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**Draft Renewal Assessment Report prepared according to the Commission
Regulation (EU) N^o 1107/2009**

FLUFENACET

**Volume 3 – Annex B.8 (AS)
Fate and Behaviour in the Environment**

**RMS: Poland
Co-RMS: France**

**Summary, evaluation and assessment of the data and information examined and the list
of studies relied upon, annotated as to the period(s) for which the particular studies are
to be protected**

November 2016

Version History

When	What
January 1998	Initial DAR
2000	Addendum fate
January 2003	Flufenacet Addendum fate
November 2016	DRAR

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B.8. – ENVIRONMENTAL FATE AND BEHAVIOUR

B.8.0. - Introduction

Flufenacet is an herbicide that was authorised for the use in the EU by its inclusion into the Annex I of the Council Directive 91/414/EEC (Commission Directive 2003/84/EC of 25 September 2003) in 2003 as entry No. 65 (at the time of inclusion as a new active substance). That authorisation entered into force from 1st January 2004 and was due to expire on the 31st December 2013. When the Directive 91/414/EEC was repealed by Council Regulation 1107/2009 of 21st October 2009, the authorisation of Flufenacet in the EU was granted by its listing, as entry No. 65, in the Part A of the Annex to the Commission Implementing Regulation (EC) 540/2011, expiring on 31st December 2013. That authorisation period was further extended to 31st October 2016 by means of the Commission Regulation (EC) No. 823/2012 of 14th September 2012.

The evaluation was based on the Draft Assessment Report prepared by the Rapporteur Member State – France, in August 1997, and Addenda to it on the basis of the documentation submitted by the Applicant – Bayer CropSciences, identified in course of the evaluation as a sole Applicant for Flufenacet. In support of the inclusion of Flufenacet into the Annex I of the Council Directive 91/414/EEC a Review Report for the active substance Flufenacet was issued (Flufenacet 7469/VI/98-final, 3 July 2003), summarising the results of the evaluation and providing the EU-agreed List of the EndPoints for this active substance.

For the purpose of the current evaluation, aimed on the renewal of the approval of Flufenacet in the EU, the Applicant provided a Dossier consisting of, in section B.8. – Environmental Fate and Behaviour, old studies, already evaluated for the previous approval for use of Flufenacet in the EU, and new studies, updating the dataset for Flufenacet in the following areas:

- Degradation in soil examined in laboratory (25 studies);
- Degradation in soil examined under field conditions (1 study);
- Soil sorption and mobility in soil of Flufenacet and its metabolites (11 studies);
- Fate and behaviour of Flufenacet the aquatic environment (7 studies);
- Fate and behaviour of Flufenacet and its degradation products in air – no new studies submitted;
- Monitoring data for Flufenacet and its degradation products (3 reports);
- Modelling exposure assessment (6 study reports).

All submitted studies, old and new, will be evaluated according to the current valid test guidelines and summarised below, under the relevant points of this Renewal Assessment Report, with exception of those considered not valid and/or being superseded by the newly submitted studies. In such cases, the studies will be cited in the Renewal Assessment Report, but not summarised. Instead, for each of them the extended rationale for its non-inclusion into the Assessment Report will be provided.

For all studies submitted for the first evaluation of Flufenacet, considered then valid and summarised in either Draft Assessment Report or Addenda to it, unless in course of the current evaluation they were found not valid, new summaries are provided to meet the current requirements.

For the first inclusion of Flufenacet into the Annex I the Applicant proposed the representative GAP comprising following uses:

- in Maize (Corn) to suppress annual grass weeds, pre-emergence, once per season in application rate 480 – 600 g/ha, in Northern and Southern European Countries;
- in Soybean and Sunflower, to suppress annual grass weeds, pre-emergence, once per season in application rate 480 – 600 g/ha, in Southern European Countries;
- in Winter Cereals (wheat, barley, rye and triticale), to suppress annual grass weeds, early post-emergence in autumn (at 2nd leaf stage of grass weeds), once per season in application rate 120 – 240 g/ha, in Northern and Southern European Countries.

The representative formulation was FOE 5043 WG 60, containing 60% of Flufenacet.

For the present evaluation the Applicant proposed the revised representative GAP, limiting the intended uses to those aimed on suppression of the annual weeds in cereals, pre-emergence and early post emergence (range of BBCH 00-22) in autumn and at early spring.

It shall be noted that, unlike for the previous assessment, the Applicant proposed the representative formulation codenamed DFF+FFA SC 600, containing 400 g/L Flufenacet and 200 g/L Diflufenican. The proposed trade names are Herold SC (to be used in both North- and South European countries), Fosburi (to be used only in NE climatic zone) and Forebird (to be used in SE climatic zone). This representative formulation was already evaluated for the purpose of the authorisation of Diflufenican in the EU (RMS – UK).

That new representative GAP, used in the evaluation in the area of environmental fate and behaviour, including the environmental exposure assessment, is presented below in the table B.8.0_CA-1. For clarity

reasons the application rates for the second active substance of the EU-representative formulation – diflufenican, were not reported in this table.

Table B.8.0_CA-1: The proposed updated representative GAP for Flufenacet.

Region	Crop	Product name	Data on application						
			Type of application	Number of Applic.	Interval between applications	Application time		Application rate - flufenacet [g/ha]	Spray volume [L/ha]
						Period	Crop's growth stage (BBCH)		
North EU	Cereals (winter wheat, winter barley, winter rye)	Herold SC (400 g/L flufenacet + 200 g/L diflufenican)	Foliar spraying	1	Not applicable – single application	Early post-emergence, Autumn only;	10-13	240	200 – 400
South EU	Cereals (wheat, winter barley)	Fosburi (400 g/L flufenacet + 200 g/L diflufenican)	Foliar spraying	1	Not applicable – single application	Early post-emergence	11-13	240	80 – 400
North EU	Cereals (winter wheat, winter barley, winter rye)	Forebird (400 g/L flufenacet + 200 g/L diflufenican)	Foliar spraying	1	Not applicable – single application	Pre-emergence and early post-emergence	00-22	120	200 – 400
South EU	Cereals (wheat, barley)	Herold SC (400 g/L flufenacet + 200 g/L diflufenican)	Foliar spraying	1	Not applicable – single application	Early post-emergence	11-13	160	200 – 400

Fulfilling the data requirement set in the Article 8 point 5 of the Regulation (EC) 1107/2009, the Applicant submitted the report presenting the results of the search of the scientific peer-reviewed open literature. This report, covering the results of the search performed for all sections, was submitted by the Applicant as a separate part of the Dossier – Document MCA, Section 9: Literature data. In this section of the Report it is summarised and evaluated under the point B.8.6. – Open literature review. All publications that were found relevant for the present assessment were summarised under the relevant points of the Report.

The findings of the evaluation performed for the previous, first authorisation of Flufenacet in the EU are presented below (in form of a short summary based of the available documentation – DAR for Flufenacet, Addenda to it and the Review Report for this compound, containing the EU-agreed List of Endpoints).

Flufenacet was found to be rapidly degraded in aerobic soil with DT₅₀ ranging from 15 to 64 days at standard conditions (T = 20-21°C, and either 40% MWHC or 75% of 1/3 bar soil moisture). The initial degradation occurred by cleavage of the C-O α-bond, resulting in formation of Thiadone (M9), which was quickly mineralised. In case of the phenyl moiety of the molecule, it was postulated that it underwent conjugation to glutathione or cysteine (forming the transient degradation product M23) or transformation to either FOE chloroacetanilide (M8) in equilibrium with M23 or FOE Alcohol (M3). The degradation product M3 was postulated to be formed either directly from Flufenacet (primary degradation product) or as secondary metabolite from M23. It was further transformed to either terminal transformation products (CO₂, NER) or to FOE Oxalate (M1), which degraded to terminal transformation products (CO₂, NER). Several degradation products were postulated to be formed from the transient metabolite M23: FOE Methylsulfoxide (M6) subsequently transformed into FOE Methylsulfone (M7), FOE Thioglycolate Sulfoxide (M4) and FOE Sulfonic Acid (M2). All they ultimately degraded to the terminal transformation products (CO₂, NER). It shall be noted that of all the metabolites listed only M23 was not found in any of the studies examining the route of degradation of Flufenacet in aerobic soils.

Of the degradation products listed above, two – FOE Sulfonic acid (M2), formed in soil in amounts up to 26.3% AR and FOE Oxalate (M1), detected in test soils in amounts up to 15.6% AR, were classified as major. In case of all remaining degradation products it was stated that they were minor, not being detected in any test soil in amounts above 5% AR.

The mineralisation level was up to 20.8% AR in case of fluorophenyl-radiolabelled compound and 31.9% for thiadiazole-radiolabelled compound. Non-extractable residues (NER) were formed in amounts up to 56.2% AR (for the fluorophenyl-radiolabelled compound), still increasing at the end of incubation period. The level of NER detected for the thiadiazole-radiolabelled compound was much lower, not surpassing 7% AR during the study.

Of the two major degradation products, FOE Sulfonic acid (M2) was demonstrated to be persistent in soil, with LoEP-reported DT_{50} in range of 189-270 days, while FOE oxalate (M1) was shown to be moderately persistent in soil, with DT_{50} values ranging from 5 days to 130 days (values reported in LoEP).

Degradation of Flufenacet in soil under anaerobic conditions was not examined on the basis that for the proposed then application pattern the compound was not expected to be exposed to anaerobic conditions.

The examination of the photolysis on the soil surface led to the conclusion that Flufenacet was photolytically stable in soil, with less than 10% of the compound transformed by the end of irradiation period.

Additionally degradation of Flufenacet in soil was examined in field dissipation studies, performed on several locations in Europe – in Germany (6 trials), Northern France (4 trials), Southern France (4 trials) and Italy (2 trials). The trials were performed on either bare or cropped soil. In those experiments Flufenacet demonstrated persistence similar to that determined in the laboratory, with DT_{50} = 38-43 days for autumn applications and DT_{50} = 15-53 days for spring applications onto bare soil and DT_{50} = 13-16 days for early spring applications and DT_{50} = 16-48 days for spring applications onto cropped soil systems. These results were not subjected to further normalisation.

In the LoEP it was declared that none of the degradation products identified in laboratory studies was detected in the field trials in amounts >LOD. In the DAR however it was stated that two of them – FOE Oxalate (M1) and FOE Sulfonic acid (M2) were sporadically detected in amounts >LOD (0.01 mg/kg), but the information provided there is not fully clear.

Additionally, in relation to the field dissipation studies, soil stability of Flufenacet and its degradation products in soil was examined, showing that Flufenacet and its three relevant degradation products – FOE Alcohol (M3), FOE Oxalate (M1) and FOE Sulfonic acid (M2) were considered to be stable in soil stored under frozen conditions for at least two years.

Neither soil residue nor soil accumulation studies were performed. They were indicated as not necessary, because the trigger values had not been exceeded.

The adsorption of Flufenacet in soil was examined in seven soils, resulting in K_{foc} = 113 – 696 mL/g and $1/n$ = 0.84 – 0.98 (values taken from the EU-agreed LoEP, including soils having OC < 0.23%). On that basis Flufenacet was classified as being moderately mobile in soil.

The soil sorption of metabolites of Flufenacet was examined in four soils. The data were collected for five metabolites – FOE Methyl sulfoxide (M5), FOE Sulfonic acid (M2), FOE Oxalate (M1), FOE Alcohol (M3) and Thiadone (M9). The obtained results were following:

- for FOE Methyl sulfoxide (M5): K_{OC} = 46 – 463 mL/g (values taken from the DAR);
- for FOE Sulfonic acid (M2): K_{OC} = 10 (6 – 19) mL/g and $1/n$ = 0.86 – 1.18 (values taken from the EU-agreed LoEP);
- for FOE Oxalate (M1): K_{OC} = 11 (7 – 23) mL/g and $1/n$ = 0.82 – 1.42 (values taken from the EU-agreed LoEP);
- for FOE Alcohol (M3): K_{OC} = 84 – 314 mL/g (values taken from the DAR);
- for Thiadone (M9): K_{OC} = 29 – 58 mL/g (values taken from the DAR).

Of the compounds listed above only FOE Oxalate and FOE Sulfonic acid were characterised as expected to have a potential to leach into deeper soil layers in significant amounts.

Column leaching studies were not performed, considered to be covered by the results of batch sorption studies.

The results of the aged residue column leaching study indicated that Flufenacet and its three metabolites found in the study – FOE Oxalate (M1), FOE Sulfonic acid (M2) and FOE Thioglycolate sulfoxide (M4), might leach to deeper soil layers, but only Flufenacet, FOE Oxalate (M1) and FOE Sulfonic acid (M2) were expected to appear there in significant amounts.

Additionally, the mobility of Flufenacet and its degradation products in soil was examined in two lysimeter studies. As a result of these studies it was concluded that even under worst-case conditions it was not expected that the active substance would leach to the groundwater in amounts posing an unacceptable threat to that environmental compartment (in concentrations ≥ 0.1 µg/L). Similar conclusion was drawn for the two degradation products detected – FOE Oxalate (M1) and FOE Thioglycolate sulfoxide (M4). In case of another metabolite of Flufenacet – FOE Sulfonic acid (M2), it was stated that that compound may be found in soil layers below 1.2 m, or in groundwater, in amounts > 0.1 µg/L. That compound however was demonstrated to be neither toxicologically nor ecotoxicologically relevant.

The examination of the fate and behaviour of Flufenacet in water showed that the compound was hydrolytically and photolytically stable in that environment. The proper study on ready biodegradability of Flufenacet was not performed, but on the basis of the results of water/sediment studies it was stated that the compound was not readily biodegradable.

The examination of the fate and degradability of Flufenacet in water/sediment systems showed that its degradation pattern in aquatic systems was very similar to that elucidated in aerobic soil. Although it was

determined that a significant portion of radioactivity was translocated to the sediment phase, it was not clearly indicated whether it was related to the parent compound or to its degradation products.

The results presented in the DAR seemed to indicate that Flufenacet was predominantly present in water phase throughout the whole study and the migration to sediment was not a significant dissipation route – the maximum amount of the compound found in sediment phase was 34.2% (on DAT 30). The kinetic endpoints were determined for the whole system and water phase and were as follows (all values taken from the EU-agreed LoEP):

- in water phase: $DT_{50} = 46.3 - 61.7$ days, $DT_{90} = 154 - 205$ days (fluorophenyl label only);
- in the whole system, for fluorophenyl label $DT_{50} = 76.4 - 84.6$ days, $DT_{90} = 254 - 281$ days, while for thiadiazole label $DT_{50} = 20 - 31$ days, $DT_{90} = 67 - 104$ days.

Of the degradation products detected only FOE Methylsulfide (M5), for the test systems treated with phenyl-radiolabelled compound, and Thiadone (M9), for the test systems treated with thiadiazole-radiolabelled compound, were classified as major degradation products.

The exposure assessment performed for the soil compartment resulted in calculation of the following initial PEC_{SOIL} values:

- for application in maize, soybean and sunflower at 600 g a. s./ha **ini** $PEC_{SOIL} = 0.8$ mg/kg;
- for application in cereals at 240 g a. s./ha **ini** $PEC_{SOIL} = 0.32$ mg/kg.

The calculations for any of the identified degradation products were not performed, nor was assessed their accumulation potential.

The model exposure assessment of the Groundwater compartment was performed twice, first using PELMO 2.01 model (“Borstel” soil scenario and Hamburg weather scenario), then using FOCUS PELMO 2.2.2.

The results of both modellings indicated no risk posed to GW compartment by Flufenacet – the calculated $PEC_{GW} < 0.1$ µg/L. Also safe uses were demonstrated for FOE Oxalate (M1), although in case of calculations performed using FOCUS PELMO 2.2.2. model for use in cereals and maize the $PEC_{GW} > 0.1$ µg/L were obtained, the highest value being that of 0.64 µg/L in Jokioinen scenario for use in cereals. In case however of FOE Sulfonic acid (M2) all calculated PEC_{GW} values were higher than the trigger value of 0.1 µg/L, peaking at 16.63 µg/L in Hamburg scenario for the use in maize. That was in good agreement with conclusions on the risk posed by that compound to the GW compartment, drawn from the lysimeter studies.

The SW exposure assessment was performed for Flufenacet and its metabolite FOE Sulfonic acid (M2), assuming the spray drift as a sole migration route of Flufenacet to SW water bodies and its 10%-conversion there to FOE Sulfonic acid (M2). The calculations were performed for static SW water bodies, considered to be representative also for slow-moving SW bodies.

The determination of the fate and behaviour of Flufenacet in air was based on the examination of its vapour pressure and Henry’s law constant. These values were following:

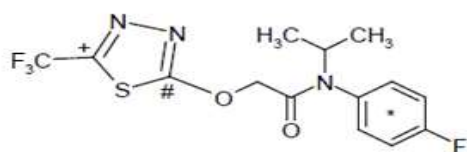
- vapour pressure (N-isomer) $V_p = 9E-5$ [Pa] ($T = 20^{\circ}C$);
- Henry’s law constant $H = 9E-4$ [$Pa \cdot m^3 \cdot mol^{-1}$] ($T = 20^{\circ}C$).

On the basis of these values it was stated that that no significant volatilization of Flufenacet is expected to occur. That was conformed by the results of the experiment on volatilization of the compound from soil, showing that within 24 hours up to 29% of the applied compound lost from the soil surface due to volatilization. The volatilization from plant surfaces was not examined.

For the process of photooxidative degradation in air the calculated (using Atkinson’s method) $DT_{50} = 4.7$ h, indicating that the compound was short-living in the atmosphere.

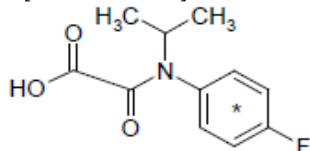
On the basis of the above results it was stated that the risk posed by Flufenacet to the atmosphere was minimal and the PEC_{AIR} values were not calculated.

In this assessment the environmental fate and behaviour of the active substance – Flufenacet, was examined using a compound radiolabelled in either phenyl ring (one radiolabelling position) or in thiadiazole moiety (two different radiolabelling positions), as shown on figure B.8.0._CA-1. The radiolabelled compounds were used also in examination of the fate and behaviour in the environment of the degradation products of Flufenacet. All radiolabelled structures used to examine the environmental fate and behaviour of Flufenacet, either as test compounds or as reference standards, are presented below on Fig. B.8.0._CA-1.

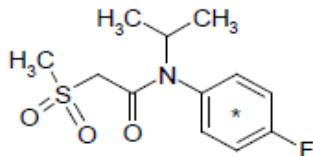


Flufenacet radiolabelled in phenyl and thiadiazole moieties;

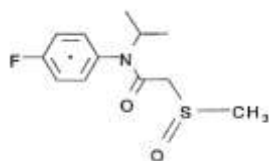
- * denotes [phenyl-UL-¹⁴C] radiolabelling position,
- # denotes [thiadiazole-2-¹⁴C] radiolabelling position;
- + denotes [thiadiazole-5-¹⁴C] radiolabelling position;



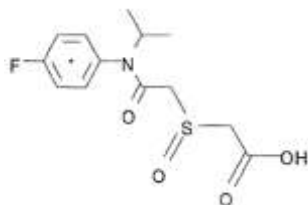
FOE Oxalate (M1);
* denotes radiolabelling position



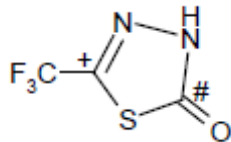
FOE Methylsulfone (M7; BCS-CO62475);
* denotes radiolabelling position



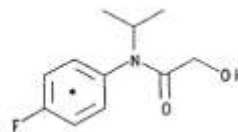
FOE Methylsulfoxide
* denotes radiolabelling position



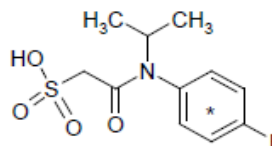
FOE Thioglycolate sulfoxide
* denotes radiolabelling position



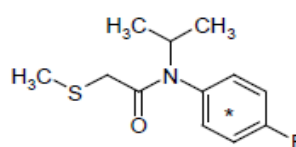
FOE-Thiadone (M9; Thiadone);
denotes [thiadiazole-2-¹⁴C] radiolabelling position;
+ denotes [thiadiazole-5-¹⁴C] radiolabelling position;



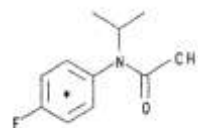
FOE Alcohol;
* denotes radiolabelling position



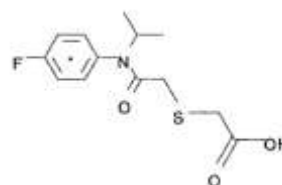
FOE Sulfonic acid (M2);
* denotes radiolabelling position



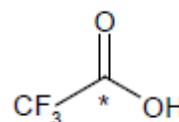
FOE Methylsulfide (M5);
* denotes radiolabelling position



FOE Amine acetate
* denotes radiolabelling position



FOE Thioglycolate sulfide
* denotes radiolabelling position



Trifluoroacetic acid (M45, TFA, BCS-AZ6567);
* denotes radiolabelling position

Figure B.8.0_CA-1: Radiolabelled forms of Flufenacet and its metabolites used in environmental fate and behaviour studies (all structures copied from the documentation provided by the Applicant).

In the documentation submitted by the Applicant following code names and alternative names for Flufenacet were used: fluthiamid, fluthiamide and FOE 5043.

B.8.1. – Fate and Behaviour in Soil

In order to adequately evaluate the studies examining the fate and behaviour of Flufenacet in soil it has become necessary to determine the application rate expressed in mass units (mg/kg) that may be subsequently used as a reference value. The analysis of the proposed EU-representative application pattern for Flufenacet (please refer to the table B.8.0._CA-1) enabled the identification of the critical use with regard to the soil exposure – 240 g Flufenacet/ha. Assuming uniform application to the top 5 cm soil layer, soil bulk density $d = 1.5 \text{ g/cm}^3$ and crop interception $CI = 0\%$ (application to bare soil), the application rate expressed in mass units (mg/kg) is **A = 0.32 mg/kg**. This value will be used as a reference in determining the validity of the studies examining fate and behaviour of flufenacet in soil.

B.8.1.1. – Route and rate of degradation in soil

Under this point are summarised the studies examining the route and rate of degradation of Flufenacet in soil under various conditions, both in the laboratory and in the field. The dossier submitted by the Applicant contained both old studies, already evaluated for the previous authorisation of Flufenacet in the EU, and the new/newly submitted (further referred to as “new”) studies, submitted specifically for the purpose of the renewal of the authorisation.

RMS – Poland, having examined the Assessment Report for Flufenacet and Addenda to it, prepared by the then-RMS France, decided to provide in this Report the summaries of all the studies submitted by the Applicant (old and new) and found acceptable. In case of the old studies RMS decided to evaluate them against the new Guidelines, but, unless it is stated that they significantly deviate from the current acceptability standards, do not change the conclusions with regard to their acceptability drawn by the former RMS – France. The old studies were summarised according to the current standards, the same as applied to the new ones.

B.8.1.1.1. – Route of degradation in soil

The route of degradation in soil was examined under aerobic and anaerobic conditions. Also was examined the relevance of the photolysis on the soil surface as the mechanism of degradation of Flufenacet in that compartment. The studies evaluated under this point provided the data for subsequent kinetic analysis, presented under the point B.8.1.1.2. In case the study report summarised under this point contained also the results of the kinetic analysis of the data, unless it was found as not meeting the current requirements, the reference to the relevant data point was made, under which that analysis was presented.

B.8.1.1.1.1. – Aerobic degradation

To address the issue of the route of degradation of Flufenacet in soil under aerobic conditions the Applicant submitted five study reports. Three of them had been evaluated for the first authorisation of this compound in the EU and summarised in the DAR prepared by the then-RMS – France. In order to maintain the consistency with the former evaluation RMS-Poland, decided to evaluate and provide the summaries of these three studies in the same order as they appeared in the former DAR. Additionally the analysis of that document revealed that to one of the studies – by Pangilinan and Smith [1994] – study Report No. MR106408, there was a supplementary study. In the previous Assessment Report both studies were summarised together. However, for the purpose of this Renewal Assessment Report RMS decided to provide for them two separate summaries.

Finally, the extensive search for open literature data enabled to identify two publications relevant in the area of the elucidation of the route of degradation of Flufenacet in aerobic soils. These publications are:

- Bloomberg A. M., Shadrick B. A., Arthur E. L., Clay V. E., “*Outdoor soil metabolism of [Phenyl- $U\text{-}^{14}\text{C}$] Flufenacet on California Soils.*”; ACS Symposium Series, 2002, vol. **813** – “Pesticide Environmental Fate” (chapter 12), 167 – 182 (book chapter);
- Lam C. K., McKinney M. K., Clay V. E., “*Evaluation of Laboratory and Field Extraction Methods: Extraction of [Phenyl- $U\text{-}^{14}\text{C}$] Flufenacet from Aged Soils.*”; ACS Symposium Series, 2002, vol. **813** – “Pesticide Environmental Fate” (chapter 11), 153 – 166 (book chapter);

Their summaries will be provided after those of the study reports submitted by the Applicant.

Study 1:

Report: Kelley I., Wood S., McKinney M., (1995): “Degradation of [Phenyl-UL-¹⁴C]FOE 5043 in Three Soil Types.”; Bayer Corporation (formerly Miles Inc), Agriculture Division, P. O. Box 4913, Kansas City, Missouri 64120, USA; study No. F3042104; unpublished Bayer Report No. MR 106664; 31 August 1995; study reference number: M-002146-01-1;

Guidelines: The study was performed to comply with the following Guidelines:

- BBA Guidelines for the Official Testing of Plant Protectants, Part IV, 4-1 (1986): Persistence, Transformation and Metabolism;
- US. EPA Guideline 162-1 Aerobic Soil Metabolism (supplemental);

GLP: Yes;

RMS comments: The study had been evaluated for the previous authorisation of Flufenacet in the EU, by its inclusion into the Annex I of the Directive 91/414/EEC. Its summary can be found under the point B.7.1.1.1.1., in section B.7 of the Annex B to the Monograph prepared by the RMS – France, for Flufenacet. The study was evaluated for its compliance with OECD Guideline 307 – Aerobic and Anaerobic Transformation in Soil. RMS stated that the study complied with the provisions of the reference Guideline, therefore it can be considered acceptable for the present assessment. It is summarised below in its part related to the route of degradation, while for the rate of degradation the information is placed under the point B.8.1.1.2.1.

Summary:

The aim of the study was to determine the route and rate of degradation of Flufenacet in soil under aerobic conditions. The experiment was performed on three European (German) soils. Their characteristic is given below in the table B.8.1.1.1.1._CA-1.

Table B.8.1.1.1.1._CA-1: The characteristic of soils used in the study.

Parameter			Soil		
			BBA 2.2	Laacherhof	Höfchen im Tal
Soil origin			Germany; EU	Germany; EU	Germany; EU
Soil type (in the DAR)			Loamy sand	Silt Loam	Silt Loam
Soil type (USDA; re-assessed)			Loamy sand	Silt Loam	Silt Loam
Particle size distribution	Sand [%]		86.2	36.9	3.6
	Silt [%]		7.7	51.1	80.8
	Clay [%]		6.1	12.0	15.6
pH value (in H ₂ O, CaCl ₂)			6.2	7.3	5.8
Organic carbon content (C _{org}) [%]			2.58	0.9	2.40
Cation Exchange Capacity – CEC [mEq/100g]			9.7	10.0	10.0
Maximum water holding capacity [%]			53.8	48.6	71.6
Soil biomass expressed in mg microbial C/kg soil	Control (no FOE 5043)	Initial (DAT 0)	350	227	490
		On DAT 56	226	270	587
		Final (DAT 120)	216	161	443
	Treated with FOE 5043	Initial (DAT 0)	315	279	520
		On DAT 56	275	256	706
		Final (DAT 120)	230	155	403
Soil biomass expressed as %OC	Control (no FOE 5043)	Initial (DAT 0)	1.3	2.52	2.04
		On DAT 56	0.88	3.0	2.45
		Final (DAT 120)	0.84	1.79	1.85
	Treated with FOE 5043	Initial (DAT 0)	1.22	3.1	2.17
		On DAT 56	1.07	2.84	2.94
		Final (DAT 120)	0.89	1.72	1.68

The test soils were selected according to BBA guidelines for examining the degradation of chemicals in soil. They were freshly collected from the agriculturally used land in Germany, from the top 15-cm layer, and sent to the test facility. There the containers were immediately opened and planted with alfalfa to maintain the biological viability of soils. The test soils were then kept for 27 days in the greenhouse, until the study began. At the beginning of the study the soils were air-dried and sieved through a 2-mm sieve.

Samples of each test soil were then taken for the textural analysis and the determination of soil properties. The soil microbial activity was controlled throughout the study by determining microbial biomass at three intervals

during the incubation period: at its beginning – on DAT 0, on DAT 56 and at its end – on DAT 120, using the method of Anderson and Domsch (method presented by Parkinson and Smith in “*Microbial Biomass*” in Page A. L (ed.), **1982**, *Methods of Soil Analysis, Part 2*; Soil Science of America Inc., Madison, pp.824-826

Also before the experiment began the soil water content at 40% MWHC was determined. This was done using soil samples that were oven-dried overnight and then passed through a 2-mm sieve. The 50-grams portions of so prepared test soils were weighed into preweighed Buchner funnels equipped with GF/C filters. The funnels were placed in beakers filled with water up to the soil level. Then the soils were allowed to soak up water for 1 hour before being drained until dripping stopped. Then the funnels were reweighed and the maximum water holding capacity of each test soil determined by difference in weight. Next the amount of water necessary for obtaining 40% MWHC was calculated.

The test substance used in the experiment was the ^{14}C -FOE 5043 radiolabelled uniformly in phenyl ring, as shown below on figure B.8.1.1.1.1._CA-1

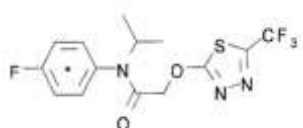


Figure B.8.1.1.1.1._CA-1: The structural formula of the radiolabelled Flufenacet (FOE 5043) used in the experiment (copied from the study report).

The specific radioactivity of the test compound used in the experiment was 66.5 mCi/mmol and the radiochemical purity of its application solution, determined by HPLC, was 96.3% (content of [^{14}C] FOE 5043).

The test substance was applied in form of the application solution containing nominally 20 ppm of the radiolabelled Flufenacet. It was prepared by adding 0.831- μL aliquot of [^{14}C] FOE 5043 solution (conc. 12.028 $\mu\text{g}/\mu\text{L}$), having the specific activity of 0.18 $\mu\text{Ci}/\mu\text{g}$, corresponding to 6.8 kBq/ μg) and 2 mL of acetonitrile (CH_3CN) to a previously sterilised 500 mL volumetric flask. Next the solution was brought to a volume with distilled water and analysed for the radiochemical concentration using LSC. The actual concentration of the test compound – Flufenacet, in so prepared solution was determined to be 19.1 $\mu\text{g}/\text{mL}$ (3.49 $\mu\text{Ci}/\text{mL}$, corresponding to 129.19 kBq/mL). The radiochemical purity of so prepared application solution was 96.3 % with relation to FOE 5043.

Additionally a second application solution, containing solely non-radiolabelled Flufenacet was prepared by dissolving 10 mg of the test compound with sterile distilled water in 500-mL volumetric flask. In order to facilitate solubilisation of the test compound 2 mL of CH_3CN were added to the volumetric flask prior to its filling in to the calibration mark with distilled water. That solution was used to treat the control samples used in determination of soil biomass.

The experiment was performed using the glass biometer flasks, presented below on figure B.8.1.1.1.1._CA-2. They consisted of 250-mL Erlenmeyer flasks with wide-diameter glass tube adapters, sealed with traps for volatile compounds. The traps consisted of a glass adapter containing of ~1g plug of glass wool soaked with 2% mineral oil in hexane to absorb possible VOC and soda lime layer (~10 g.) to capture formed $^{14}\text{CO}_2$, capped with a layer of glass wool (separator) above which further ~4-grams. layer of soda lime was placed to prevent soda-lime sorbent from being saturated with atmospheric CO_2 . On the top 4-grams layer of glass wool was placed. The side-arm inlet tube, sealed with a rubber septum was set to enable the adjustment of soil moisture by adding the necessary amounts of distilled water during the study.

Each test vessel contained the equivalent of 100 grams d. w. test soil, with soil moisture adjusted to ~40% MWHC by addition of the appropriate amount of the distilled water. That level was maintained throughout of the incubation period, lasting up to 120 days.

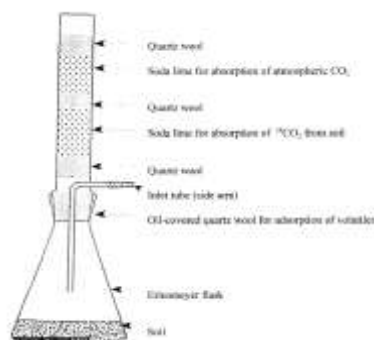


Figure B.8.1.1.1._CA-2: The biometer flask used in the experiment (scheme copied from the study report).

The test compound was applied onto the test soils in form of the application solution described above, having the nominal concentration of 20 mg/L, and actual concentration of 19.1 mg/L.

The test substance was applied at two different application rates: 750 g a. s./ha (0.67 lb a. s./acre) in case of two test soils and 1500 g a. s./ha (1.34 lb a. s./acre) in case of one soil. The appropriate volumes of the application solution were evenly distributed over the soil surface. The details of the application of Flufenacet to the test soils are presented below in the table B.8.1.1.1._CA-2.

Table B.8.1.1.1._CA-2: The characteristics of the treatment of test soils with Flufenacet.

Test soil	Target application rate [g/a. s./ha]	Volume of application solution [mL]	Concentration of the test compound in treated soil	
			Concentration [ppm]	Assumptions made
BBA 2.2 (Loamy sand)	750	5	1	soil depth: 5 cm soil density: 1.5 g/cm ³
Laacherhof (Silt loam)	750	5	1	soil depth: 5 cm soil density: 1.5 g/cm ³
Höfchen im Tal (Silt loam)	1500	10	2	soil depth: 5 cm soil density: 1.5 g/cm ³

After treatment the appropriate amounts of distilled water were sprinkled onto each test soil to establish a soil moisture of ~40% MWHC. The amounts of water used for each test soil were:

- 1.92 mL for BBA 2.2 soil;
- 1.43 mL for Laacherhof soil;
- 0.97 mL for Höfchen im Tal soil.

Controls were treated with the solution of non-radiolabelled Flufenacet in such amount to obtain its concentration of 1 ppm. As it was in case of treated soils the controls were then brought to ~40% MWHC by adding the appropriate amount of distilled water.

After treatment the Erlenmayer incubation flask were sealed with traps for volatile compounds, weighed and covered with aluminium foil to exclude light.

So prepared incubation systems were placed in a walk-in, temperature controlled environmental chamber and incubated in the darkness at $T = 20 \pm 1^{\circ}\text{C}$ for up to 120 days. The temperature in the incubation chamber was recorded continuously with circular charts changed every 7th day. Treated samples were removed for the analysis at DAT (Days After Treatment) 0, 7, 14, 28, 56, 70, 100 and 120. Control samples were removed for analysis at DAT 0, 56 and 120. For each time point duplicate samples were prepared. The adjustment of soil moisture was performed in 2-weeks intervals by weighing the incubation flasks and, when necessary, introducing the appropriate amounts of distilled water through the side-arm inlet tube.

At the designated time points duplicate test flask for each soil were removed from the incubation chamber and for 15 minutes purged gently with N₂ in order to flush the produced CO₂ and VOCs into the traps.

Next soils from each test vessel were analysed. That was done by extracting the entire soil samples in multistep extraction procedure.

In case of DAT 0 samples it consisted of two following steps:

- Step 1: extraction with water – twice 150 mL, lasting for two hours (stir extraction at room temperature), to determine the residues immediately available for plants or leaching to groundwater. The extracts were combined, their volume recorded and triplicate aliquots analysed by LSC.

- Step 2: organic extraction with two 150-mL portions of 0.01N HCl in CH₃CN (stir extraction). So obtained organic extracts were combined, their volumes recorded and 100-μL or 500-μL aliquots analysed by LSC. The remaining organic extracts were then evaporated under reduced pressure, redissolved in small amounts of MeOH and analysed by using HPLC.

For all samples collected at later time points, with exception of those collected at DAT 100 and DAT 120, three-step extraction procedure was used, consisting of:

- Step 1: extraction with water – twice 150 mL, lasting for two hours (stir extraction at room temperature), to determine the residues immediately available for plants or leaching to groundwater. The extracts were combined, their volume recorded and triplicate aliquots analysed by LSC.
- Step 2: organic extraction with two 150-mL portions of 0.01N HCl in CH₃CN (stir extraction). So obtained organic extracts were combined, their volumes recorded and 100-μL or 500-μL aliquots analysed by LSC. The remaining organic extracts were then evaporated under reduced pressure, redissolved in small amounts of MeOH and analysed by using HPLC (that extract will be further called “**organic extract 1**”).
- Step 3: additional harsher organic extraction with two 100-mL portions of CH₃CN: 0.1N HCl_{aq} 1:1 v/v solution (stir extraction). The obtained extracts were treated in the same manner as described above for Step-2 organic extracts. That step was introduced because it was stated that with time the amount of bound residues increased significantly. (That extract will be further called “**organic extract 2**”).

Finally for soils collected at DAT 100 and DAT 120 Step 2 was omitted and the extraction procedure consisted again of only two, following steps:

- Step 1: extraction with water – twice 150 mL, lasting for two hours (stir extraction at room temperature), to determine the residues immediately available for plants or leaching to groundwater. The extracts were combined, their volume recorded and triplicate aliquots analysed by LSC.
- Step2 (formerly Step 3): harsher organic extraction with two 100-mL portions of CH₃CN: 0.1N HCl_{aq} 1:1 v/v solution (stir extraction). The obtained extracts were treated in the same manner as described above for Step-2 organic extracts. That step was introduced because it was stated that with time the amount of bound residues increased significantly. (That extract will be further called “**organic extract 2**”).

Additionally, DAT 120 samples were further extracted for the additional RA using following extraction methods:

- Soxhlet extraction with 0.1N HCl_{aq}:CH₃CN solution;
- Soxhlet extraction with CH₃COOC₂H₅ (ethyl acetate);
- Soxhlet extraction with CH₂Cl₂ (methylene chloride)
- Soxhlet extraction with CH₃OH;
- Stir heating extraction with 1N HCl_{aq};
- Stir extraction with 1N NaOH.

The extracted soils were subsequently analysed for NER fraction. To do that each soil sample was allowed to air-dry overnight, after what it was ground to the fine powder, weighed, and its triplicate aliquots analysed for radioactivity content after combustion by LSC.

Traps for volatile compounds, recovered from test vessels were dissected into soda lime trap and mineral oil coated glasswool plug sections.

The filling of each soda lime trap section was ground, weighed, oxidised and analysed by LSC. In the same way were analysed unexposed soda lime traps and spiked soda lime traps.

Mineral oil coated glasswool plugs were extracted with ~100 mL CH₃COOC₂H₅ in 30-min. sonication. The volumes of extract were recorded and triplicate 500-μL or 1000-μL aliquots analysed by LSC. Unexposed plugs were used as blanks. As the levels of radioactivity recovered from plugs were low, samples from later intervals were combined, 10 μL of C₁₀H₂₁OH added to minimise losses during processing and combined samples were evaporated at Rotovap. The oily residue was redissolved in 1.5 mL CH₃CN and 250-μL aliquots of so prepared solution analysed by HPLC.

The extracts from DAT 0 samples were used to verify the stability of the test compound during sample treatment. Additionally the stability of the test compound in the application solution was tested.

All samples were analysed for the content of radioactivity using LSC method. The LSC (Liquid Scintillation Counting) analysis was performed using a Packard Tri-Carb Model 4640 counter equipped with automatic external standardisation.

Liquid samples were radioassayed after addition of 15-20 mL of Ultima Gold solution to 100 – 1000 μ L aliquots, depending on sample. The minimum sensitivity of LSC analysis for those samples was 0.00018 ppm, and when expressed as Lowest Acceptable Gross Count Rate (LAGC) it was 70 cpm, while as Lowest Acceptable Net Count Rate (LANC) – 35 cpm.

Solid samples were oxidised using Packard Model 306 sample oxidizer, generated $^{14}\text{CO}_2$ trapped on 6 mL Carbo-sorb E and 15 mL Perma Fluor E. The minimum sensitivity of LSC analysis for those samples was 0.00091 ppm, and when expressed as Lowest Acceptable Gross Count Rate (LAGC) it was 70 cpm, while as Lowest Acceptable Net Count Rate (LANC) – 35 cpm.

Sample extracts were analysed using the following techniques:

- HPLC – major identification and quantitation method for parent compound and its degradation products;
- TLC – conformatory method for identification of degradation products;
- LC-MS - identification and quantitation method for parent compound and its degradation products.

The RP-HPLC analysis was performed in a gradient mode. The system, consisted of Hewlett Packard 1090 chromatograph equipped Spherisorb 3 μ ODS2 (7 cm * 10 mm) chromatographic column and two detectors – UV absorbance flow detector, set at 254 nm, and Raytest Ramona radioactivity detector. It worked in the following gradient regime:

- Mobile phase A: Water + 0.4% CH_3COOH ,
- Mobile phase B: CH_3CN + 0.4% CH_3COOH ,
- Gradient mode: linear from 0% B at 0 min to 100% B at 60 min.

The flow rate in the system was set to 1 mL/min.

The TLC method – conformatory for identification of metabolites, used pre-coated 0.25-mm thick silica gel plates with fluorescent indicator. Plates were developed in $\text{CHCl}_3/\text{CH}_3\text{COOC}_2\text{H}_5$ 3:1 solution and further separation was performed on the same plate using a solvent system $\text{CH}_3\text{CN}/(\text{CH}_3)_2\text{CHOH}/\text{CH}_3\text{COOH}/\text{H}_2\text{O}$ (20:3:2:1 v/v). Radioactive bands were detected by exposing the plates to X-Ray film.

The LC-MS analysis was performed using Varian 5400 HPLC equipped with a C18 (5- μ) Novapak column (15 cm * 3.9 mm) working in a gradient mode, and Finnigan MAT 90 MS detector. The parameters of gradient were following:

- Mobile phase A: Water + 0.1% CH_3COOH ,
- Mobile phase B: CH_3OH ,
- Gradient mode: linear from 0% B at 0 min to 100% B at 30 min.

The flow rate in the system was set to 1 mL/min.

The parameters of MS detector were following:

- source temperature: 250 $^\circ\text{C}$,
- aerosol temperature: 210 $^\circ\text{C}$,
- vaporiser temperature gradient : 170 $^\circ$ at 100% H_2O to 148 $^\circ\text{C}$ at 100% CH_3OH ,
- scans collected at: 150-600 amu at rate 10 sec/dec,
- 0.2 M ammonium acetate added post column at rate of 0.5 mL/min.

The identification of Flufenacet and its degradation products in HPLC and TLC analysis was performed by means of comparison of the R_t (HPLC) and R_f (TLC) factors in examined extracts with those of the standards. The R_t and R_f values for each of the analysed compounds in HPLC and TLC analysis are given in the table B.8.1.1.1.1._CA-3 below.

Table B.8.1.1.1._CA-3: Chromatographic (HPLC and TLC) identification of Flufenacet and its degradation products in the study.

Compound	Compound's identity	Identification with:	
		HPLC – R_t [min]	TLC – R_f
Parent	Flufenacet	44.7	0.93
Metabolite 1	FOE Sulfonic acid	16.4	0.52
Metabolite 2	FOE Oxalate	18.4	0.38
Metabolite 3	FOE Thioglycolate sulfoxide	25.7	0.30
Metabolite 4	FOE Methylsulfoxide	30.3	0.62
Metabolite 5	FOE Methylsulfone	33.8	0.84
Metabolite 6	FOE Amine acetate	37.5	0.81
Metabolite 7	FOE Methylsulfide	40.6	0.62
Metabolite 8	FOE Alcohol	37.6	0.74

The identification of Flufenacet and its degradation products in LC/MS analysis was performed by comparison of mass spectra of each chromatographic peak with those obtained for the standards, for which base signals and protonated molecular ion signals were identified. These are presented below in the table B.8.1.1.1.1_CA-4. It shall be noted that of all compounds listed in the table B.8.1.1.1.1_CA-3 above, the identification with LC/MS was performed for the parent compound and the metabolites either present in amounts > 10% AR in combined aqueous and organic extracts, or those <10% AR in combined aqueous and organic extracts, but not exhibiting a decreasing trend towards the end of the study.

Table B.8.1.1.1.1_CA-4: LC/MS identification of Flufenacet and its degradation products in the study.

Compound	Representative signals used in identification	
	Position – m/z	Description
Flufenacet	364	Protonated molecular ion $[M+H]^+$ = base peak
	381	Ammonia adduct $[M + NH_4]^+$
FOE sulfonic acid	274	Base Peak $[M - H]^-$ = molecular ion
FOE oxalate	226	Protonated molecular ion $[M+H]^+$
	243	Base peak (Ammonia adduct $[M + NH_4]^+$)
FOE methylsulfone	274	Protonated molecular ion $[M+H]^+$
	291	Base peak (Ammonia adduct $[M + NH_4]^+$)

Results and their discussion:

The stability tests performed using DAT 0 samples demonstrated that Flufenacet was stable during application and routine extraction procedure. In case however of extraction with 1N NaOH the compound was undergoing the decomposition, what complicated the interpretation of the results obtained during the additional analysis of the NER fraction (bound residues).

It was also shown that in the application solution the compound was stable for the period of at least 9 months, when the solution was stored in refrigerator at 4°C.

The analysis of the soil biomass showed that in all three soils it was > 1% OC at the beginning of the study and although decreasing towards it end it was still above that level in two of them – Laacherhof (1.72-1.79% OC) and Höfchen im Tal (1.68-1.85% OC). In case of BBA 2.2 soil on DAT 120 (end of the incubation period) it dropped below the level of 1% OC – to 0.84-0.89% OC.

In all three soils the microbial biomass decreased towards the end of the study – by 27.0% (control treated with Flufenacet) – 38.3% (untreated control) in case of BBA 2.2 soil, 29.1% (untreated control) – 44.4% (control treated with Flufenacet) in case of Laacherhof soil and by 9.59% (untreated control) – 22.5% (control treated with Flufenacet) in case of for Höfchen im Tal soil. It shall be pointed out however, that while in BBA 2.2 soil that decline was steady, in case of the two remaining soils the amount of biomass was higher at DAT 56 than that at DAT 0.

In the study report it was stated that the decline of soil microbial biomass was attributed rather to the storage of the samples and test conditions, while the addition of the test compound had little effect on that phenomenon.

The recovery of the applied radioactivity in all three experimental soils was generally good, in line with the recommendations of the relevant Guidelines. For the individual soils it looked as follows:

- for BBA 2.2 soil: 91.3 – 106.0% AR (average 98.3% AR);
- for Laacherhof soil: 92.4 – 100.5% AR (average 95.9% AR);
- for Höfchen im Tal soil: 91.3 – 100.4% AR (average 97.7% AR).

The level of mineralization gradually increased throughout the study, to reach at its end (DAT 120) 14.2% AR in BBA 2.2 soil, 23.8% AR in Laacherhof soil and 12.0% AR in Höfchen im Tal soil (determined as $^{14}CO_2$ captured in volatile compounds trap). Also the NER fraction increased with time to reach at the end of the study – DAT 120, the levels of 42.3% AR in BBA 2.2 soil, 37.1% AR in Laacherhof soil and 58.0% AR in Höfchen im Tal soil.

The amount of AR present as combined extractable fraction decreased with time all three soils, to reach at the end of the study (DAT 120) the level of 37.4% AR in BBA 2.2 soil, 31.5% AR in Laacherhof soil and 26.1% AR in Höfchen im Tal soil. It was also noted that for samples collected from DAT 7 to DAT 70 the amount of radioactivity extracted with **organic extract 2** (harsher extraction) increased with time, while that extracted with **organic extract 1** (milder extraction) decreased.

The following compounds were identified in extracts from all three soils:

- Flufenacet,
- FOE Sulfonic acid,
- FOE Oxalate,

- FOE Thioglycolate sulfide,
- FOE Methylsulfoxide,
- FOE Methylsulfone,
- Other fraction consisting of 5-6 specified and several unspecified constituents.

The maximum concentrations of identified degradation products recorded in each test soil are given below in the table B.8.1.1.1.1._CA-5.

Table B.8.1.1.1.1._CA-5: The maximum amounts of identified degradation products of Flufenacet observed in each test soil.

Compound	Maximum concentration, expressed in %AR, observed in soil:		
	BBA 2.2 (Loamy sand)	Laacherhof (Silt loam)	Höfchen im Tal (Silt loam)
<i>FOE Sulfonic acid</i>	25.4 (DAT 100)	26.3 (DAT 100)	13.5 (DAT 100)
<i>FOE Oxalate</i>	6.6 (DAT 28)	15.6 (DAT 28)	10.0 (DAT 28)
<i>FOE Thioglycolate sulfide</i>	3.3 (DAT 56)	5.5 (DAT 28)	1.9 (DAT 28)
<i>FOE Methylsulfoxide</i>	1.1 (DAT 28, DAT 56)	3.5 (DAT 56)	1.5 (DAT 56)
<i>FOE Methylsulfone</i>	6.6 (DAT 100)	4.3 (DAT 120)	5.6 (DAT 120)

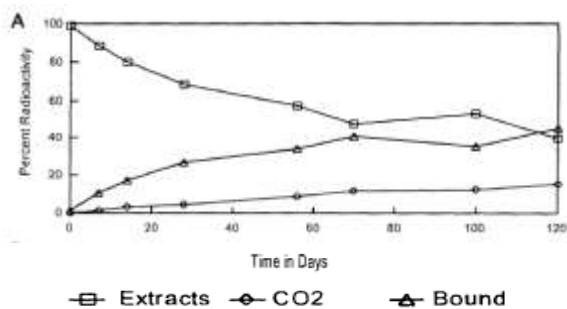
The detailed results are presented below, separately for each soil, in tables B.8.1.1.1.1._CA-6 – B.8.1.1.1.1._CA-8 (the values were rounded to one digit after the decimal point). Additionally they are presented in graphical form, on the paired graphs, presenting the distribution of radioactivity among extracts, NER fraction and CO₂ (left-hand side graph) and distribution of Flufenacet and its degradates (right-hand side graph) in each test soil, on figures B.8.1.1.1.1._CA-3 – B.8.1.1.1.1._CA-5, individually for each soil.

Table B.8.1.1.1.1._CA-6: The detailed results obtained in BBA 2.2 soil.

% AR		Results obtained for sample collected at DAT ¹⁾ :							
		0	7	14	28	56	70	100	120
<i>Extracted as:</i>	Water extract	20.7	23.2	20.5	22.8	18.7	17.9	18.9	17.1
	Organic extract 1	77.2	55.2	53.8	38.8	28.4	20.8	n. d. ⁵⁾	n. d. ⁶⁾
	Organic extract 2 ²⁾	n. d. ⁴⁾	2.5	4.1	7.5	8.2	9.3	37.2	20.3
	Total extracted	97.9	80.9	78.4	69.1	55.3	48.0	56.0	37.4
<i>In extracts identified as:</i>	Flufenacet	97.3	73.1	66.4	43.6	27.7	19.9	16.8	10.0
	FOE Sulfonic acid	0.0	2.4	3.9	9.5	12.3	17.8	25.4	22.6
	FOE Oxalate	0.0	3.7	5.4	6.6	4.0	0.6	0.0	0.0
	FOE Thioglycolate sulfoxide	0.0	1.6	2.2	3.1	3.3	0.9	0.3	0.0
	FOE Methylsulfoxide	0.0	0.0	0.0	1.1	1.1	0.5	0.3	0.0
	FOE Methylsulfone	0.0	0.0	0.2	1.1	2.8	2.6	6.6	4.7
	Unknown 1 (~6 min.)	0.3	0.0	0.0	1.9	3.3	5.7	2.7	0.0
	Unknown 2 (~31 min.)	0.0	0.0	0.2	0.3	0.1	0.0	0.0	0.0
	Unknown 3 (~32 min.)	0.2	0.0	0.2	0.5	0.1	0.0	0.0	0.0
	Unknown 4 (~38 min.)	0.0	0.0	0.0	0.3	0.0	0.0	0.0	0.0
	Unknown 5 (~40 min.)	0.1	0.0	0.0	1.2	0.3	0.0	4.0	0.0
	Total identified	97.9	80.8	78.5	68.9	55.2	48.0	56.1	37.3
Bound residues (NER fraction)		1.4	9.3	16.6	27.3	33.3	41.1	37.3	42.3⁷⁾
<i>Volatile compounds</i>	VOC	0.0 ⁸⁾	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	CO ₂	0.0 ⁸⁾	1.1	2.8	4.5	8.1	11.6	12.6	14.2
	Total volatile compounds³⁾	0.0	1.1	2.8	4.5	8.1	11.6	12.6	14.2
Total recovered AR		99.3	91.3	97.8	100.9	96.4	100.7	106.0	93.9

Footnotes to the table:

- 1) Values given as % theoretically Applied Radioactivity;
- 2) For samples collected on DAT 100 and DAT 120 that was major, sole organic extraction step, for the remaining samples additional extraction;
- 3) Values calculated by the RMS by adding the results obtained for VOC and those for CO₂;
- 4) Extraction not performed because milder extraction ("organic extract 1") considered sufficient by the Applicant;
- 5) For sample collected at that data point extraction with milder organic extrahent not performed, as considered insufficient;
- 6) For sample collected at that data point extraction with milder organic extrahent not performed, as considered insufficient; results of further Soxhlet and base extractions not taken into account;
- 7) Results of Soxhlet and base extractions, performed to further characterise NER fraction at that sampling point not taken into account;
- 8) Default value – it was assumed that at that time point level of volatile compounds formed would be negligible.

Distribution of AR among extractable, NER and CO₂ fractions:

Distribution of Flufenacet and its degradation products:

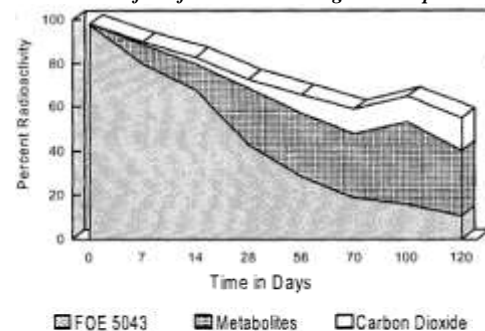


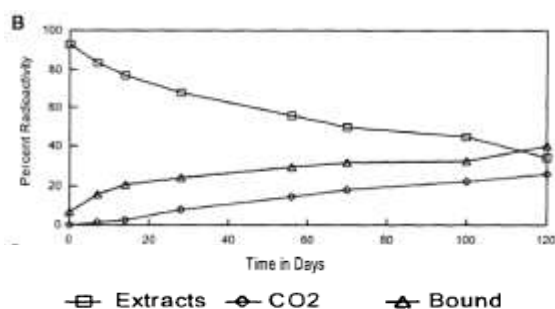
Figure B.8.1.1.1._CA-3: Graphical presentation of the results obtained in BBA 2.2 soil (copied from the study report).

Table B.8.1.1.1._CA-7: The detailed results obtained in Laacherhof soil.

% AR		Results obtained for sample collected at DAT ¹⁾ :							
		0	7	14	28	56	70	100	120
Extracted as:	Water extract	42.2	44.0	36.0	36.8	32.8	30.4	26.6	19.9
	Organic extract 1	44.5	29.0	32.2	20.8	10.6	8.2	n. d. ⁵⁾	n. d. ⁶⁾
	Organic extract 2 ²⁾	n. d. ⁴⁾	4.8	6.9	10.9	11.2	10.7	15.1	11.6
	Total extracted	86.7	77.8	75.1	68.5	54.6	49.3	41.7	31.5
In extracts identified as:	Flufenacet	85.3	57.2	47.2	23.6	6.2	4.7	3.2	2.8
	FOE Sulfonic acid	0.6	3.9	9.0	14.6	22.2	21.0	26.3	21.8
	FOE Oxalate	0.0	7.0	10.9	15.6	10.0	7.3	1.6	0.0
	FOE Thioglycolate sulfoxide	0.0	4.1	4.3	5.5	2.5	1.8	0.9	0.0
	FOE Methylsulfoxide	0.0	1.0	1.6	3.4	3.5	3.2	2.4	0.7
	FOE Methylsulfone	0.0	0.2	0.5	1.7	4.0	4.1	3.1	4.3
	Unknown 1 (~6 min.)	0.5	3.3	0.4	2.1	4.8	5.7	2.0	1.0
	Unknown 2 (~31 min.)	0.0	0.6	0.4	0.4	0.0	0.0	0.0	0.0
	Unknown 3 (~32 min.)	0.3	0.3	0.5	0.0	0.0	0.0	1.5	0.0
	Unknown 4 (~38 min.)	0.0	0.1	0.1	0.0	0.1	0.1	0.0	0.0
	Unknown 5 (~40 min.)	0.0	0.0	0.1	1.1	0.9	0.9	0.2	0.3
	Unknown 6 (~50 min.)	0.0	0.0	0.0	0.4	0.4	0.4	0.5	0.2
Total identified		86.7	77.7	75.0	68.4	54.6	49.2	41.7	31.1
Bound residues (NER fraction)		6.5	14.5	20.3	24.1	29.0	32.0	29.9	37.1⁷⁾
Volatile compounds	VOC	0.0 ⁸⁾	0.0	0.0	0.0	0.0	0.1	0.0	0.1
	CO ₂	0.0 ⁸⁾	1.2	2.6	7.9	14.2	18.1	20.8	23.8
	Total volatile compounds³⁾	0.0	1.2	2.6	7.9	14.2	18.2	20.8	23.9
Total recovered AR		93.2	93.5	98.0	100.5	97.8	99.5	92.4	92.5

Footnotes to the table:

- 1) Values given as % theoretically Applied Radioactivity;
- 2) For samples collected on DAT 100 and DAT 120 that was major, sole organic extraction step, for the remaining samples additional extraction;
- 3) Values calculated by the RMS by adding the results obtained for VOC and those for CO₂;
- 4) Extraction not performed because milder extraction ("organic extract 1") considered sufficient by the Applicant;
- 5) For sample collected at that data point extraction with milder organic extrahent not performed, as considered insufficient;
- 6) For sample collected at that data point extraction with milder organic extrahent not performed, as considered insufficient; results of further Soxhlet and base extractions not taken into account;
- 7) Results of Soxhlet and base extractions, performed to further characterise NER fraction at that sampling point not taken into account;
- 8) Default value – it was assumed that at that time point level of volatile compounds formed would be negligible.

Distribution of AR among extractable, NER and CO₂ fractions:

Distribution of Flufenacet and its degradation products:

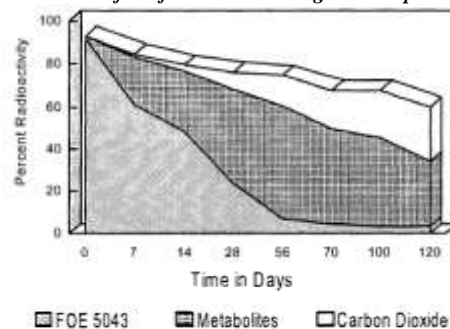


Figure B.8.1.1.1._CA-4: Graphical presentation of the results obtained in Laacherhof soil (copied from the study report).

Table B.8.1.1.1._CA-8: The detailed results obtained in Höfchen im Tal soil.

% AR		Results obtained for sample collected at DAT:							
		0	7	14	28	56	70	100	120
Extracted as:	Water extract	24.5	22.8	22.5	23.2	16.9	13.3	13.1	10.6
	Organic extract 1	68.4	62.0	43.9	31.7	17.8	15.8	n. d. ⁶⁾	n. d. ⁷⁾
	Organic extract 2	n. d. ⁵⁾	3.3	4.9	9.0	10.7	9.9	11.8	15.4
	Total extracted	92.9	88.2	71.2	63.9	45.4	39.0	24.9	26.1
In extracts identified as:	Flufenacet	91.4	76.9	54.5	37.2	14.0	11.1	4.9	5.6
	FOE Sulfonic acid	0.1	2.6	4.3	8.7	13.0	11.2	13.5	12.5
	FOE Oxalate	0.0	4.9	8.9	10.0	6.4	3.7	0.9	0.0
	FOE Thioglycolate sulfoxide	0.0	1.8	1.8	1.9	1.1	0.7	0.1	0.0
	FOE Methylsulfoxide	0.0	0.8	0.5	1.3	1.5	1.1	0.2	0.2
	FOE Methylsulfone	0.0	0.1	0.2	1.6	2.9	4.1	3.6	5.6
	Unknown 1 (~6 min.)	0.0	0.2	0.0	1.2	3.2	6.3	1.1	0.9
	Unknown 2 (~31 min.)	0.0	0.2	0.4	0.4	0.4	0.1	0.0	0.0
	Unknown 3 (~32 min.)	0.3	0.3	0.3	0.2	0.5	0.2	0.3	0.3
	Unknown 5 (~40 min.)	1.1	0.2	0.2	0.9	1.9	0.5	0.1	0.0
	Unknown 6 (~50 min.)	0.0	0.0	0.0	0.0	0.1	0.0	0.2	0.0
	Other ³⁾	0.0	0.1	0.0	0.6	0.2	0.0	0.1	0.0
	Total identified	92.9	88.1	71.1	64.0	45.2	39.0	25.0	26.1
Bound residues (NER fraction)		4.4	15.0	23.7	32.1	44.2	50.5	56.2	58.0
Volatile compounds	VOC	0.0 ⁹⁾	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	CO ₂	0.0 ⁹⁾	0.8	1.7	4.4	7.2	9.4	10.2	12.0
	Total volatile compounds⁴⁾	0.0	0.8	1.7	4.4	7.2	9.4	10.2	12.0
Total recovered AR		97.3	103.9	96.7	100.4	96.8	98.9	91.3	96.0

Footnotes to the table:

- 1) Values given as % theoretically Applied Radioactivity;
- 2) For samples collected on DAT 100 and DAT 120 that was major, sole organic extraction step, for the remaining samples additional extraction;
- 3) Various minor peaks occurring only once per HPLC retention time;
- 4) Values calculated by the RMS by adding the results obtained for VOC and those for CO₂;
- 5) Extraction not performed because milder extraction ("organic extract 1") considered sufficient by the Applicant;
- 6) For sample collected at that data point extraction with milder organic extrahent not performed, as considered insufficient;
- 7) For sample collected at that data point extraction with milder organic extrahent not performed, as considered insufficient; results of further Soxhlet and base extractions not taken into account;
- 8) Results of Soxhlet and base extractions, performed to further characterise NER fraction at that sampling point not taken into account;
- 9) Default value – it was assumed that at that time point level of volatile compounds formed would be negligible.

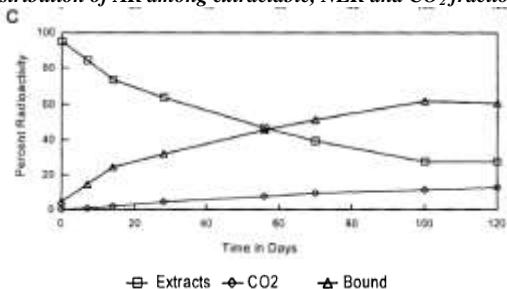
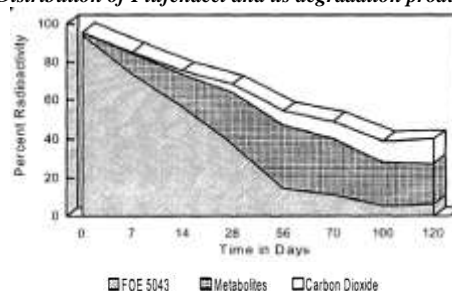
Distribution of AR among extractable, NER and CO₂ fractions:*Distribution of Flufenacet and its degradation products:*

Figure B.8.1.1.1.-CA-5: Graphical presentation of the results obtained in Höfchen im Tal soil (copied from the study report).

The results of the further examination of Bound Residues (NER) fraction are presented below, in the table B.8.1.1.1.-CA-9. For all three soils was performed a two-step extraction:

- **Step 1:** Soxhlet extraction with 0.1N HCl_{aq}:CH₃CN solution;
- **Step 2:** Stir heating extraction with 1N NaOH.

Only for Höfchen im Tal soil, in which the amount of the formed NER fraction was the highest – 58.0% AR, the additional steps were included.

The **Step 1** extraction resulted in extracting additional 2.6 – 3.5% TAR (theoretically applied radioactivity). The chromatographic (HPLC) analysis of that fraction demonstrated that it consisted mainly of degradation products, as shown on figure B.8.1.1.1.-CA-6.

Step 2 extraction enabled to recover further 19.9 – 31.4% TAR, consisting mostly of degradation products, as demonstrated chromatographic (HPLC) analysis of the extract. It was however pointed out that results of the identification and quantitation of that extract's constituents were of limited reliability, because the extraction method was demonstrated to be too harsh and destructive for Flufenacet (it was shown that Flufenacet added to Höfchen im Tal soil and then extracted using that method was partly degraded).

No further attempts to identify the NER fraction were undertaken.

Table B.8.1.1.1.-CA-9: The results of characterisation of NER fraction in DAT 120 samples.

Process		Results [%AR] obtained for soil:		
		BBA 2.2 (Loamy sand)	Laacherhof (Silt loam)	Höfchen im Tal (Silt loam)
<i>Original extraction method (see tables B.8.1.1.1.-CA-6 – B.8.1.1.1.-CA-8 above)</i>	Water extract	17.53	19.61	10.87
	Organic extract	20.61	12.21	15.06
	NER fraction	43.02	38.11	58.05
<i>Additional extraction for NER characterisation</i>	NER – initial level	43.02	38.11	58.05
	Soxhlet, 0.1N HCl:CH ₃ CN	2.61	3.48	2.97
	Soxhlet, CH ₃ COOC ₂ H ₅	Not performed	Not performed	0.17
	Soxhlet, CH ₂ Cl ₂	Not performed	Not performed	0.53
	Soxhlet, MeOH	Not performed	Not performed	0.60
	Stir heating with 1N HCl	Not performed	Not performed	2.02
	Stir with 1N NaOH	25.77	19.92	31.44
	Total extracted	28.38	23.40	45.73
	NER remaining	14.64	14.71	12.32

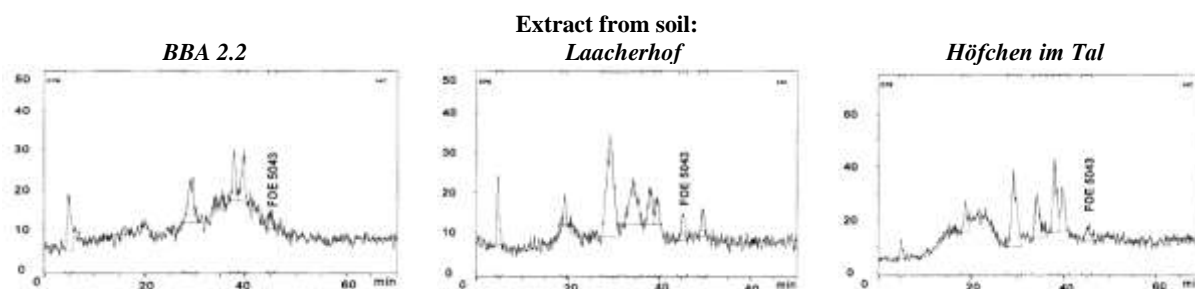


Figure B.8.1.1.1._CA-6: The results of the HPLC analysis of Step1 extracts from each test soil (copied from the study report).

The results obtained for Flufenacet in each soil were kinetically evaluated to obtain the kinetic endpoints – DT_{50} and DT_{90} values. Although that kinetic analysis was presented in details in the study report, it was not included into the summary as not complying with the current standards.

The results were kinetically re-examined, and the results of that examination presented in the separate report, which will be summarised under the relevant point of this Assessment Report – B.8.1.1.2.1.1.

Conclusions:

The obtained results showed that Flufenacet was extensively degraded in all three soils during 120 days, reaching the level of 2.8 – 10.0% AR at the end of the study.

Several degradation products were detected, of which five were identified: FOE Sulfonic acid, FOE Oxalate, FOE Thioglycolate sulfoxide, FOE Methylsulfoxide and FOE Methylsulfone. Three of them are considered major according to the current Guidelines: FOE Sulfonic acid (max. 13.5 – 26.3% AR), FOE Oxalate (max. 6.6 – 15.6% AR) and FOE Methylsulfone (max. 4.3 – 6.6% AR). It shall be noted that FOE Methylsulfone met the relevance criteria due to the fact that it was still forming, with concentrations increasing, at the end of the study. All other detected degradates, both identified and unknown, may be considered as minor degradates and transformation products.

The level of mineralization, measured by the amounts of $^{14}CO_2$ formed, was 12.0 – 23.8% AR. Formation of NER was significant, reaching the level of 37.1 – 58.0% AR. The additional extraction using the non-destructive methods enabled to obtain only 2.6 – 3.5% of additional AR, mainly identified as degradation products.

Extraction of NER with much harsher method, destructive for Flufenacet, led to additional extraction of 20 – 31.5% AR, mainly in form of degradation products.

On the basis of obtained results the Applicant proposed the following transformation pathway of Flufenacet in aerobic soil, determined for the compound radiolabelled uniformly in phenyl ring – Fig B.8.1.1.1._CA-7. It shall be noted that the proposed transformation scheme takes into account also the findings of the earlier study by Pangilinan and Smith [1994], summarised below as **Study 2**. It contains two degradation products – FOE Chloroacetanilide and FOE Alcohol not found in this study, but in that by Pangilinan and Smith [1994]. It shall be also pointed out that the proposed by-product – FOE Cysteine Conjugate was not detected in any study examining the route of degradation of Flufenacet in soil, but it was assumed to be formed as a logical intermediate.

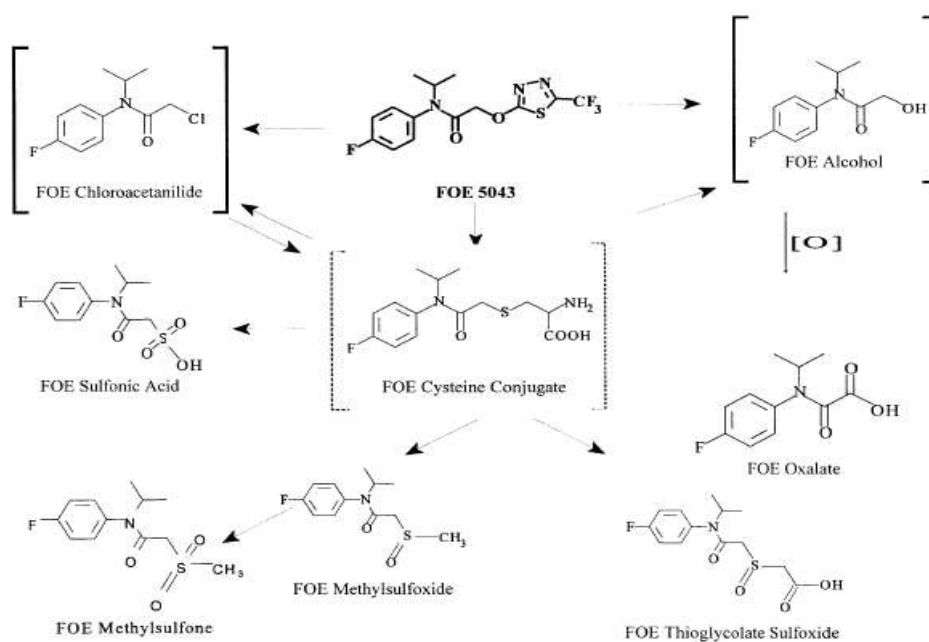


Figure B.8.1.1.1._CA-7: The transformation pathway of Flufenacet in aerobic soil, determined for the compound radiolabelled in phenyl ring (scheme copied from the study report).

The results obtained for Flufenacet were kinetically examined and the results of that kinetic assessment were presented as a part of the study report. However, as it did not comply with the current standards, set by FOCUS Kinetics Guidance Document [FOCUS, 2006] it was decided not to present it in the summary.

Study 2:

Report: Pangilinan N. C., Smith D. M., (1994): “Aerobic Soil Metabolism of [Phenyl-U-¹⁴C] FOE 5043”; Miles Inc., Agriculture Division, Research and Development Department, P. O. Box 4913, Kansas City, Missouri 64120-0013, USA; study No. F3042102; unpublished Miles Report No. MR 106408; 12 May 1994; study reference number: M-002166-01-1;

Guidelines: The study was performed to comply with the following Guidelines:

- US. EPA Guidelines for Pesticide Registration, Subdivision N, Section 162-1;

GLP: Yes;

RMS comments: The study had been evaluated for the previous authorisation of Flufenacet in the EU. Its summary can be found under the point B.7.1.1.1.1., in section B.7 of the Annex B to the Monograph prepared by the RMS – France, for Flufenacet. At present the study was evaluated for its compliance with OECD Guideline 307 – Aerobic and Anaerobic Transformation in Soil. Additionally RMS checked its compliance with the SETAC Guidelines on performing the laboratory test on aerobic degradation in soils, presented in *M. Lynch (ed.) “Procedures for Assessing the Environmental Fate and Ecotoxicity of Pesticides.”*, SETAC, 1995. Also the US EPA Guideline indicated by the Applicant - US. EPA Guidelines for Pesticide Registration, Subdivision N, Section 162-1, was consulted. In course of that verification the following deviations from the Guidelines and problems were stated:

- The test soil displayed a very low average OM/OC content, well below the recommended OC = 0.5%, and highly variable. In the study report not only the declared average OM = 0.6%, corresponding to OC = 0.35%, but also it was in range 0.2 – 1.2%, depending on the year, in which the test soil was characterised. That may indicate that the test soil was very inhomogeneous with regard to OC content, what in turn might have influenced the obtained results. That feature was reported in the previous Assessment Report for Flufenacet prepared by the RMS – France, but not indicated as deviation disqualifying the study as not valid;
- There was a significant decrease in soil microbial activity observed in the test soil. It was stated that the phenomenon occurred at 30-th day after application of the test substance, when the collapse of the soil microbial activity was observed. Afterwards the steady decline in microbial activity occurred. The results however were not definitive, as two different methods of the determination of microbial activity in the test soil were used. The phenomenon was examined thoroughly by Applicant and the results of that examination presented in the study by Hellpointner (1995) in the report submitted as a part of the Dossier evaluated for the first authorisation of Flufenacet in the EU. The same study was evaluated and will be summarised under this point of the DRAR, as **Study 3**, immediately below the summary of this study. It shall be noted that the problem was noticed by the former RMS – France, but not considered as disqualifying the study;
- The test soil was preconditioned prior to its use by storing it in greenhouse in two 5-gallon (~19-L) buckets. Soybean plants were planted on the soil surface during that period to maintain its microbial viability. The samples of the test soil samples taken to the laboratory at the beginning of the experiment were pre-treated by sieving and air-drying, but afterwards they were not pre-conditioned as recommended by OECD 307 Guideline. That fact was not stated in the summary provided in the previous Assessment Report. It may possibly be the reason for the sudden collapse of soil microflora observed in the test systems ~30 days after the experiment started;
- Test substance was applied in form of the treatment solution being a mixture of CH₃CN: H₂O in ratio 1:4. That deviation from the Guidelines (OECD 307 Guideline recommends to prepare the treatment solution with water and only a small addition of any organic solvent not demonstrated to inhibit microbial activity; also the verification of the influence of such treatment solution on soil microbial activity is recommended prior to the treatment) was also not indicated in the previous DAR.

No other deviations were found in the study report. Despite those listed above RMS decided to consider the study acceptable, mainly because it provides the data on the route of degradation of Flufenacet in soil not reported in the summarised above **Study 1**. It is summarised below in its part related to the route of degradation, while for the rate of degradation the information is placed under the point B.8.1.1.2.1.

Summary:

The aim of the study was to investigate the fate – route and rate of degradation, of Flufenacet in soil incubated under controlled (in the laboratory) aerobic conditions. The experiment was performed using one test soil originating from the US (Howe, Indiana). Its characteristic is provided below in the table B.8.1.1.1.1_CA-10. It shall be noted that in the study report the table on soil characterisation provides the results for three different batches, then averaged. RMS decided to present all the results of that characterisation, as they were reported in the original study's report. The results of the determination of the microbial biomass are presented separately in the table B.8.1.1.1.1_CA-11 immediately following the main table presenting the test soil properties.

Table B.8.1.1.1.1_CA-10: The characteristic of soil used in the study.

Parameter		Soil: 395			
Soil origin		Howe, Indiana, USA			
Batch analysed		A ¹⁾	B ²⁾	C ³⁾	Average
Soil type (USDA)		Sandy loam	Sandy loam	Sandy loam	Sandy loam
Particle size distribution	Sand [%]	72.5	77.5	70.4	73.5
	Silt [%]	20.0	17.2	20.0	19.1
	Clay [%]	7.5	5.3	9.6	7.5
pH value (in water, 1:1)		6.1	6.4	6.2	6.2
pH value in CaCl ₂ ⁴⁾		5.5	5.9	5.6	5.6 ⁵⁾
Organic matter content (OM) [%]		0.2	0.4	1.2	0.6
Organic carbon content (C _{org}) [%] ⁵⁾		0.12	0.23	0.70	0.35
Cation Exchange Capacity – CEC [mEq/100g]		6.9	7.4	5.1	6.5
Bulk density (disturbed) [g/cm ³]		1.31	1.33	1.47	1.37
Moisture holding capacity at ½ bar [%]		14.8	13.1	11.4	13.1

Footnotes to the table:

- 1) Analysis performed by Agvise Inc. on 13 August 1991;
- 2) Analysis performed by Agvise Inc. on 4 February 1992;
- 3) Analysis performed by A&L Great Lakes Laboratories Inc. on 29 March 1993;
- 4) Value recalculated by the RMS using the following equation: $pH_{H_2O} = 0.982 pH_{CaCl_2} + 0.648$;
- 5) Value calculated from the corresponding pH in water;
- 6) Value calculated by RMS using the following relationship: OC = OM/1.724.

Table B.8.1.1.1.1_CA-11: The results of the determination of soil microbial biomass.

Time point - DAT	Results of the determination of the soil microbial biomass obtained in					
	biomass test I ¹⁾ , expressed as:		biomass test II ²⁾ , expressed as:			
	mg microbial C/kg soil	% of OC ³⁾	mg microbial C/kg soil		% of OC ³⁾	
			Rep. 1.	Rep. 2	Rep. 1.	Rep. 2
0	n. a. ⁴⁾	----	266	258	7.6	7.4
14	n. a.	----	211	202	6.0	5.8
30/33	157 ⁵⁾	4.49	181	181	5.2	5.2
104	29	0.83	n. a. ⁶⁾	n. a. ⁶⁾	n. a. ⁶⁾	n. a. ⁶⁾
327	18	0.51	n. a. ⁶⁾	n. a. ⁶⁾	n. a. ⁶⁾	n. a. ⁶⁾
369	27	0.77	n. a. ⁶⁾	n. a. ⁶⁾	n. a. ⁶⁾	n. a. ⁶⁾

Footnotes to the table:

- 1) The measurements performed specifically for the determination of the biomass in soil during the experiment;
- 2) The measurement performed independently at the Institute for Metabolism Research, Bayer AG, Germany, to determine the effects of storage on soil microbial population, on soils not treated with the test compound; samples were analysed using the method described by Anderson and Domsch;
- 3) Values calculated using the average OC content – 0.35%, reported in the table B.8.1.1.1.1_CA-10 above;
- 4) Value not reported as the samples were not analysed using either the method by Anderson and Domsch or that by Vance;
- 5) Analysis performed for soil sample collected on DAT 33, using the method by Vance;
- 6) Not available – the experiment was still ongoing when the currently summarised study report was finalised, so its full results will be presented as a summary of **Study 3** (Hellpointner; 1995).

Soil biomass in the test soil was determined using one of the following three methods:

- 1) analysis for ester-linked phospholipid fatty acids (PLFA);
- 2) soil fumigation method described by Vance et al;
- 3) method described by Anderson and Domsch.

The test soil was taken from a Miles Research Farm in Howe, Indiana, USA and placed in two ~19L buckets in the greenhouse. In order to maintain its microbiological viability soil was planted with soybean until the beginning of the study.

Immediately before the experiment began, ~2 kg of soil from the top 5-6 inch (corresponding to 12-15 cm) layer was taken to the laboratory, where the soybean plants were removed and moist soil sieved through 2-mm sieve. Then the test soil was air-dried for 2 hours to the level of 75% of $\frac{1}{3}$ bar (the soil moisture level kept throughout the experiment) and placed in the test vessels.

The test substance used in the experiment was the ^{14}C -FOE 5043 radiolabelled uniformly in phenyl ring, as shown below on figure B.8.1.1.1.1._CA-8.

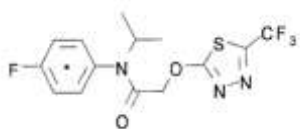


Figure B.8.1.1.1.1._CA-8.: The structural formula of the radiolabelled Flufenacet (FOE 5043) used in the experiment (copied from the study report).

The specific radioactivity of the test compound used in the experiment was 66.5 mCi/mmol and its radiochemical purity, determined with TLC, was 98.9%. Its radiochemical purity determined at the time of the treatment was 98.4%. It was applied to the test soil in incubation vessels in form of the application solution prepared in the following way: 296 μg of [phenyl- ^{14}C]-Flufenacet was evaporated to dryness under gentle stream of nitrogen and then redissolved in 2 mL of CH_3CN (acetonitrile), to which 8 mL of distilled water was added next. The so prepared solution was stirred and 60 mL of $\text{CH}_3\text{CN}:\text{H}_2\text{O}$ 1:4 solution was added. The concentration of so prepared solution was verified by LSC. It was determined to be 55.06 mg Flufenacet/L.

The experiment was performed using the glass biometer flasks, presented below on figure B.8.1.1.1.1._CA-9.

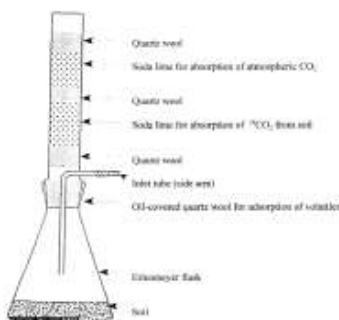


Figure B.8.1.1.1.1._CA-9: The biometer flask used in the experiment (scheme copied from the study report).

They consisted of 250-mL Erlenmeyer flasks with wide-diameter glass tube adapters, sealed with traps for volatile compounds. The traps consisted of a glass adapter containing ~1g plug of glass wool soaked with 2% mineral oil in hexane to absorb possible VOC, and soda lime layer (~10 g.) to capture formed $^{14}\text{CO}_2$. These sorbents were capped with a layer of glass wool (separator) above which further ~4-grams layer of soda lime was placed to prevent soda-lime sorbent from being saturated with atmospheric CO_2 . On the top 4-grams layer of glass wool was placed. The side-arm inlet tube, sealed with a rubber septum was set to enable the adjustment of soil moisture by adding the necessary amounts of distilled water during the study.

Each test vessel contained the equivalent of 100 grams of oven-dried test soil, adjusted to soil moisture content of 75% of $\frac{1}{3}$ bar by addition of the appropriate amount of the distilled water. That level was maintained throughout of the incubation period, lasting up to 365 days.

In total 43 incubation flask were prepared, of which 25 were used for kinetic tests, 3 for the non-sterile control, 3 for microbial biomass determination, 7 as test spares and 5 for metabolite isolation.

The test flasks were treated with the test substance, applied to the soil surface in form of the application solution described above, at a rate of 1.101 mg/kg. Applicant declared that it corresponded to approximately field application rate of 0.8 lbs a. i./acre, assuming soil depth of 3 inches and soil bulk density of 1.33 g/cm^3 . When recalculated by the RMS as g/ha, assuming soil depth of 5 cm and soil bulk density of 1.5 g/cm^3 , the exact

application rate was **825.75** g Flufenacet/ha. The use of the measured average soil bulk density – $d = 1.37 \text{ g/cm}^3$, resulted in the application rate of **754.185** g Flufenacet/ha.

The amount of the application solution introduced into each test vessel was 2 mL, applied dropwise to the soil surface using Hamilton 500 μL syringue, what resulted in 110 μg Flufenacet per flask. Each flask was gently shaken after introducing each 500 μL -portion of the application solution, to grant the even distribution of the test compound in soil.

Control and microbial biomass flasks were treated with 2-mL portions of blank solvent carrier ($\text{CH}_3\text{CN}:\text{H}_2\text{O}$ 1:4 v/v).

After treatment the appropriate amount of distilled water was added to each test vessel to establish a soil moisture of 75% of $\frac{1}{3}$ bar.

After treatment the Erlenmeyer incubation flask were sealed with traps for volatile compounds, weighed and covered with aluminium foil to exclude light.

So prepared incubation systems were placed in an incubator chamber and incubated in the darkness at $T = 21 \pm 1^\circ\text{C}$ (temperature range $T = 20.7 - 21.6^\circ\text{C}$) for up to 365 days. The temperature in the incubation chamber was monitored continuously. Soil moisture was monitored every week and corrected adequately, when necessary.

Trapping towers for formed volatile compounds were replaced at 6th month of incubation. Additionally, at the 11th month of incubation top layer of the soda lime (trap for atmospheric gasses) was replaced.

Samples were removed for the analysis at DAT (Days After Treatment) 0, 7, 14, 21, 28, 44, 65, 76, 91, 180, 271 and 365. In case of DAT 0 sampling point triplicate analysis was performed, while for all remaining 11 sampling points duplicate samples were prepared. In case of DAT 0 samples the traps for volatile compounds were not set and the soils were analysed almost immediately (1 hour) after treatment with the test compound.

The adjustment of soil moisture was performed in 1-week intervals by weighing the incubation flasks and, when necessary, introducing the appropriate amounts of distilled water through the side-arm inlet tube.

At the designated time points duplicate test flasks were removed from the incubation chamber and for 10 minutes purged with N_2 , administered at the flow rate of 500 mL/min, in order to flush the produced CO_2 and VOCs into the traps.

The collected traps for volatile compounds were removed and analysed for their content of trapped radioactivity. That was done in a following way: the traps were dissected, mineral oil coated glass wool transferred into 250-mL Erlenmeyer flask and extracted by sonication for at least 30 min with 50 mL of $\text{CH}_3\text{COOC}_2\text{H}_5$. The organic extract was then collected by decantation and its triplicate aliquots analysed by LSC. Soda lime traps were transferred to 150-mL flasks, being a part of a specially designed extraction apparatus, shown below on figure B.8.1.1.1.1.-CA-10, to which 10 mL of water was added next.

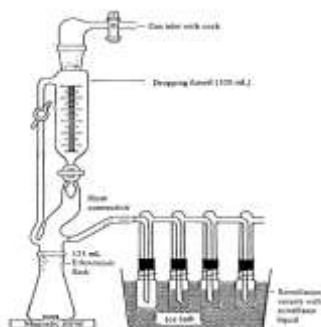


Figure B.8.1.1.1.1.-CA-10: The apparatus used for the liberation of $^{14}\text{CO}_2$ (copied from the study report).

The system was put under the constant flow of N_2 (~20 mL/min) and 50 mL of 12N HCl was gently added. The released CO_2 was trapped in three vessels, each containing 10 mL of the mixture of Carbo-sorb E and Permafluor-E⁺ (3:5), and analysed by LSC.

Next soils from each test vessel were analysed. That was done by extracting the entire soil samples in a sequential multistep extraction procedure, shown below on figure B.8.1.1.1.1.-CA-11. ACN stands for acetonitrile (CH_3CN).

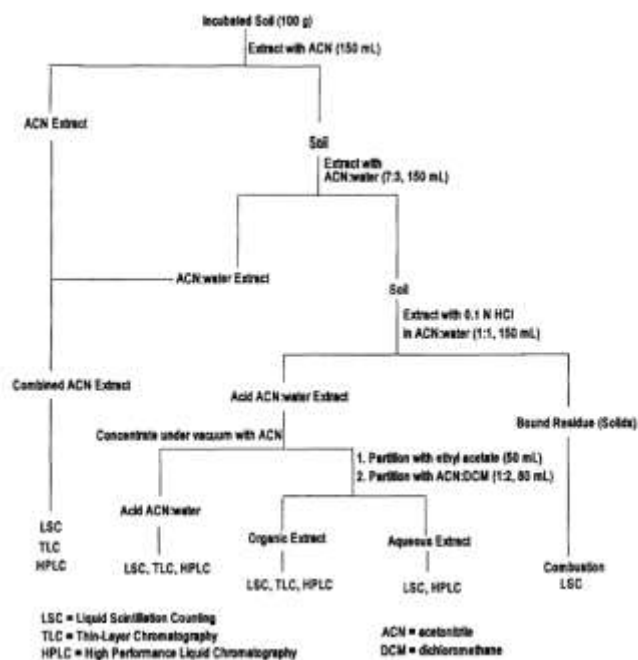


Figure B.8.1.1.1.-CA-11: A multistep soil extraction procedure used in the experiment (scheme copied from the study report).

The ACN and ACN:H₂O extracts were combined and concentrated under vacuum, then analysed. The acid extracts – 0.1N HCl_{aq}:ACN (1:1), were treated in three different ways:

- Acid extracts from DAT 0, DAT 7 and DAT 14 samples were evaporated under vacuum to ~50 mL and fractionated with ethyl acetate (CH₃COOC₂H₅). The ethyl acetate fractions were collected, dried over anhydrous Na₂SO₄ and halved. One half of each extract was concentrated under the stream of N₂ and passed through pre-conditioned Sep-Pak C-18 cartridges, subsequently eluted with CH₃CN and CH₃CN:H₂O (3:7 v/v). The cleaned-up residues were dissolved in CH₃CN:H₂O (3:7 v/v) and analysed by HPLC.
- All acid extracts from DAT 28 and DAT 65 and ½ of those from DAT 21 and DAT 44 were azeotropically concentrated using CH₃CN under vacuum. That was done to minimise the would be losses from excessive sample work-up. Extracts were concentrated, without prior partitioning with any organic solvent, to ~5 mL and transferred quantitatively, by subsequent flushing the evaporation vessels with small portions of MeOH, to 13-mL centrifuge tubes. The aliquots were analysed, after filtration through 5-µm PTFE filters, by HPLC. No losses of radioactivity were observed as a result of azeotropic concentration followed by filtration procedure.
- Acid extracts from DAT 76, DAT 91, DAT 180, DAT 271 and DAT 365 samples were initially concentrated to 60 mL, partitioned with 100 mL of CH₂Cl₂, followed by partitioning twice with CH₃CN:CH₂Cl₂ (1:2) solution (~80 mL). Organic and aqueous extracts were radioassayed and concentrated under vacuum to ~5 mL, after what quantitatively transferred to 13-mL centrifuge tubes.

In some extracts soil residues were observed upon their concentration. In such cases residues were repeatedly washed with either CH₃CN:H₂O (3:7 v/v) solution or MeOH and obtained extracts combined with supernatant solutions. Remaining residues were analysed by LSC for radioactivity content.

In case of solely DAT 180 samples the post-extraction residues were additionally extracted for ~1 hour with 150 mL of 0.1N NaOH solution in CH₃CN:H₂O. Extracts were then fractionated 3 times with 150 mL of CH₃CN:CH₂Cl₂ (1:2) solution. That extraction step was not repeated for any other samples as it was considered too harsh and expected to produce the analytical artefacts.

The extracted soil pellets were subsequently analysed for NER fraction. To do that each soil sample was allowed to air-dry overnight, after what its triplicate aliquots (50 – 100 mg) were oxidized by combustion. Formed ¹⁴CO₂ was trapped in alkaline solution and, after mixing with scintillation cocktail, analysed by LSC.

All samples were analysed for the content of radioactivity using LSC method. The LSC (Liquid scintillation counting) analysis was performed using a Packard Tri-Carb Model 4640 counter equipped with automatic external standardisation.

Liquid samples were radioassayed after addition of 15-20 mL of Ultima Gold solution to their 100 – 1000 μL aliquots, depending on sample. The minimum sensitivity of LSC analysis for these samples was 2.488 E-4 ppm , corresponding to $0.0226 \% \text{AR}$. When expressed as Lowest Acceptable Gross Count Rate (LAGC) it was 64 cpm, while as Lowest Acceptable Net Count Rate (LANC) – 32 cpm, assuming average background (BCGK) of 32 cpm ($\text{LAGC} = 2 \cdot \text{BCGK}$ and $\text{LANC} = \text{LAGC} - \text{BCGK}$). The greatest probable error $\text{GPE} = 9.24\%$.

Solid samples were oxidised using Packard Model 306 sample oxidizer, generated $^{14}\text{CO}_2$ trapped on 6 mL Carbo-sorb E and 15 mL Perma Fluor E. The minimum sensitivity of LSC analysis for those samples was 8.735 E-6 ppm , corresponding to $7.95 \text{ E-4 } \% \text{AR}$, and when expressed as Lowest Acceptable Gross Count Rate (LAGC) it was 64 cpm, while as Lowest Acceptable Net Count Rate (LANC) – 32 cpm, assuming average background (BCGK) of 32 cpm ($\text{LAGC} = 2 \cdot \text{BCGK}$ and $\text{LANC} = \text{LAGC} - \text{BCGK}$). The greatest probable error $\text{GPE} = 9.24\%$.

Sample extracts were analysed using the following techniques:

- HPLC – major identification and quantitation method for parent compound and its degradation products;
- TLC – secondary quantitation method for the parent compound and its degradation products;
- LC-MS – identification method for parent compound and its degradation products;
- GC/MS – supplementary identification method for parent compound and its degradation products.

The HPLC analysis was performed using a Hewlett Packard Model 1090 chromatograph coupled to Ramona 5-LS radioactivity monitor. Three following HPLC methods were used:

- Method A: gradient mode analysis performed using PRP-1, 5 μm , 150 x 4.1 mm chromatographic column (Hamilton Co., Reno) and PRP-1 cartridge as a guard column. The mobile phase consisted of water + 0.4% CH_3COOH as **Solvent A** and CH_3CN + 0.4% CH_3COOH as **Solvent B**. Gradient elution lasted 95 minutes. Its parameters are shown below in the table B.8.1.1.1.1._CA-12. The flow rate was set to 2 mL/min. The method was used generally, to analyse all extracts and was able to detect and radioactive residues $>1.0\% \text{ AR}$.
- Method B: gradient mode analysis performed using Selectosil 5, C-18, 5 μm , 250 x 4 mm chromatographic column (Phenomenex, California) and Brownlee cartridge, 5 μm , RP-18, as a guard column. The mobile phase consisted of water + 0.4% CH_3COOH as **Solvent A** and CH_3CN + 0.4% CH_3COOH as **Solvent B**. Gradient elution lasted 95 minutes. Its parameters are shown below in the table B.8.1.1.1.1._CA-12. The flow rate was set to 1 mL/min. The method was developed as first, but subsequently replaced by Method A, demonstrated to give the better resolution of Flufenacet from its degradation products. As a result only DAT 0 acid extracts were analysed using that method.
- Method C: gradient mode analysis performed using Spherisorb 32 (ODS2), 3 μm , 70 x 10 mm chromatographic column (Phenomenex, California) and RP-18 Spheri-5 cartridge as a guard column. The mobile phase consisted of water as **Solvent A** and CH_3OH as **Solvent B**. Gradient elution lasted 40 minutes. Its parameters are shown below in the table B.8.1.1.1.1._CA-12. The flow rate was set to 1 mL/min. The method was used to further purify the degradation products isolated from acid $\text{CH}_3\text{CN}:\text{H}_2\text{O}$ extracts from DAT 28 samples.

The LOD for the listed above chromatographic methods, in reference to the performance of the used radioactivity detector, was determined to be 1000 dpm, what corresponded to $1.0\% \text{ AR}$. The value was determined experimentally on the basis of the comparison of radioactivity injected and eluted (expressed in dpm, as determined by LSC). The results of that examination, aimed on the determination of both LOD and the linearity of HPLC analysis, are presented below in the table B.8.1.1.1.1.-CA-13. The linearity of the analysis, expressed as r^2 was: $r^2 = 0.999983$.

The identification of the chromatographic peaks was performed by means of the comparison of their retention times R_t with those of the standards. The retention times of each examined compound and for each HPLC method used in the experiment are presented below in the table B.8.1.1.1.1._CA-14.

Table B.8.1.1.1.1_CA-12: The HPLC gradient modes used in the study.

Method A:		
Time [min]	Solvent ratio	
	<i>Solvent A – Water + 0.4% CH₃COOH</i>	<i>Solvent B – Acetonitrile + 0.4% CH₃COOH</i>
0	100	0
0-25	Linear gradient	
25	75	25
25 - 40	75	25
40 - 75	Linear gradient	
75	30	70
75 - 85	Linear gradient	
85	0	100
85 - 95	0	100
Method B:		
Time [min]	Solvent ratio	
	<i>Solvent A – Water + 0.4% CH₃COOH</i>	<i>Solvent B – Acetonitrile + 0.4% CH₃COOH</i>
0	100	0
0-25	Linear gradient	
25	75	25
25 - 40	75	25
40 - 75	Linear gradient	
75	30	70
75 - 85	Linear gradient	
85	5	95
85 - 95	5	95
Method C:		
Time [min]	Solvent ratio	
	<i>Solvent A – Water</i>	<i>Solvent B – MeOH</i>
0	40	60
0 - 20	40	60
20 - 40	Linear gradient	
40	10	90

Table B.8.1.1.1.1_CA-13: The results of the determination of linearity and LOD of the HPLC analysis.

Sample No.	Radioactivity in [dpm]:		Integration ^{3, 4)}
	<i>Injected¹⁾</i>	<i>Eluted²⁾</i>	
1	1080734	1037270	86167
2	212100	203520	17118
3	106050	101760	8415
4	35350	33920	2592
5	7734	7422	628
6	2062	1979	184
7 ⁵⁾	1031	990	102

Footnotes to the table (for 1,2,3, as given in the study report):

- 1) Values determined by LSC analysis of the aliquots of the [¹⁴C]-Flufenacet standard solution injected, radioassayed prior to HPLC analysis;
- 2) Values determined by LSC analysis of the aliquots of HPLC eluents;
- 3) Regions of interest were integrated with background correction, determined at the beginning and the end of analysis;
- 4) Linearity of the analysis, expressed as r² value, was determined to be r² = 0.999983;
- 5) The value corresponding to LOD (by averaging the amount of injected and eluted it was set to LOD = 1000 dpm)

Table B.8.1.1.1.1_CA-14: Chromatographic – HPLC, identification of Flufenacet and its degradation products in the study.

Compound	HPLC identification – retention time (R_t) [min] determined for:		
	HPLC Method A	HPLC Method B	HPLC Method C
<i>Flufenacet (FOE 5043)</i>	78	74	30
<i>FOE Oxalate</i>	24	27	n. a. ¹⁾
<i>FOE Alcohol</i>	52	n. a. ¹⁾	n. a. ¹⁾
<i>FOE Sulfonic acid</i>	26	30	n. a. ¹⁾
<i>FOE Methylsulfide</i>	71	n. a. ¹⁾	21.5
<i>FOE Methylsulfoxide</i>	36	n. a. ¹⁾	n. a. ¹⁾
<i>FOE Methylsulfone</i>	58	n. a. ¹⁾	n. a. ¹⁾
<i>FOE Amine acetate</i>	60	n. a. ¹⁾	n. a. ¹⁾
<i>FOE Thioglycolate sulfoxide</i>	31	n. a. ¹⁾	n. a. ¹⁾
<i>FOE Amine</i>	26.5	n. a. ¹⁾	n. a. ¹⁾
<i>FOE Thiol acetate</i>	70	n. a. ¹⁾	16.6
<i>Hydroxy FOE Alcohol</i>	29.5	n. a. ¹⁾	n. a. ¹⁾
<i>FOE Cysteine conjugate</i>	29	n. a. ¹⁾	n. a. ¹⁾
<i>FOE N-Acetyl conjugate</i>	48	n. a. ¹⁾	n. a. ¹⁾
<i>des-Fluoro FOE Alcohol</i>	50	n. a. ¹⁾	n. a. ¹⁾
<i>4-FluoroAcetanilide</i>	36	n. a. ¹⁾	n. a. ¹⁾
<i>FOE 5043 N-isomer</i>	80	n. a. ¹⁾	n. a. ¹⁾
<i>Hydroxy Isopropyl FOE Sulfone</i>	n. a. ¹⁾	n. a. ¹⁾	5
<i>Hydroxy Isopropyl FOE Sulfoxide</i>	n. a. ¹⁾	n. a. ¹⁾	5
<i>FOE Chloroacetanilide</i>	70	n. a. ¹⁾	16

Footnotes to the table:

1) n. a. = not analysed using that method;

The TLC analysis of the extracts was performed in two modes:

- as RP-TLC (reversed phase TLC);
- as NP-TLC (normal phase TLC).

The RP-TLC analysis was performed using Whatman KC₁₈F TLC plates, having a dimensions 20x20 cm and 200- μ m thick, with a fluorescent indicator. The solvent system used in the analysis was CH₃CN:CH₃OH:0.5N NaCl_{aq} 2:2:1 (v/v) solution.

The NP-TLC analysis was performed using silica gel TLC plates, having a dimensions 20x20 cm and 250- μ m thick, with a fluorescent indicator. The solvent system used in the analysis was CHCl₃:CH₃COOC₂H₅:CH₃COOH 75:25:1 (v/v) solution.

The LOD was set to 1% AR for each individual compound detected. The quantitative analysis was performed using RITA 68000 Radio-TLC analyser. The LOD for this detector was determined to be 150 dpm. The results of determination of linearity and LOD of the detector are presented below in the table B.8.1.1.1.1.-CA-15.

The identification was performed by means of the comparison with the R_f values of the known standards. These values are provided below in the table B.8.1.1.1.1.-CA-16.

Table B.8.1.1.1.1_CA-15: The results of the determination of linearity and LOD of the TLC analysis.

Sample No.	LSC Counts Total dpm/band	Scanner Counts	
		dpm/ 600 sec	dpm/ 1200 sec
1	145	23	32
2	329	43	58
3	512	57	131
4	1033	103	224
5	1919	158	366
6	5594	549	1099
7	8788	962	1871
<i>Background</i>	----	9	15
<i>Correlation coefficient</i>	----	0.994	0.997

Table B.8.1.1.1.1_CA-16: Chromatographic – TLC, identification of Flufenacet and its degradation products in the study.

Compound	TLC identification – R_f value determined for:	
	RP-TLC	NP-TLC
<i>Flufenacet (FOE 5043)</i>	0.46	0.54
<i>FOE Oxalate</i>	0.84	0.00
<i>FOE Alcohol</i>	0.68	0.22
<i>FOE Sulfonic acid</i>	0.84	0.00
<i>FOE Methylsulfide</i>	0.57	0.41
<i>FOE Methylsulfoxide</i>	0.69	0.003
<i>FOE Methylsulfone</i>	0.72	0.23
<i>FOE Amine acetate</i>	0.59	0.34
<i>FOE Thioglycolate sulfoxide</i>	0.86	0.00
<i>FOE Amine</i>	0.53	0.51
<i>FOE Thiol acetate</i>	0.61	0.48
<i>Hydroxy FOE Alcohol</i>	0.85	0.008
<i>FOE Cysteine conjugate</i>	0.72	0.00
<i>FOE N-Acetyl conjugate</i>	0.82	0.00
<i>des-Fluoro FOE Alcohol</i>	0.72	0.26
<i>4-FluoroAcetanilide</i>	0.76	0.16
<i>Hydroxy Isopropyl FOE Sulfone</i>	0.85	0.01
<i>Hydroxy Isopropyl FOE Sulfoxide</i>	0.87	0.00
<i>FOE 5043 N-isomer</i>	0.48	0.59

The LC-MS analysis was performed using Varian 5040 HPLC equipped with a Regis Spherisorb S50DS column working in a gradient mode and Berthold LB 505-HPLC Radioactivity Monitor, coupled with Finnigan MAT 90 MS detector. The parameters of gradient were following:

- Mobile phase A: Water,
- Mobile phase B: CH₃OH,
- Gradient mode: linear from 0% B at 0 min to 100% B at 30 min.

The flow rate was set to 0.8 mL/min.

The reported parameters of MS detector were following:

- Spectrometer operated in either positive or negative mode,
- aerosol temperature: 210°C,
- 0.2 M ammonium acetate added post column at rate of 0.2 mL/min.

The identification of Flufenacet and its degradation products in LC/MS analysis was performed by comparison of mass spectra of each chromatographic peaks with those obtained for the standards, for which base peaks and protonated molecular ion peaks were identified. These are presented below in the table B.8.1.1.1.1_CA-17.

Table B.8.1.1.1.1_CA-17: LC/MS identification of Flufenacet and its degradation products in the study.

Compound	Representative signals used in identification	
	Position – m/z	Description
Flufenacet	364	Protonated molecular ion $[M+H]^+$
	381	Ammonia adduct $[M + NH_4]^+$
FOE Sulfonic acid	274	Peak for $[M - H]^-$ (negative-ion mode)
FOE Oxalate	226	Protonated molecular ion $[M+H]^+$
	243	Ammonia adduct $[M + NH_4]^+$
	224	Peak for $[M - H]^-$ (negative-ion mode)
FOE Methylsulfoxide	275	Protonated molecular ion $[M+H]^+$
	291	Ammonia adduct $[M + NH_4]^+$
FOE Alcohol	212	Protonated molecular ion $[M+H]^+$
FOE Thioglycolate sulfoxide	302	Protonated molecular ion $[M+H]^+$
	316	Protonated molecular ion $[M+H]^+$ for methylated derivative
FOE Chloroacetanilide	230	Protonated molecular ion $[M+H]^+$
	247	Ammonia adduct $[M + NH_4]^+$

GC/MS analysis was performed to confirm the identity of Flufenacet and FOE chloroacetanilide. It was carried out with HP Model 5995 Gas Chromatograph/Mass Spectrometer. GC was equipped with an Ultra-1 column (12 m x 0.2 mm x 0.3 µm film thickness).

Two different programmes were used:

- for Flufenacet GC oven was programmed to start at $T = 90^{\circ}\text{C}$, held at that level for $t = 1$ min, then the temperature increased linearly at rate of $20^{\circ}\text{C}/\text{min}$ up to $T = 250^{\circ}\text{C}$ and held at that level for $t = 1$ min; the injector's temperature was $T = 250^{\circ}\text{C}$; MS detector operated in the electron impact mode with a mass range 50 – 400 amu;
- for FOE Chloroacetanilide GC oven was programmed to start at $T = 85^{\circ}\text{C}$, held at that level for $t = 1$ min, then the temperature increased linearly at rate of $10^{\circ}\text{C}/\text{min}$ up to $T = 210^{\circ}\text{C}$ and held at that level for $t = 3$ min; the injector's temperature was $T = 255^{\circ}\text{C}$; MS detector operated in the electron impact mode with a mass range 50 – 400 amu.

Additionally two tests were carried out to determine the mechanism of the formation of FOE Chloroacetanilide – biotic (microbial degradation of Flufenacet or one of its degradation products) or abiotic (chemical degradation of Flufenacet or one of its degradation products) process.

Test 1 was performed in a test system with soil. Four flask were prepared, each containing 100 g (d.w.) of the test soil. Two flask were treated with [^{14}C]-Flufenacet at rate 1 ppm, the other two with [^{14}C]-FOE Alcohol at the same application rate. Since FOE Chloroacetanilide was primarily detected in acid extracts from samples collected at DATs 21, 28, 48 and 65, the samples in that experiment were similarly extracted and analysed by HPLC.

Test 2 was performed to determine the possibility of the formation of FOE Chloroacetanilide as a result of chemical reactions taking place during the sample processing. For that purpose the remaining acid extracts from DAT 44 samples were partitioned with $\text{CH}_3\text{CN}:\text{CH}_2\text{Cl}_2$ (1:2) solution. The resulting organic extracts were then partitioned and analysed by HPLC in the manner similar to that used for acid extracts obtained from samples collected at DATs 76, 91, 180, 271 and 365.

Results and their discussion:

The stability tests performed using DAT 0 samples demonstrated that the Flufenacet was stable during application and routine extraction procedure. It was also stated that the acidic extraction with 0.1N $\text{HCl}_{\text{aq}}:\text{ACN}$ (1:1) followed by the direct azeotropic concentration under vacuum may have resulted in some degradation of Flufenacet, but the phenomenon is expected to have a small impact on the obtained results.

As it was indicated, the extraction with 1N NaOH resulted in the decomposition of the test compound.

The analysis of the soil biomass showed that it was $> 1\%$ OC, although it shall be noted that the level of soil OC was very low – 0.35% on average, at the beginning of the study. Its sudden collapse was observed ~4 weeks after the beginning of incubation. At 30th day of incubation it was determined that ~30% die-out of the microbial population occurred and the process continued until ~3 months of incubation, when the steady state was reached. That might have influenced the obtained results, in particular the rate of degradation of Flufenacet, what demonstrated itself in bi-phasic degradation pattern.

The recovery of the applied radioactivity in the experimental soil was generally good, in line with the recommendations of the relevant Guidelines: 91.5 – 99.6% AR (average 95.4% AR).

The level of mineralization gradually increased throughout the study, to reach at its end (DAT 365) 5.9% AR. At the same time it shall be noted that it was not very high, in comparison to the results of other experiments with the compound radiolabelled at the same position, probably due to the significant decrease of microbial soil activity with time.

The amount of NER fraction also increased with time from 0.3% AR on DAT 0 to 17.7% AR on DAT 271. A slight decrease in the content of that fraction was observed at the end of the study. Also between the DAT 76 and DAT 271 it fluctuated – after reaching the level of 17.0% AR on DAT 76 it declined to 15.8% AR on DAT 180 to increase once again to 17.7% AR on DAT 271.

The amount of AR present as combined extractable fraction decreased with time, to reach at the end of the study (DAT 365) the level of 73.0% AR. It was also noted that while the amount of radioactivity extracted in combined acetonitrile (CH_3CN extract and $\text{CH}_3\text{CN}:\text{H}_2\text{O}$ 7:3 extract) extract decreased from 93.9% AR on DAT 0 to 52.7% AR on DAT 365, it increased in acidic 0.1N $\text{HCl}_{\text{aq}}:\text{ACN}$ (1:1) extracts from 0.9% AR on DAT 0 to 20.3 % AR on DAT 365.

The following compounds were identified in extracts:

- Flufenacet,
- FOE Sulfonic acid,
- FOE Oxalate,

- FOE Alcohol,
- FOE Thioglycolate sulfide,
- FOE Methylsulfoxide,
- FOE Chloroacetanilide,
- Other 7 unknown degradation products or degradation products fractions.

Of the compounds listed above the following may be considered as major on the basis of the criteria set by SANCO/211/2000 Guidance Document on the Assessment of the Relevance of Metabolites:

- FOE Oxalate: max 26.5% AR (DAT 365);
- FOE Sulfonic acid: max. 7.7% AR (DAT 180), with highest-occurrence profile on DATs: DAT 65 – 4.7% AR, DAT 76 – 6.0 % AR, DAT 91 – 5.5% AR, DAT 180 – 7.% AR, DAT 271 – 5.8 % AR.

The remaining four identified degradation products should be considered as minor with regard to their relevance to GW, and occurred in max amounts:

- FOE Alcohol: 2.1% AR (DAT 44 and DAT 65),
- FOE Thioglycolate sulfide: 3.7% AR (DAT 180),
- FOE Methylsulfoxide: 0.6% AR (DAT 28),
- FOE Chloroacetanilide: 5.1% AR (DAT 44).

The detailed results are presented below, in table B.8.1.1.1.1._CA-18 (the values were rounded to one digit after the decimal point) and additionally in graphical form, on figure B.8.1.1.1.1._CA-12.

Table B.8.1.1.1.1._CA-18: The detailed results obtained in the study.

% AR		Results obtained for sample collected at DAT ¹⁾ :											
		0	7	14	21	28	44	65	76	91	180	271	365
<i>Extracted as:</i>	Combined ACN extracts ²⁾	93.9	76.5	75.0	67.4	68.5	70.2	64.6	60.0	62.9	57.1	53.2	52.7
	Acidic extract ³⁾	0.9	8.5	9.6	9.9	11.0	12.2	13.9	18.1	11.9	18.5	18.7	20.3
	Total extracted	94.8	85.0	84.6	77.3	79.5	82.4	78.5	78.1	74.8	75.6	71.9	73.0
<i>In extracts identified as:</i>	Flufenacet	93.3	76.1	67.3	59.7	51.4	51.2	48.0	51.3	47.5	44.6	38.6	35.2
	FOE Oxalate	0.1	4.7	10.1	10.6	12.2	11.9	14.0	14.1	15.2	14.6	17.0	26.5
	FOE Sulfonic acid	<0.1	1.0	2.6	3.5	4.7	5.1	4.7	6.0	5.5	7.7	5.8	5.3
	FOE Alcohol	0.6	0.7	0.2	0.2	1.3	2.1	2.1	1.3	1.1	0.9	0.5	n.d ⁷⁾
	FOE TGS ⁴⁾	n.d ⁷⁾	0.4	1.6	1.7	1.7	1.7	1.8	2.4	2.3	3.7	3.6	2.8
	FOE Methylsulfoxide	n.d ⁷⁾	0.1	0.3	0.2	0.6	0.5	0.4	0.3	0.4	0.2	0.2	n.d ⁷⁾
	FOE Chloroacetanilide ⁵⁾	n.d ⁷⁾	n.d ⁷⁾	n.d ⁷⁾	0.4	4.2	5.1	4.1	0.1	n.d ⁷⁾	n.d ⁷⁾	n.d ⁷⁾	n.d ⁷⁾
	Unknown 1 (69 min.)	n.d ⁷⁾	n.d ⁷⁾	n.d ⁷⁾	n.d ⁷⁾	1.3	2.2	1.2	n.d ⁷⁾	n.d ⁷⁾	n.d ⁷⁾	n.d ⁷⁾	n.d ⁷⁾
	Unknown 2 (26.5 min.)	n.d ⁷⁾	n.d ⁷⁾	n.d ⁷⁾	n.d ⁷⁾	0.5	0.2	0.1	n.d ⁷⁾	1.1	2.4	0.7	0.7
	Unknown 3 (27 min.)	n.d ⁷⁾	n.d ⁷⁾	n.d ⁷⁾	n.d ⁷⁾	0.3	n.d ⁷⁾	n.d ⁷⁾	n.d ⁷⁾	0.9	0.3	n.d ⁷⁾	n.d ⁷⁾
	Unknown 4 (58 min.)	n.d ⁷⁾	n.d ⁷⁾	n.d ⁷⁾	0.1	0.6	0.6	0.7	0.9	0.8	0.7	0.9	n.d ⁷⁾
	Unknown 5 (60 min.)	n.d ⁷⁾	n.d ⁷⁾	0.1	0.3	0.2	0.5	0.4	0.4	0.1	n.d ⁷⁾	0.6	n.d ⁷⁾
	Unknown 6 (81 min.)	n.d ⁷⁾	1.4	1.4	0.2	1.0	1.0	0.9	1.1	1.6	0.8	0.7	0.6
	Unknown 7 (82 min.)	0.7	0.1	n.d ⁷⁾	0.5	n.d ⁷⁾	n.d ⁷⁾	0.2	n.d ⁷⁾	n.d ⁷⁾	0.4	0.5	n.d ⁷⁾
	Total identified⁶⁾	94.7	84.5	83.6	77.4	79.5	82.4	78.7	78.0	74.5	75.6	71.1	71.1
Bound residues (NER fraction)		0.3	6.7	11.8	13.0	15.0	15.2	16.1	17.0	16.3	15.8⁸⁾	17.7	16.5
<i>Volatile compounds</i>	VOC	n. a. ⁹⁾	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	CO ₂	n. a. ⁹⁾	0.4	0.6	1.2	1.3	2.0	2.2	2.3	2.7	4.0	4.6	5.9
	Total volatile compounds¹⁰⁾	n.a.	0.4	0.6	1.2	1.3	2.0	2.2	2.3	2.7	4.0	4.6	5.9
Total recovered AR¹¹⁾		95.1	92.0	97.0	91.5	95.8	99.6	96.8	97.4	93.8	95.4	94.2	95.4

Footnotes to the table:

- 1) Values presented are the averages of triplicate analysis for DAT 0 and of duplicate analysis for remaining time points;
- 2) Represents combined CH₃CN and CH₃CN:H₂O (7:3 v/v) extracts;
- 3) Represents 0.1N HCl in CH₃CN:H₂O (1:1 v/v) extract;
- 4) FOE TGS = FOE Thioglycolate sulfide;
- 5) It was postulated that FOE Chloroacetanilide might have formed in soil as a genuine degradation product and/or during sample work-up as a result of chemical transformation of either Flufenacet or FOE Alcohol;
- 6) The difference between the Total Extracted AR the Total identified AR was declared in the study report to be possibly due to three following factors: rounding of figures (1), presence of other HPLC resolvable degradation products, individually not exceeding 0.1% AR (2), presence of radiocarbon residues in acidic extracts that were below LOD for HPLC method (3);
- 7) n. d = not detected;
- 8) Includes residues released by alkaline extraction with 0.1N NaOH in CH₃CN:H₂O (1:1 v/v);
- 9) n. a. = not analysed – it was assumed that at that time point no volatile degradates were formed;
- 10) Value calculated by the RMS by adding the results obtained for VOC and those for CO₂;
- 11) Expressed as % of theoretically applied radioactivity.

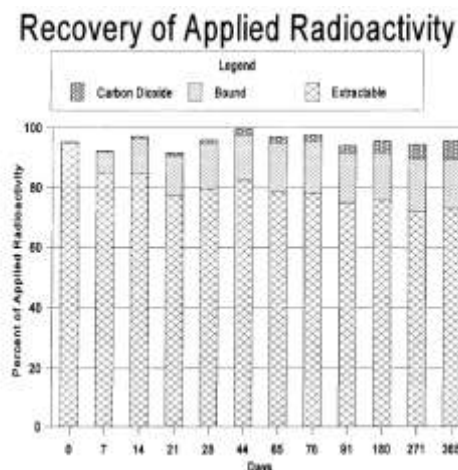


Figure B.8.1.1.1._CA-12: Graphical presentation of the obtained results (copied from the study report).

Additionally, below are presented the results of the HPLC analysis of combined ACN extracts – table B.8.1.1.1.1._CA-19, and acidic extracts – table B.8.1.1.1.1._CA-20.

Table B.8.1.1.1.1._CA-19: The detailed results of the examination of combined ACN extracts.

Compound	Results obtained for sample collected at DAT ^{1,2} :											
	0	7	14	21	28	44	65	76	91	180	271	365
<i>Flufenacet</i>	92.6	69.1	60.8	53.6	49.9	50.2	44.4	43.4	41.8	35.3	28.4	25.1
<i>FOE Oxalate</i>	n.d ⁶	4.2	9.0	9.0	10.6	11.0	11.8	8.3	11.3	9.3	11.9	19.2
<i>FOE Sulfonic acid</i>	n.d ⁶	1.0	2.6	3.0	3.9	4.4	4.0	3.9	4.5	5.8	5.8	5.3
<i>FOE Alcohol</i>	0.6	0.6	n.d ⁶	n.d ⁶	0.6	0.8	0.9	0.9	0.8	0.5	0.2	n.d ⁶
<i>FOE TGS³</i>	n.d ⁶	0.3	1.3	1.3	1.6	1.7	1.7	1.3	1.7	2.5	2.4	1.7
<i>FOE Methylsulfoxide</i>	n.d ⁶	n.d ⁶	n.d ⁶	n.d ⁶	n.d ⁶	n.d ⁶	n.d ⁶	n.d ⁶	n.d ⁶	1.1	2.4	0.7
<i>FOE Chloroacetanilide⁴</i>	n.d ⁶	n.d ⁶	n.d ⁶	n.d ⁶	0.4	0.5	0.2	0.2	0.3	0.2	0.2	n.d ⁶
<i>Unknown 1 (69 min.)</i>	Compound not reported in the relevant summary table in the study report.											
<i>Unknown 2 (26.5 min.)</i>	n.d ⁶	n.d ⁶	n.d ⁶	n.d ⁶	n.d ⁶	n.d ⁶	n.d ⁶	n.d ⁶	n.d ⁶	1.1	2.4	0.7
<i>Unknown 3 (27 min.)</i>	n.d ⁶	n.d ⁶	n.d ⁶	n.d ⁶	n.d ⁶	n.d ⁶	n.d ⁶	n.d ⁶	n.d ⁶	0.9	0.3	n.d ⁶
<i>Unknown 4 (58 min.)</i>	n.d ⁶	n.d ⁶	n.d ⁶	n.d ⁶	0.6	0.6	0.7	0.7	0.7	0.7	0.8	n.d ⁶
<i>Unknown 5 (60 min.)</i>	n.d ⁶	n.d ⁶	n.d ⁶	n.d ⁶	n.d ⁶	n.d ⁶	n.d ⁶	0.1	n.d ⁶	n.d ⁶	n.d ⁶	n.d ⁶
<i>Unknown 6 (81 min.)</i>	n.d ⁶	1.3	1.2	n.d ⁶	1.0	1.0	0.8	0.9	1.5	0.6	0.5	0.6
<i>Unknown 7 (82 min.)</i>	0.7	n.d ⁶	n.d ⁶	0.5	n.d ⁶	n.d ⁶	0.2	n.d ⁶	n.d ⁶	0.3	0.4	n.d ⁶
Total⁵	93.9	76.5	74.9	67.4	68.6	70.2	64.7	59.7	62.6	57.2	53.3	49.6

Footnotes to the table:

- 1) Values presented are the averages of triplicate analysis for DAT 0 and of duplicate analysis for remaining time points;
- 2) Represents combined CH₃CN and CH₃CN:H₂O (7:3 v/v) extracts;
- 3) FOE TGS = FOE Thioglycolate sulfoxide;
- 4) It was postulated that FOE Chloroacetanilide might have formed in soil as a genuine degradation product and/or during sample work-up as a result of chemical transformation of either Flufenacet or FOE Alcohol;
- 5) The difference between the **Total** value reported here and the (**extracted as**): **Combined ACN extracts** reported in the table B.8.1.1.1.1._CA-18 above, was postulated in the study report to be possibly due to the two following factors: rounding of figures (1), presence of other HPLC resolvable degradation products, individually not exceeding 0.1% AR (2);
- 6) n. d = not detected.

Table B.8.1.1.1.1. CA-20: The detailed results of the examination of acidic extracts.

Compound	Results obtained for sample collected at DAT ^{1, 2} :											
	0	7	14	21	28	44	65	76	91	180	271	365
Flufenacet	0.7	7.0	6.5	6.1	1.6	1.0	3.6	7.9	5.6	9.3	10.1	10.1
FOE Oxalate	0.1	0.4	1.1	1.6	1.6	1.0	2.1	5.8	3.9	5.3	5.1	7.2
FOE Sulfonic acid	<0.1	n.d ⁽⁶⁾	n.d ⁽⁶⁾	0.5	0.8	0.7	0.7	2.1	1.0	1.9	n.d ⁽⁶⁾	n.d ⁽⁶⁾
FOE Alcohol	n.d ⁽⁶⁾	0.1	0.2	0.2	0.7	1.3	1.2	0.4	0.3	0.3	0.3	n.d ⁽⁶⁾
FOE TGS ⁽³⁾	n.d ⁽⁶⁾	0.1	0.4	0.4	0.1	n.d ⁽⁶⁾	0.2	0.1	<0.1	n.d ⁽⁶⁾	n.d ⁽⁶⁾	1.1
FOE Methylsulfoxide	n.d ⁽⁶⁾	0.1	0.3	0.2	0.2	n.d ⁽⁶⁾	0.2	0.1	<0.1	n.d ⁽⁶⁾	n.d ⁽⁶⁾	n.d ⁽⁶⁾
FOE Chloroacetanilide ⁽⁴⁾	n.d ⁽⁶⁾	n.d ⁽⁶⁾	n.d ⁽⁶⁾	0.4	4.2	5.1	4.1	0.1	n.d ⁽⁶⁾	n.d ⁽⁶⁾	n.d ⁽⁶⁾	n.d ⁽⁶⁾
Unknown 1 (69 min.)	n.d ⁽⁶⁾	n.d ⁽⁶⁾	n.d ⁽⁶⁾	n.d ⁽⁶⁾	1.3	2.2	1.2	n.d ⁽⁶⁾	n.d ⁽⁶⁾	n.d ⁽⁶⁾	n.d ⁽⁶⁾	n.d ⁽⁶⁾
Unknown 2 (26.5 min.)	n.d ⁽⁶⁾	n.d ⁽⁶⁾	n.d ⁽⁶⁾	n.d ⁽⁶⁾	n.d ⁽⁶⁾	0.5	0.2	0.1	n.d ⁽⁶⁾	n.d ⁽⁶⁾	n.d ⁽⁶⁾	n.d ⁽⁶⁾
Unknown 3 (27 min.)	n.d ⁽⁶⁾	n.d ⁽⁶⁾	n.d ⁽⁶⁾	n.d ⁽⁶⁾	0.3	n.d ⁽⁶⁾	n.d ⁽⁶⁾	n.d ⁽⁶⁾	n.d ⁽⁶⁾	n.d ⁽⁶⁾	n.d ⁽⁶⁾	n.d ⁽⁶⁾
Unknown 4 (58 min.)	n.d ⁽⁶⁾	n.d ⁽⁶⁾	n.d ⁽⁶⁾	0.1	n.d ⁽⁶⁾	n.d ⁽⁶⁾	n.d ⁽⁶⁾	0.2	0.1	n.d ⁽⁶⁾	0.1	n.d ⁽⁶⁾
Unknown 5 (60 min.)	n.d ⁽⁶⁾	n.d ⁽⁶⁾	0.1	0.3	0.2	0.5	0.4	0.2	0.1	n.d ⁽⁶⁾	0.6	n.d ⁽⁶⁾
Unknown 6 (81 min.)	n.d ⁽⁶⁾	0.1	0.1	0.2	<0.1	n.d ⁽⁶⁾	0.1	0.2	0.1	0.3	0.2	n.d ⁽⁶⁾
Unknown 7 (82 min.)	n.d ⁽⁶⁾	0.1	n.d ⁽⁶⁾	n.d ⁽⁶⁾	n.d ⁽⁶⁾	n.d ⁽⁶⁾	n.d ⁽⁶⁾	n.d ⁽⁶⁾	n.d ⁽⁶⁾	0.1	0.1	n.d ⁽⁶⁾
Total ⁽⁵⁾	0.8	7.9	8.7	10.0	11.0	12.3	14.0	16.1	10.1	16.3	17.8	18.4

Footnotes to the table:

- 1) Values presented are the averages of triplicate analysis for DAT 0 and duplicate analysis for remaining time points;
- 2) Represents 0.1N HCl in CH₃CN:H₂O (1:1 v/v) extract;
- 3) FOE TGS = FOE Thioglycolate sulfoxide;
- 4) It was postulated that FOE Chloroacetanilide might have formed in soil as a genuine degradation product and/or during sample work-up as a result of chemical transformation of either Flufenacet or FOE Alcohol;
- 5) The difference between the **Total** value reported here and the (**extracted as:**) **Acidic extracts** reported in the table B.8.1.1.1.1. CA-18 above, was postulated in the study report to be possibly due to the three following factors: rounding of figures (1), presence of other HPLC resolvable degradation products, individually not exceeding 0.1% AR (2), presence of radiocarbon residues in acidic extracts that were below LOD for HPLC method (3);
- 6) n. d = not detected.

The results of the additional TLC analysis were following:

- **NP-TLC** enabled the identification and quantitation of Flufenacet and following four fractions:
 - **Metabolite 1:** the mixture of FOE Oxalate, FOE Sulfonic acid and FOE Thioglycolate sulfoxide, detected in extracts from all sampling points, in most of them in amounts >10% AR and in max. amount of 37.5% AR in DAT 44 sample;
 - **Metabolite 2:** FOE alcohol, detected in some of the analysed samples and in none of them in amounts ≥1.5% AR, the maximum amount quantified was 1.2% AR in DAT 271 sample;
 - **Metabolite 3:** not further identified fraction, reaching max. amount of 1.0% AR (DAT 180 sample);
 - **Others:** fraction characterised in the study report as “*resolvable FOE 5043 metabolites, none of which individually contained as much as 1% of applied radioactivity*”, however detected continuously throughout the study in low quantities (~0.0 – 3.6% AR), reaching the maximum amount of 3.6% AR in DAT 44 sample.
- **RP-TLC** enabled the identification and quantitation of Flufenacet and following six fractions:
 - **FOE Chloroacetanilide**, the fraction once surpassing the level of 5% AR, in DAT 44 sample (5.6% AR);
 - **Metabolite 1:** the mixture of FOE Oxalate and FOE Sulfonic acid, detected in extracts from all sampling points, in most of them in amounts >10% AR and in max. amount of 33.8% AR in DAT 365 sample;
 - **Metabolite 2:** postulated to be possibly “*a mixture of FOE 5043 metabolites that were retained at the origin by the soil matrix*”, never surpassing the amount of 5% AR (max. amount 3.2% AR in DAT 28 sample);
 - **Metabolite 3:** fraction not further identified, unless it was postulated mixture of FOE Alcohol and FOE Methoxysulfoxide mistakenly assigned to **Metabolite 4**, the fraction detected for the first time in DAT 44 samples, then detected continuously, although in low quantities – max. 1.5% AR (DAT 65 and DAT 91 samples);
 - **Metabolite 4:** postulated to be possibly a mixture of FOE Alcohol and FOE Methoxysulfoxide, however that identification in the study report is uncertain as the reference is given to **Metabolite 3**, the fraction sporadically detected and in max. amounts of 1.0% AR (DAT 44 and DAT 65 samples);
 - **Others:** fraction characterised in the study report as “*resolvable FOE 5043 metabolites, none of which individually contained as much as 1% of applied radioactivity*”, however detected continuously throughout the study in low quantities (~0.0 – 2.5% AR), reaching the maximum amount of 2.5% AR in DAT 28 sample.

The examination of the possible mechanisms of formation of FOE Chloroacetanilide showed that the formation of that compound may be possibly attributed to the chemical transformation of Flufenacet, but not FOE alcohol, during the sample work-up. It was demonstrated that although FOE Alcohol was stable in worked-up extracts, the same cannot be stated for Flufenacet, which was transformed, in 2 - 4% of its initial dose, to FOE Chloroacetanilide during the processing of the extracts. At the same time it was indicated, on the basis of the analysis of the data from acidic extraction of DAT 21, DAT 28, DAT 44 and DAT 65 samples, that the process of chemical degradation of Flufenacet to FOE Chloroacetanilide varied in intensity.

It was also stated that although the results suggest that FOE Chloroacetanilide was an analytical artefact formed during the sample processing, its microbial formation in soil could not be ruled out, as that compound was identified in another experiment – an outdoor soil metabolism study, in which soils were extracted only with acetonitrile, so chlorine atoms were not involved. That implicated that the process was biologically mediated, what in turn was conformed by open literature studies.

All that taken into account it was proposed in the study report to consider both microbial and chemical transformation during sample work-up transformation processes of Flufenacet as responsible for formation of FOE Chloroacetanilide, without however indicating which of them is considered to be predominating.

Additional attempt was made to further identify the **Unknown 1** fraction found in HPLC analysis using **Method A**. That was done by means of purification using HPLC **Method C**, followed by LC/MS analysis. It was demonstrated that that fraction consisted of two peaks: **Peak 1** having $R_t = 11.5$ min, and **Peak 2** having $R_t = 32$ min. **Peak 1** was the major component of the mixture – it accounted for 84% of it (1.1% AR). Further attempts to identify it by LC/MS did not provide sufficient information to enable its proper identification. **Peak 2** accounted for 16% of the mixture (0.2% AR). The MS spectrum of that peak was very similar to that obtained for Flufenacet, although not identical. However it was not explained why that fraction displayed R_t different from that determined for Flufenacet in HPLC **Method 1**. As a result no definitive conclusion with regard to the identity of that fraction was drawn.

There were no further attempts to identify the remaining Unknowns (2, 3, 4, 5, 6, 7). That was due to the fact that each of them was detected in amounts < 2.5% AR throughout the study.

On the basis of the obtained results the possible transformation pathway of Flufenacet in soil was proposed. It was also stated that the degradation was predominantly, if not exclusively biotically mediated.

The sudden collapse in the soil microbial activity was observed 4 weeks after the initiation of the experiment, followed by further, gentler decline. It was attributed to the natural factors rather than to the influence of the test compound or of the treatment solution's solvents.

Finally, it was postulated that, because of the collapse of the soil microbial activity ~4 weeks after the initiation of the experiment, the degradation should have followed bi-phasic pattern and the kinetic endpoints were calculated accordingly.

Conclusions:

The obtained results showed that Flufenacet was extensively degraded in the experimental soil during 365 days of the experiment, reaching the level of ~35% of the initial dose at the end of the study. There was a slow-down in degradation observed at the later time points, attributed to the sudden collapse of the soil microbial activity around 30th day after the beginning of the incubation.

Applicant explained that by the natural factors, not related to the experiment set-up, or influence of any of the constituents of the treatment solution. It shall be pointed out that the test soil was not pre-conditioned after being prepared for the experiment (atmosphere-dried and sieved), but before being treated with the test compound. That might have contributed to the observed collapse. It shall be also pointed out that the OC content of the test soil was very low, below the recommended 0.5%, although the results presented in that area are not very clear.

The level of mineralisation was relatively low, in comparison to the results obtained in other soils for the same radiolabelling position – 5.9% AR (approx. half of the level reached in other soils). That may also be explained by low soil microbial activity, especially at later time points.

The level of NER formed was also lower than in other soils treated with the compound radiolabelled in the same position, what may be explained not only by slowed degradation of the test compound and its degradation products, but also by the fact that the test soil displayed low OC content.

Several degradation product were detected, of which six were identified. Of them FOE Sulfonic acid, FOE Oxalate, FOE Thioglycolate sulfoxide and FOE Methylsulfoxide were found in other soils. The remaining two – FOE Alcohol and FOE Chloroacetanilide, were identified solely in this experiment. It shall be noted that FOE Chloroacetanilide was postulated to be both genuine degradation product, resulting from microbially-mediated transformation of Flufenacet, and the analytical artefact formed during the sample processing after acidic extraction. However, as it was not possible to determine which process was predominant, RMS, on the basis of

the weight of evidence and the worse-case principle, proposes to consider it being a **genuine degradation product**.

Of the compounds listed above two should be considered major, in line with the recommendations given by SANCO/221/2000 Guidance Document – FOE Oxalate, peaking at 26.5 % AR on DAT 365 and FOE Sulfonic acid, peaking at 7.7% AR on DAT 180, but being detected in amounts > 5% AR on several consecutive time points from DAT 76 to DAT 365.

It shall be noted that, due to the stated problems with soil microbial activity the metabolite profiling may not fully reflect the situation really occurring in soil. Therefore in practice other degradation products identified in the study, but not demonstrated to be major, may be formed in amounts enabling their classification as major with regard to their relevance for GW exposure and risk assessment.

On the basis of the results obtained in this study the following transformation pathway of Flufenacet in aerobic soil, shown on the Fig B.8.1.1.1.1._CA-13, was proposed:

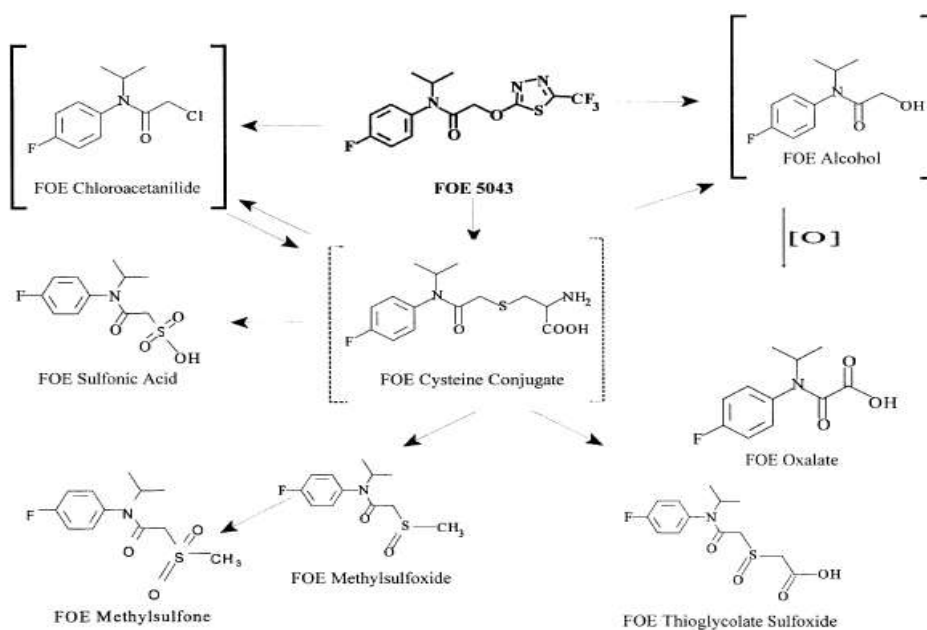


Figure B.8.1.1.1.1._CA-13: The transformation pathway of Flufenacet in aerobic soil, determined for the compound radiolabelled in phenyl ring (scheme copied from the study report).

RMS's conclusions with regard to the validity of the study:

On the basis of the thorough examination of the study protocol RMS proposes to consider the study valid, despite the deficiencies it displays, because it provides vital information in the area of the determination of the route of degradation of Flufenacet in soil. It shall be pointed out that the results of that study in the area of identification of the degradation products and elucidation of the degradation pathway of Flufenacet within its phenyl moiety were conformed by the results of the other, open literature studies, summarised further down this Assessment Report.

The problem of the sudden collapse of the soil microbial activity observed in the experimental soil was thoroughly examined and satisfactorily explained in an independent study, summarised below as **Study 3**. In light of the findings of that study, the study summarised above can be considered acceptable and relevant for the purpose of the regulatory assessment of Flufenacet.

Study 3:

Report: Hellpointner E., (1995): “Evolution of the microbial biomass in the biometer flask system (supportive to study no. F3042102, aerobic metabolism of FOE 5043).”; Bayer AG, Agrochemicals Division, Development, Institute for Metabolism Research & Residue Analysis, D51368 Leverkusen; Germany; unpublished Report No. PF 4066; 20 June 1995; study reference number: M-002164-01-1;

Guidelines: The study was not declared to follow any specific Guidelines, but it was indicated that it was performed in order to meet the specific requirements set by the US EPA Guidelines for Pesticide Registration, Subdivision N, Section 162-1 - Aerobic Soil Metabolism;

GLP: Yes – study was declared to be conducted in compliance with GLP standards;

RMS comments: The study was submitted as an additional explanatory study, examining the reasons for the sudden collapse of soil microbial activity observed in the study by Pangilinan and Smith [1994], examining the degradation of [¹⁴C-phenyl] Flufenacet in aerobic soil (**Study 1**). The study was evaluated and found acceptable by the RMS. It is summarised below. It shall be noted that tit was referred to in the previous Assessment Report, prepared by the RMS – France, for the purpose of the first authorisation of Flufenacet in the EU.

Summary:

The aim of the study was to examine the survival of the living, metabolically active, microbial biomass in a moist loamy sand soil incubated in the dark under aerobic conditions at $T = 20 \pm 1^{\circ}\text{C}$ for 1 year. The additional aim of the study was to determine the reasons for the sudden collapse of the soil microbial activity, observed in the study by Pangilinan and Smith [1994], examining the degradation of [¹⁴C-phenyl] Flufenacet in aerobic soil (**Study 1**), after ~ 4 weeks of incubation.

The experiment was performed in the premises of Bayer AG in Monheim, Germany, on the same soil as used in two studies by Pangilinan and Smith [1994, 1994a], examining the degradation of Flufenacet radiolabelled in two different positions – in phenyl ring (**Study 1**) and in C2-thiadazole position (**Study 2**), in one soil incubated under aerobic conditions.

The characteristic of the test soil is presented below in the table B.8.1.1.1.1._CA-21.

Table B.8.1.1.1.1._CA-21: The characteristic of soil used in the study.

Parameter		Soil:		
		395 (A)		
Soil origin		Howe, Indiana, USA		
Soil type (USDA)		Sandy loam		
Particle size distribution	Sand [%]	77.5		
	Silt [%]	17.2		
	Clay [%]	5.3		
pH value (in water, 1:1)		6.4		
Organic matter content (OM) [%]		0.4		
Organic carbon content (C _{org}) [%] ¹⁾		0.23		
Cation Exchange Capacity – CEC [mEq/100g]		7.4		
Bulk density (disturbed) [g/cm ³]		1.33		
Moisture holding capacity at ½ bar [%]		13.1		
Moisture holding capacity at 15 bar [%]		3.4		
Available nutrients ²⁾	Ca	1700 [lb/ac]	1905.053 [kg/ha]	1884.70 [mg/kg]
	Mg	250 [lb/ac]	280.155 [kg/ha]	277.16 [mg/kg]
	Na	24 [lb/ac]	26.895 [kg/ha]	26.61 [mg/kg]
	K	312 [lb/ac]	349.633 [kg/ha]	345.90 [mg/kg]
	H	34 [lb/ac]	38.101 [kg/ha]	37.69 [mg/kg]
P (Olsen)		57 [lb/ac]	63.875 [kg/ha]	63.19 [mg/kg]
Total N [%]		0.062		
Soluble Salts [mmhos/cm]		0.24		

Footnotes to the table:

- 1) Value recalculated by the RMS from that reporting OM content given in the study report using the following equation: $\text{OM} = 1.724 * \text{OC}$;
- 2) In the study report only the values in [lb/ac] (US pound/US acre) were given. RMS recalculated them to first kg/ha and then to mg/kg soil using the following assumptions: for transformation to kg/ha it was assumed that 1 kg = 0.4535 US pound and 1 ha = 0.4046873 US acre; to calculate the amount in mg/kg soil Escape modelling tool was used with the following assumptions: soil density $d = 1.33 \text{ g/cm}^3$ and soil depth 7.6 cm – the equivalent to 3 inches (value used to calculate the application rate in lb/ac in the **Study 2**).

The test soil was treated in the similar way to that described in the summary of the **Study 2** [Pangilinan and Smith; 1994] – after shipment by air to the test facility in Germany, the test soil was stored, for a not defined

period, in a greenhouse. In order to maintain it biologically viable until being used, the soil surface was planted with grass. Immediately before the experiment began ~1.5 kg of the test soil was taken to the laboratory where the plant material was removed and moist soil was swiftly air-dried. Next it was sieved through 2-mm sieve. The dry weight of sieved soil was determined to be 92.5% of the moist one.

So prepared soil was introduced, in amounts of 100 g d.w./incubation vessel (108.1 g sieved soil/incubation vessel) to the biometer flasks, identical to those used in the **Study 1**, shown below on figure B.8.1.1.1.1._CA-14. After placing the soil in incubation vessels its moisture content was brought to the level of 75% of $\frac{1}{3}$ bar (~9.83 g H₂O/100 g soil) by adding 1.73g of Milli-Q water to each incubation flask. Soil moisture was controlled in 1-month intervals by reweighing the test vessels and, if necessary adjusting that factor by introducing the adequate amount of water.

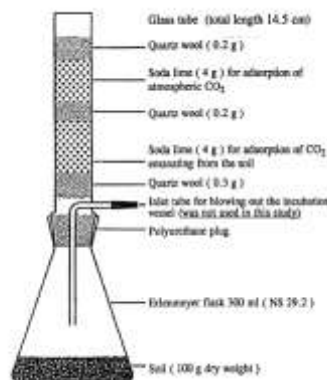


Figure B.8.1.1.1.1._CA-14: The biometer flask used in the experiment (scheme copied from the study report).

The incubation vessels were prepared in duplicate for each sampling point. The incubation flask were then placed in the dark, in the incubation chamber, and incubated at $T = 20 \pm 1^{\circ}\text{C}$ for up to 52 weeks (1 year). At the designated intervals duplicate samples were taken for the determination of the soil biomass. The detailed information on the sampling protocol is presented below in the table B.8.1.1.1.1._CA-22.

Table B.8.1.1.1.1._CA-22: The detailed information on the sampling protocol.

Sampling date (dd/mm/yyyy)	Duration of aerobic incubation [weeks]	Number of vessels collected	Termination date of Biomass Evaluation (dd/mm/yyyy)
06/12/1993	0	2	08/12/1993
20/12/1993	2	2	21/12/1993
03/01/1994	4	2	05/01/1994
31/01/1994	8	2	01/02/1994
07/03/1994	13	2	08/03/1994
06/06/1994	26	2	07/06/1994
07/09/1994	39	2	09/09/1994
05/12/1994	52		07/12/1994
----	Total duration: 1 year	Total = 16	----

Soil samples taken at each sapling point were analysed for viable soil microbial biomass and pH within 3 days after sampling. The determination of the soil microbial biomass was performed using Anderson&Domsch method. Soil pH was measured in 1M KCl. Also the soil moisture of sampled soils was determined at the time of sampling.

Results and their discussion:

It was stated that aerobic conditions were maintained in the test vessels during the study via the diffusion of air through the trapping towers, what was also conformed in other experiments using the same incubation vessels' system.

The observed at the adjustment points decrease in soil moisture content during the study was to the level of 57% of $\frac{1}{3}$ bar – 62% of $\frac{1}{3}$ bar, so it dropped by 17 - 24% in comparison to the assumed level of 75% of $\frac{1}{3}$ bar.

The incubation temperature was demonstrated to be stable throughout the experiment – $T = 20 \pm 1^\circ\text{C}$. All relevant numerical results of the experiment are presented below in the table B.8.1.1.1.1_CA-23.

Table B.8.1.1.1.1_CA-23: The numerical results of the experiment

Sampling point – weeks after incubation	Soil moisture determined [%] ¹⁾		Soil pH in 1N KCl		Soil microbial biomass [mg C/kg soil d.w.] ²⁾		
	Replicate A	Replicate B	Replicate A	Replicate B	Replicate A	Replicate B	Average ³⁾
0	9.45	8.85	5.6	5.6	266	258	262
2	7.75	8.10	5.6	5.6	211	202	207
4	9.60	8.55	5.6	5.6	181	181	181
8	9.10	9.00	5.8	5.8	186	188	187
13	7.50	8.50	6.0	6.0	149	148	149
26	7.00	7.10	6.0	6.1	102	123	113
39	7.20	7.50	6.7	6.9	66	89	78
52	7.25	7.40	6.2	6.4	95	37	66

Footnotes to the table:

- 1) expressed as g H₂O/100 g soil d.w.;
- 2) d.w. stands for dry weight;
- 3) the value is mean value of the Replicates 1 and 2.

The soil pH was stable during initial four weeks of incubation. After that it increased to peak at 6.8 on 39th week after the beginning of incubation. Afterwards it decreased. That change is demonstrated in graphical form on figure B.8.1.1.1.1.-CA-15.

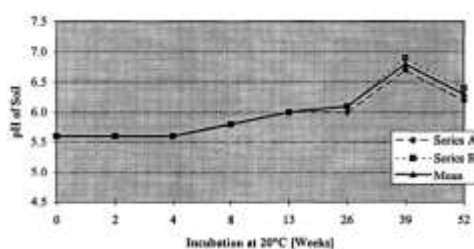


Figure B.8.1.1.1.1_CA-15: The change in the soil pH during the incubation (as presented in the study report).

In general the decrease in soil microbial biomass was observed in the test soil during the 52-weeks lasting incubation. On average the microbial biomass decreased from 262 mg C/kg soil d.w. at the beginning of the study (0 week) to 66 mg C/kg soil d.w., so by 74.81%. It shall be noted that while the soil biomass accounted for 11.29% OC at the beginning of the experiment, at its end, after 52 weeks, it was on the level of 2.87% OC, so within the limits set by the OECD 307 Guidance.

For the individual replicates the decrease looked as follows:

- for replicate A from 266 mg C/kg soil d.w. at the beginning of the study (0 week) to 95 mg C/kg soil d.w., so by 64.29%; the soil biomass in that replicate accounted for 11.46% OC at the beginning of the experiment, at its end, after 52 weeks, it was on the level of 4.09% OC;
- for replicate B from 258 mg C/kg soil d.w. at the beginning of the study (0 week) to 37 mg C/kg soil d.w., so by 85.57%; the soil biomass in that replicate accounted for 11.12% OC at the beginning of the experiment, at its end, after 52 weeks, it was on the level of 1.59% OC.

In graphical form the results are presented below on figure B.8.1.1.1.1_CA-16. It shall be noted that the decline in soil microbial biomass was not linear – after steady decrease up to the 4th week of incubation, the level of soil microbial carbon stabilised up to the 8th week on the level of 180-200 mg C/kg soil d.w., to then drop significantly within the remaining incubation period.

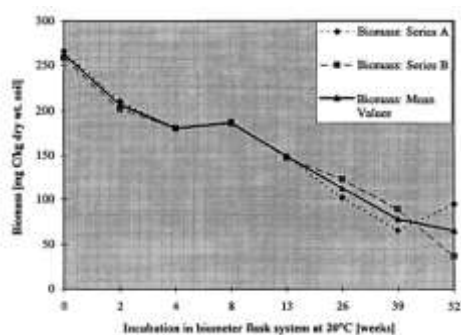


Figure B.8.1.1.1._CA-16: The decrease of the microbial biomass in the test soil during incubation (as presented in the study report).

Additionally the linearity of the decrease of microbial biomass, rate constant and a “half-life” for that process, in each replicate series (A and B) as well as for averaged results was determined. The graphical and numerical results are presented below on figure B.8.1.1.1._CA-17.

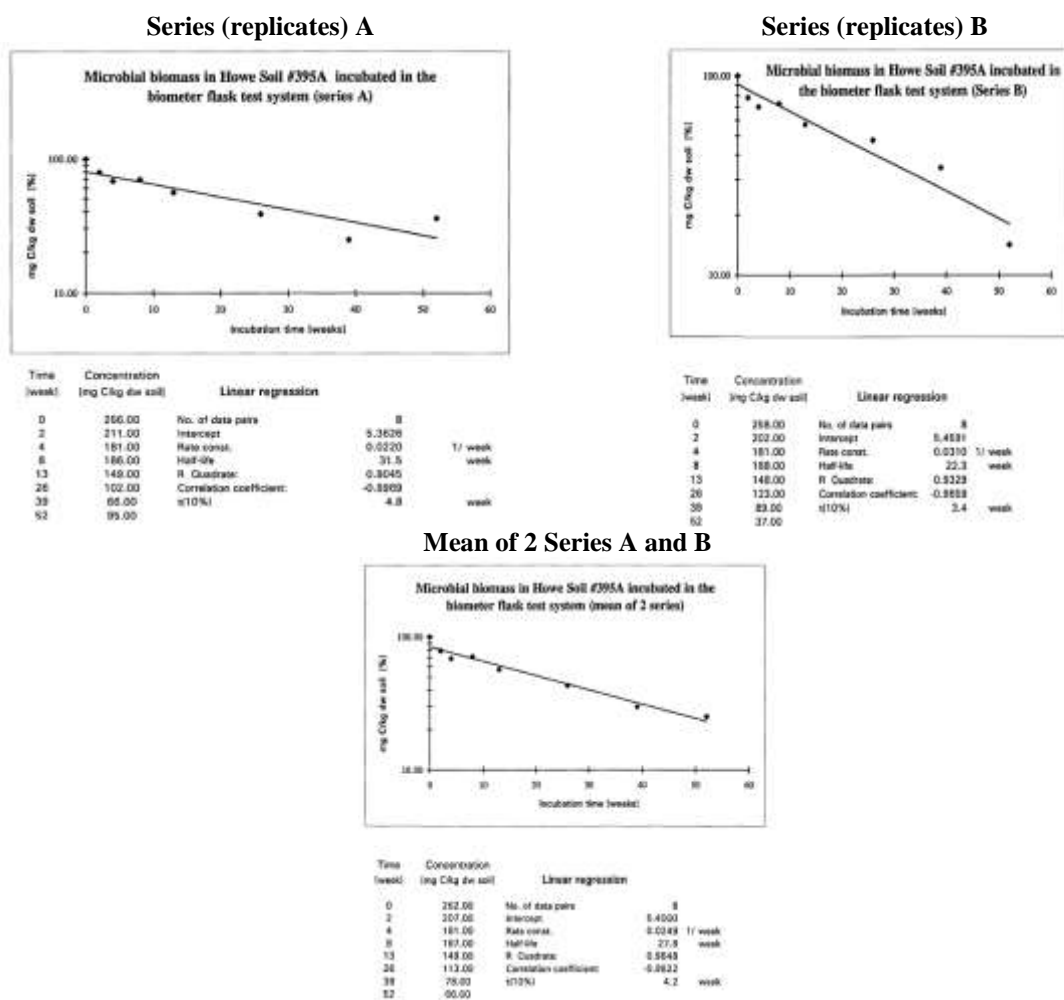


Figure B.8.1.1.1._CA-17: The linearity and kinetic parameters of the decline of microbial biomass in the test soil (as presented in the study report).

Conclusions:

In conclusions to the study it was stated that the decrease of the living microbial biomass during 1 year incubation of small portions of soil in isolated test systems could be attributed to the exhaustion of available carbon and other nutrients in soil and consequent starvation and death of microbial cells – the explanation usually given for that phenomenon. It was stated that that fact, in general and in case of Howe soil in particular, should be taken into account in examining the degradation kinetics – in order to get reliable kinetic endpoints the study should not exceed 6 months.

The possible causes of sudden collapse of soil microbial activity during the first 4 weeks of incubation were not given in the study report, but as the decline pattern in soil microbial activity similar to that determined in the study by Pangilinan and Smith [1994] was observed here, it may be assumed that it was not related to the solvent system used in the application solution, but rather was due to the incubation conditions.

The results of the study conform that the observed in the studies by Pangilinan and Smith [1994, 1994a] (**Study 2** and **Study 4**) decrease in soil microbial activity with time is a natural phenomenon. Therefore, from that point of view, both studies may be considered valid.

Study 4:

Report: Pangilinan N. C., Smith D. M., (1994): “Aerobic Soil Metabolism of [Thiadiazole -2-¹⁴C] FOE 5043”; Miles Inc., Agriculture Division, Research and Development Department, P. O. Box 4913, Kansas City, Missouri 64120-0013, USA; study No. F3042103; unpublished Miles Report No. MR 106420; 30 June 1994; study reference number: M-002165-01-1;

Guidelines: The study was performed to comply with the following Guidelines:

- US. EPA Guidelines for Pesticide Registration, Subdivision N, Section 162-1;

GLP: Yes

RMS comments: The study has been evaluated for the previous authorisation of Flufenacet in the EU. Its summary can be found under the point B.7.1.1.1.1., in section B.7 of the Annex B to the Monograph prepared by the RMS – France, for Flufenacet. At present the study was evaluated for its compliance with OECD Guideline 307 – Aerobic and Anaerobic Transformation in Soil. Additionally RMS checked its compliance with the guidelines on performing the laboratory test on aerobic degradation in soils, presented in *M. Lynch (ed.) “Procedures for Assessing the Environmental Fate and Ecotoxicity of Pesticides.”, SETAC, 1995*. Also the US EPA Guideline indicated by the Applicant - US. EPA Guidelines for Pesticide Registration, Subdivision N, Section 162-1, was consulted. During that verifications the following deviations from the Guidelines and problems were stated:

- The test soil displayed a very low average OM/OC content, well below the recommended OC = 0.5%, and highly variable. In the study report not only the declared average OM = 0.6%, corresponding to OC = 0.35%, but also it was in range 0.2 – 1.2%, depending on the year in which the test soil was characterised. That may indicate that the test soil was very inhomogeneous with regard to OC content, what in turn might have influenced the obtained results. That feature was signalled in the previous Assessment Report for Flufenacet prepared by the RMS – France, but not indicated as deviation disqualifying the study;
- There was a significant decrease in soil microbial activity observed in the test soil. It accounted for 62.8% after 8 months of incubation and 77.5% after 12 months of incubation. As the soil microbial biomass was measured only at three time points during the study – at the beginning, and at 8th and 12th month of incubation, it was not possible to determine how it was looking like in time. However, the good insight to the phenomenon provides the supplementary study by Hellpointner [1995], summarised above as **Study 3**. The report of that study was submitted for evaluation as a part of the Dossier evaluated for the first authorisation of Flufenacet in the EU. It shall be noted that the problem was noticed by the former RMS – France, but not considered as disqualifying the study;
- The test soil was preconditioned prior to its use by storing it in greenhouse in two 5-gallon (~19-L) buckets. Soybean plants were planted on the soil surface during that incubation period to maintain its microbiological viability. The test soil samples taken to the laboratory prior to the beginning of the experiment were pre-treated by sieving and air-drying, but afterwards were not pre-conditioned as recommended by OECD 307 Guideline. That fact was not stated in the summary provided in the previous Assessment Report, but may be the reason for the substantial decrease of soil microflora observed after 8 months of incubation;
- Test substance was applied in form of the treatment solution being a mixture of CH₃CN: H₂O in ratio 1:4. That deviation from the Guidelines (OECD 307 Guideline recommends to prepare the treatment solution with water and only a small addition of any organic solvent not demonstrated to inhibit microbial activity; also the verification of the influence of such treatment solution on soil microbial activity is recommended prior to the treatment) was also not indicated in the previous DAR.

No other deviations were found in the study report. Despite those listed above the study may still be considered acceptable and as such is summarised below in its part related to the route of degradation, while for the rate of degradation the information is placed under the point B.8.1.1.2.1.

Summary:

The aim of the study was to investigate the fate – route and rate of degradation, of Flufenacet in soil incubated under controlled (in the laboratory) aerobic conditions. The experiment was performed using one test soil originating from the US (Howe, Indiana). Its characteristic is provided below in the table B.8.1.1.1.1._CA-24. It shall be noted that in the study report the table on soil characterisation provides the results of the soil characterisation performed for three different batches, then averaged. RMS decided to present all the results of that characterisation, as they were reported in the original study's report.

Table B.8.1.1.1.1._CA-24: The characteristic of soil used in the study.

Parameter		Soil: 395			
Soil origin		Howe, Indiana, USA			
Batch analysed		A ¹⁾	B ²⁾	C ³⁾	Average
Soil type (USDA)		Sandy loam	Sandy loam	Sandy loam	Sandy loam
Particle size distribution	Sand [%]	72.5	77.5	70.4	73.5
	Silt [%]	20.0	17.2	20.0	19.1
	Clay [%]	7.5	5.3	9.6	7.5
pH value (in water, 1:1)		6.1	6.4	6.2	6.2
pH value in CaCl ₂ ⁴⁾		5.5	5.9	5.6	5.6 ⁵⁾
Organic matter content (OM) [%]		0.2	0.4	1.2	0.6
Organic carbon content (C _{org}) [%] ⁵⁾		0.12	0.23	0.70	0.35
Cation Exchange Capacity – CEC [mEq/100g]		6.9	7.4	5.1	6.5
Bulk density (disturbed) [g/cm ³]		1.31	1.33	1.47	1.37
Moisture holding capacity at ½ bar [%]		14.8	13.1	11.4	13.1
Soil biomass expressed in mg microbial C/kg soil in samples collected on DAT ⁷⁾ :	0	-----	-----	-----	129
	8 months	-----	-----	-----	48
	12 months	-----	-----	-----	29
Soil biomass expressed as %OC ⁸⁾ in samples collected on DAT:	0	-----	-----	-----	3.7
	8 months	-----	-----	-----	1.4
	12 months	-----	-----	-----	0.8

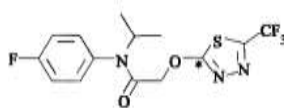
Footnotes to the table:

- 1) Analysis performed by Agvise Inc. on 13 August 1991;
- 2) Analysis performed by Agvise Inc. on 4 February 1992;
- 3) Analysis performed by A&L Great Lakes Laboratories Inc. on 29 March 1993;
- 4) Value recalculated by the RMS using the following equation: $pH_{H_2O} = 0.982 pH_{CaCl_2} + 0.648$;
- 5) Value calculated from the corresponding pH in water;
- 6) Value calculated by RMS using the following relationship: $OC = OM/1.724$.
- 7) The soil microbial biomass was determined in soil samples using Anderson and Domsch method;
- 8) Values calculated using the average OC content – 0.35%;

The test soil was taken from a Miles Research Farm in Howe, Indiana, USA, and placed in two ~19L buckets in the greenhouse. In order to maintain its microbiological viability soil was planted with soybean prior to the conduct of the study.

Immediately before the experiment began, ~2 kg of soil from the top 5-6 inch (corresponding to 12-15 cm) layer was taken to the laboratory, where the soybean plants were removed and moist soil sieved through 2-mm sieve. Then the test soil was air-dried for 2 hours to the level of 75% of ½ bar (the soil moisture level kept throughout the experiment) and placed in the test vessels.

The test substance used in the experiment was the ¹⁴C-FOE 5043 radiolabelled in 2-thiadiazole position, as shown below on figure B.8.1.1.1.1._CA-18.

**Figure B.8.1.1.1.1._CA-18.:** The structural formula of the radiolabelled Flufenacet (FOE 5043) used in the experiment (scheme copied from the study report).

The specific radioactivity of the test compound used in the experiment was 18.47 mCi/mmol and its radiochemical purity, determined with TLC, was 99.5%. Its radiochemical purity determined at the time of the treatment was 97.5%. It was applied to the test soil in incubation vessels in form of the application solution prepared in the following way: 366 µg of [Thiadiazole-2-¹⁴C]-Flufenacet was evaporated to dryness under gentle stream of nitrogen and then redissolved in first 5 mL of CH₃CN (acetonitrile), to which 20 mL of distilled water was added next. The so prepared solution was stirred and then was controlled for its concentration by radioassaying. It was determined that the concentration was 291 mg Flufenacet/L.

The experiment was performed using the glass biometer flasks, presented below on figure B.8.1.1.1.1._CA-19.

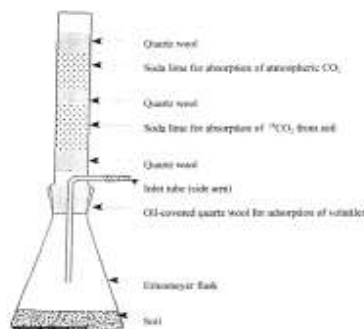


Figure B.8.1.1.1.1._CA-19: The biometer flask used in the experiment (scheme copied from the study report).

They consisted of 250-mL Erlenmeyer flasks with wide-diameter glass tube adapters, sealed with traps for volatile compounds. The traps were glass tubes with adapter containing of ~1g plug of glass wool soaked with 2% mineral oil in hexane to absorb possible VOC and soda lime layer (~10 g.) to capture formed ¹⁴CO₂, capped with a layer of glass wool (separator) above which further ~4-grams. layer of soda lime was placed to prevent soda-lime sorbent from being saturated with atmospheric CO₂. On the top 4-grams of glass wool was placed. The side-arm inlet tube, sealed with a rubber septum, was set to enable the adjustment of soil moisture by adding the necessary amounts of distilled water during the study.

Each test vessel contained the equivalent of 100 grams of oven-dried test soil, adjusted to 75% of ½ bar by addition of the appropriate amount of the distilled water. That level was maintained throughout the incubation period, lasting up to 365 days.

In total 28 incubation flask were prepared, of which 21 were treated with the test compound (4 of them were test spares), 3 were used for the non-sterile control and remaining 4 for microbial biomass determination.

The test flasks were treated with the test substance, applied to the soil surface in form of the application solution described above, at rate of 2.9 mg/kg. Applicant declared that that rate corresponded to approx. three times field application rate of 0.8 lbs a. i./acre – i. e. 2.32 lbs a. i./acre, assuming soil depth of 3 inches and soil bulk density of 1.33 g/cm³. When recalculated by the RMS as g/ha, assuming soil depth of 5 cm and soil bulk density of 1.5 g/cm³, the exact application rate was **2175 g Flufenacet/ha**. The use of the measured average soil bulk density – d = 1.37 g/cm³, resulted in the application rate of **1986.5 g Flufenacet/ha**.

The amount of the application solution introduced into each test vessel was 1 mL, applied dropwise to the soil surface. Control and microbial biomass flasks were treated with 1-mL portions of blank solvent carrier (CH₃CN:H₂O 1:4 v/v).

After treatment the appropriate amount of distilled water was added to each test vessel to establish soil moisture of 75% of ½ bar.

After treatment the Erlenmeyer incubation flask were sealed with traps for volatile compounds, weighed and covered with aluminium foil to exclude light.

So prepared incubation systems were placed in an incubation chamber and incubated in the darkness at T = 21 ± 1°C for up to 368 days. The temperature in the incubation chamber was monitored continuously. Soil moisture was monitored every week and corrected adequately, when necessary.

Trapping towers for formed volatile compounds were replaced on 4th month of incubation.

Samples were removed for the analysis on DATs (Days After Treatment) 0, 7, 14, 32, 90, 181, 27 and 368. In case of DAT-0 sampling point triplicate analysis was performed, while for all remaining sampling points duplicate samples were prepared. Also in case of two DAT-0 replicates the traps for volatile compounds were not set and the soils were analysed almost immediately (1 hour) after treatment with the test compound.

The adjustment of soil moisture was performed in 1-week intervals by weighing the incubation flasks and, when necessary, introducing the appropriate amounts of distilled water through the side-arm inlet tube.

At the designated time points duplicate test flasks were removed from the incubation chamber and for 5 minutes purged with N₂ in order to flush the produced CO₂ and VOCs into the traps.

The collected traps for volatile compounds were analysed for their content of trapped radioactivity. That was done in a following way: first the traps were dissected, mineral-oil-coated glass wool transferred into 250-mL Erlenmeyer flask and extracted by sonication for at least 30 min with 50 mL of CH₃COOC₂H₅. The organic extract was then collected by decantation and its triplicate aliquots analysed by LSC. Soda lime traps were transferred to 125-mL flasks, being a part of a specially designed extraction apparatus, shown below on figure B.8.1.1.1.1.-CA-20, to which 10 mL of water was added next.

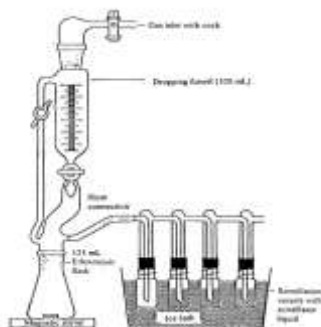


Figure B.8.1.1.1.-CA-20: The apparatus used for the liberation of ¹⁴CO₂ (scheme copied from the study report).

The system was put under the constant flow of N₂ (~20 mL/min) and 50 mL of 12N HCl was gently added. The released CO₂ was trapped in three vessels, each containing 10 mL of the mixture of Carbo-sorb E and Permafluor-E⁺ (3:5), and analysed by LSC.

Next soils from each test vessel were analysed. That was done by extracting the entire soil samples in a sequential multistep extraction procedure. Initially it consisted of the following extraction steps:

- **Step 1:** 1-hour extraction with 150 mL of CH₃CN, and the collection (decantation) of the liquid phase,
- **Step 2:** 1-hour extraction with 150 mL of CH₃CN: H₂O (7:3) solution and the collection (decantation) of the liquid phase,
- **Step 3:** 2-hours extraction with 0.1N HCl in CH₃CN: H₂O (1:1) solution and the collection (decantation) of the liquid phase.

The procedure was identical to that used in the summarised above **Study 2** [Pangilinan and Smith, 1994], but was applied solely to DAT 0 samples. The reason for that was the fact that although it displayed good efficiency – the amount of extracted AR was >90%, it was determined that Thiadone – the expected degradation product of Flufenacet, was potentially volatile. Since it was necessary to process the CH₃CN: H₂O (7:3) extracts by azeotropic concentration prior to chromatographic analysis, what implied possible losses of the volatile Thiadone, that step was removed from the extraction procedure. The modified extraction procedure, used to process all samples collected at the remaining time points, is shown below on figure B.8.1.1.1.1.-CA-21. ACN stands for acetonitrile (CH₃CN).

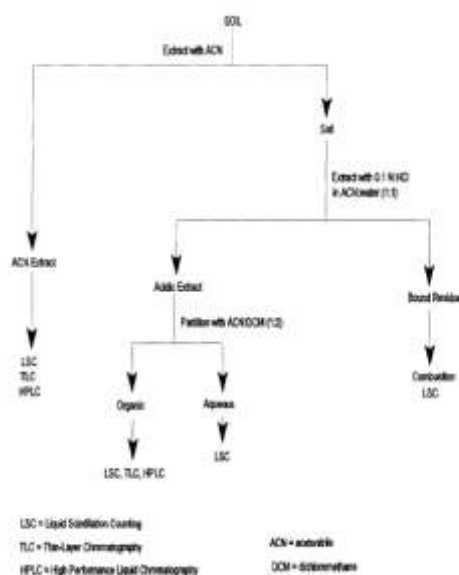


Figure B.8.1.1.1.-CA-21: A multistep soil extraction procedure used in the experiment (scheme copied from the study report).

Additionally, to maintain the consistency of the analytical procedure, also the analysis of DAT 0 samples was repeated. That was done in the following way:

The test soil was prepared and treated with the test compound in the same manner as presented above. The purity of Flufenacet used to prepare the treatment solution, determined by TLC, was 98.8% and its concentration in soil, determined by LSC, was 2.7 ppm. When recalculated by the RMS to application rate in g/ha, assuming soil depth of 5 cm and soil bulk density of 1.5 g/cm³, it was **2025 g** Flufenacet/ha. The use of the measured average soil bulk density – $d = 1.37 \text{ g/cm}^3$, resulted in the application rate of **1849.5 g** Flufenacet/ha. Volatile traps were not set as it was demonstrated that in the volatile traps from the initial DAT 0 samples <0.1% AR was detected.

The extracted soil pellets were analysed for NER fraction. To do that each soil sample was allowed to air-dry overnight, after what its triplicate aliquots (50 – 100 mg) were oxidized by combustion, and formed ¹⁴CO₂ trapped in alkaline solution. That solution, after mixing with scintillation cocktail, was analysed by LSC.

All samples were analysed for the content of radioactivity using LSC method. The LSC (Liquid scintillation counting) analysis was performed using a Packard Tri-Carb Model 4640 counter equipped with automatic external standardisation.

Liquid samples were radioassayed after addition of 15 mL of Ultima Gold solution. The minimum sensitivity of LSC analysis for those samples was 8.96 E-6 ppm, corresponding to 3.08 E-4% AR. When expressed as Lowest Acceptable Gross Count Rate (LAGC) it was 64 cpm, while as Lowest Acceptable Net Count Rate (LANC) – 32 cpm, assuming average background (BCGK) of 32 cpm (LAGC = 2*BCGK and LANC = LAGC – BCGK). The greatest probable error GPE = 9.24%.

Solid samples were oxidised using Packard Model 306 sample oxidizer, generated ¹⁴CO₂ trapped on 6 mL Carbo-sorb E and 15 mL Perma Fluor E. The minimum sensitivity of LSC analysis for those samples was 3.15 E-3 ppm, corresponding to 0.11% AR. When expressed as Lowest Acceptable Gross Count Rate (LAGC) it was 64 cpm, while as Lowest Acceptable Net Count Rate (LANC) – 32 cpm, assuming average background (BCGK) of 32 cpm (LAGC = 2*BCGK and LANC = LAGC – BCGK). The greatest probable error GPE = 9.24%.

Sample extracts were analysed using the following techniques:

- HPLC – major identification and quantitation method for parent compound and its degradation products;
- TLC – secondary quantitation method for the parent compound and its degradation products;
- LC-MS – identification method for parent compound and its degradation products;
- GC/MS – supplementary identification method for parent compound and its degradation products.

The RP-HPLC analysis was performed in a gradient mode. The system consisted of Hewlett Packard 1090 chromatograph coupled with Ramona 5-LS radioactivity monitor, equipped with RP-18 Spheri-5 cartridge in function of the guard column and Spherisorb 3 μ ODS2 (7 cm * 10 mm) chromatographic column. It worked in the following gradient regime:

- Mobile phase A: Water + 0.4% CH₃COOH,
- Mobile phase B: CH₃OH
- Gradient mode: linear from 100% AB at 0 min to 30% AB at 40 min, hold for next 20 min and linear to 0% A at 70 min.

The flow rate was set to 1 mL/min.

The LOD for the chromatographic method, in relation to the performance of the used radioactivity detector, was determined to be 500 dpm, corresponding to 1.0% AR. That value was determined experimentally on the basis of the comparison of radioactivity injected and eluted (expressed in dpm, as determined by LSC). The results of that examination, aimed on the determination of both LOD and the linearity of HPLC analysis, are presented below in the table B.8.1.1.1.1.-CA-25. The linearity of the analysis, expressed as r^2 , was: $r^2 = 0.9995$.

The identification of the chromatographic peaks was performed by means of the comparison of their retention times R_t with those of the standards. The HPLC retention times of each of the examined compounds are presented further down the document, in the table B.8.1.1.1.1.-CA-27, together with R_f values for NP-TLC and RP-TLC methods.

Table B.8.1.1.1.1.-CA-25: The results of the determination of linearity and LOD of the HPLC analysis.

Sample No.	Radioactivity in [dpm]:		Integration ^{3, 4)}
	Injected ¹⁾	Eluted ²⁾	
1	330204	308860	57035
2	211148	196266	37931
3	141516	129698	23364
4	64073	67713	10874
5	35191	n. d. ⁶⁾	5928
6	10495	10191	1872
7	4939	4806	682
8	3704	n. d. ⁶⁾	748
9 ⁵⁾	468	559	86

Footnotes to the table (for 1,2,3, as given in the study report):

- 1) Values determined by LSC analysis of the aliquots of the [¹⁴C]-Flufenacet standard solution injected, radioassayed prior to HPLC analysis;
- 2) Values determined by LSC analysis of the aliquots of HPLC eluents;
- 3) Regions of interest were integrated with background correction, determined at the beginning and the end of analysis;
- 4) Linearity of the analysis, expressed as r^2 value, was determined to be $r^2 = 0.9995$;
- 5) The value corresponding to LOD (by averaging the amount of injected and eluted it was set to LOD = 500 dpm);
- 6) n. d. = represents not determined.

The TLC analysis of the extracts was performed in two modes:

- as RP-TLC (reversed phase TLC);
- as NP-TLC (normal phase TLC).

The RP-TLC analysis was performed using Whatman KC₁₈F TLC plates, having a dimensions 20x20 cm and 200- μ m thick, with a fluorescent indicator. The solvent system used in the analysis was CH₃CN:CH₃OH:0.5N NaCl_{aq} 2:2:1 (v/v) solution.

The NP-TLC analysis was performed using silica gel TLC plates, having a dimensions 20x20 cm and 250- μ m thick, with a fluorescent indicator. The solvent system used in the analysis was CHCl₃:CH₃COOC₂H₅:CH₃COOH 75:25:1 (v/v) solution.

The LOD was set to 1 %AR for each individual compound detected. The quantitative analysis was performed using RITA 6800 Radio-TLC analyser. The LOD for this detector was determined to be 150 dpm, corresponding to 1.0% AR. The complete results of the determination of linearity and LOD of the detector are presented below in the table B.8.1.1.1.1.-CA-26.

The identification was performed by means of the comparison with the R_f values of the known standards. These values are provided below in the table B.8.1.1.1.1.-CA-27, together with R_t values for HPLC method.

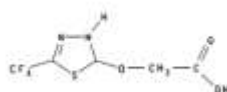
Table B.8.1.1.1.1._CA-26: The results of the determination of linearity and LOD of the TLC analysis.

Sample No.	LSC Counts Total dpm/band	Scanner Counts	
		dpm/ 600 sec	dpm/ 1200 sec
1	145	23	32
2	329	43	58
3	512	57	131
4	1033	103	224
5	1919	158	366
6	5594	549	1099
7	8788	962	1871
Background	----	9	15
Correlation coefficient	----	0.994	0.997

Table B.8.1.1.1.1._CA-27: Chromatographic identification of Flufenacet and its degradation products in the study.

Compound	Chromatographic identification – retention time R_t [min] (HPLC)/ R_f value (TLC) determined for:		
	HPLC Method	RP-TLC Method	NP-TLC Method
<i>Flufenacet (FOE 5043)</i>	52	0.45	0.47
<i>FOE Thiadone</i>	35.5	0.74	0.17
<i>WAK-5958</i>	23.0	0.93	0.00

WAK-5958 is 3-Trifluoromethyl-1,3,4-thiadiazol-2-oxy acetic acid, presented below (structural formula) on figure B.8.1.1.1.1._CA-22.

**Figure B.8.1.1.1.1._CA-22:** Structural formula of WAK-5958 (scheme copied from the study report).

The LC-MS analysis was performed using Varian 5040 HPLC equipped with a Regis Spherisorb S50DS column working in a gradient mode and Berthold LB 505-HPLC Radioactivity Monitor, coupled with Finnigan MAT 90 MS detector. The parameters of gradient were following:

- Mobile phase A: Water,
- Mobile phase B: CH₃OH,
- Gradient mode: linear from 0% B at 0 min to 100% B at 30 min.

The flow rate in the system was set to 0.8 mL/min.

The reported parameters of MS detector were following:

- Spectrometer operated in either positive or negative mode,
- aerosol temperature: 210°C,
- 0.2 M ammonium acetate added post column at rate of 0.2 mL/min.

The identification of Flufenacet and its degradation products in LC/MS analysis was performed by comparison of mass spectra of each chromatographic peaks with those obtained for the standards, for which base signals and protonated molecular ion signals were identified. These are presented below in the table B.8.1.1.1.1._CA-28.

Table B.8.1.1.1.1._CA-28: LC/MS identification of Flufenacet and its degradation products in the study.

Compound	Representative signals used in identification	
	Position – m/z	Description
Flufenacet	364	Protonated molecular ion $[M+H]^+$
	381	Ammonia adduct $[M + NH_4]^+$
Thiadone	169	Peak for $[M - H]^-$ (negative-ion mode)

GC/MS analysis was performed to conform the identity of Flufenacet. It was carried out on HP Model 5990A Gas Chromatograph/Mass Spectrometer. GC was equipped with a DB5-MS column (15 m x 0.25 mm x 0.25 µm film thickness).

The following chromatographic programme was used in analysis:

- GC oven was programmed to start at $T = 80^{\circ}\text{C}$, held at that level for $t = 1$ min, then the temperature increased linearly at rate of $20^{\circ}\text{C}/\text{min}$ up to $T = 250^{\circ}\text{C}$ in 20 min and held at that level for $t = 1$ min; the injector's temperature was $T = 250^{\circ}\text{C}$; MS detector operated in the electron impact mode with a mass range 50 – 400 amu.

Results and their discussion:

The stability tests, performed using DAT-0 samples, demonstrated that the Flufenacet was stable during application, routine extraction procedure and chromatographic analysis of the sample. The same was demonstrated for the acid extraction procedure - with 0.1N HCl_{aq} :ACN (1:1) followed by organic solvent partitioning.

The analysis of the soil biomass showed its decline from 129 mg microbial C/kg soil to 48 mg microbial C/kg soil – 37.21% of initial level, after 8-months lasting incubation (decrease by 62.79%) and further down to 29 mg microbial C/kg soil – 22.48% of the initial level after 12 months of incubation (decrease by 77.52%). That decline pattern was examined in detail in another study, summarised above as **Study 3**. It shall be noted that the microbial biomass throughout the incubation period accounted for 3.7% OC on DAT 0, 1.4% OC after 8 months of incubation and 0.8% OC after 12 months of incubation, but that was due to the low level of soil OC – 0.32% on average. That might have influenced the obtained results, in particular the rate of degradation of Flufenacet.

The recovery of the applied radioactivity in the experimental soil was generally good, in line with the recommendations of the relevant Guidelines: 96.3 – 106.5% AR (average 101.46 % AR).

The level of mineralization for that radiolabelling position was high – it reached 50.9% AR at the end of the study (DAT 368) and gradually increased throughout the study.

The amount of NER fraction also increased with time, from 0.3% AR on DAT 0 to 6.9% AR on DAT 270. A slight decrease in the content of that fraction was observed at the end of the study. It can be stated that the level of NER formed for that radiolabelling position was not very high and ~3 times lower than that observed in the same soil for the compound radiolabelled in phenyl ring.

That may indicate that, unlike the phenyl moiety of the molecule, for the thiadone moiety mineralisation was more important ultimate transformation process in comparison to the formation of NER.

The amount of AR present as combined extractable fraction decreased with time, to reach at the end of the study (DAT 368) the level of 45.5% AR. It was also noted that the AR recovered as extracted was found predominantly in ACN extracts, although it decreased with time, while the amount of AR extracted with acidic extract increased.

The following compounds were identified in extracts:

- Flufenacet,
- Thiadone,
- Other 5 unknown degradation products or degradation products fractions.

Of the compounds listed above none may be considered as major on the basis of the criteria set by SANCO/211/2000 Guidance Document on the Assessment of the Relevance of Metabolites.

The detailed results are presented below, in table B.8.1.1.1.1_CA-29 (the values were rounded to one digit after the decimal point) and additionally in graphical form, on figure B.8.1.1.1.1_CA-23.

Table B.8.1.1.1.1._CA-29: The detailed results obtained in the study.

% AR		Results obtained for sample collected at DAT ¹⁾ :							
		0	7	14	32	90	181	270	368
<i>Extracted as:</i>	ACN extracts ²⁾	95.9	80.3	72.3	59.6	52.9	41.5	35.2	29.1
	Acidic extract ³⁾	6.5	12.6	13.5	12.8	15.5	15.1	15.3	16.4
	Total extracted	102.4	92.9	85.8	72.4	68.4	56.6	50.5	45.5
<i>In extracts identified as:</i>	Flufenacet	100.6	87.7	81.6	69.7	66.7	54.5	48.0	43.7
	Thiadone	1.2	3.9	2.6	1.4	1.0	1.0	1.4	0.9
	Unknown 1 (34.5 min.)	n. d. ⁶⁾	n. d. ⁶⁾	n. d. ⁶⁾	n. d. ⁶⁾	n. d. ⁶⁾	n. d. ⁶⁾	n. d. ⁶⁾	0.2
	Unknown 2 (54.0 min.)	n. d. ⁶⁾	0.1	0.2	0.6	0.4	0.5	0.2	n. d. ⁶⁾
	Unknown 3 (54.5 min.)	0.7	0.7	0.4	0.1	<0.1	0.1	0.2	n. d. ⁶⁾
	Unknown 4 (55.0 min.)	n. d. ⁶⁾	0.1	0.2	n. d. ⁶⁾	n. d. ⁶⁾	<0.1	0.2	n. d. ⁶⁾
	Unknown 5 (57.0 min.)	n. d. ⁶⁾	n. d. ⁶⁾	0.1	0.1	n. d. ⁶⁾	n. d. ⁶⁾	n. d. ⁶⁾	n. d. ⁶⁾
Total identified⁴⁾		102.5	92.5	85.1	71.9	68.1	56.1	50.0	44.8
<i>Bound residues (NER fraction)</i>		0.3	2.7	4.8	5.9	6.2	6.0	6.9	6.5
<i>Volatile compounds</i>	CO ₂	<0.1	4.5	10.1	18.0	31.9	37.9	42.7	50.9
	VOC	<0.1	<0.1	<0.1	<0.1	<0.1	0.1	0.1	1.7
	Total volatile compounds⁵⁾	<0.1	4.5	10.1	18.0	31.9	38.0	42.8	52.6
Total recovered AR		102.7	100.1	100.7	96.3	106.5	100.65	100.2	104.6

Footnotes to the table:

- 1) Values presented are the averages of triplicate repeated analysis for DAT 0 and of duplicate analysis for remaining time points;
- 2) Represents CH₃CN extract;
- 3) Represents 0.1N HCl in CH₃CN:H₂O (1:1 v/v) extract;
- 4) The difference between the Total Extracted AR and the Total identified AR was declared in the study report to be possibly due to three following factors: rounding of figures (1), presence of other HPLC resolvable degradation products, individually not exceeding 0.1% AR (2), presence of radiocarbon residues in acidic extracts that were below LOD for HPLC method (3);
- 5) Value calculated by adding the results obtained for VOC and those for CO₂
- 6) n. d. = not detected.

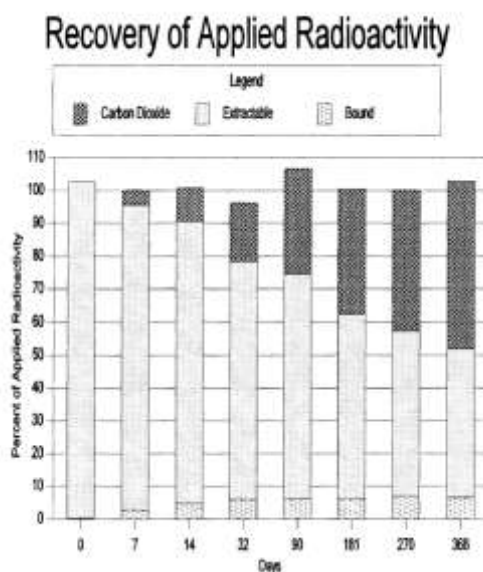


Figure B.8.1.1.1.1._CA-23: Graphical presentation of the obtained results (scheme copied from the study report).

Additionally, below are presented the results of the HPLC analysis of ACN extracts – table B.8.1.1.1.1._CA-30, and acidic extracts – table B.8.1.1.1.1._CA-31.

Table B.8.1.1.1.1_CA-30: The detailed results of the examination of ACN extracts.

Compound	Results obtained for sample collected at DAT ¹⁾ :							
	0	7	14	32	90	181	270	368
<i>Flufenacet</i>	94.1	76.5	69.3	57.5	51.8	40.1	33.7	28.2
<i>FOE Thiadone</i>	1.2	3.0	2.2	1.2	0.8	0.7	1.0	0.6
<i>Unknown 1 (34.5 min.)</i>	n. d. ³⁾	n. d. ³⁾	n. d. ³⁾	n. d. ³⁾	n. d. ³⁾	n. d. ³⁾	n. d. ³⁾	0.2
<i>Unknown 2 (54.0 min.)</i>	n. d. ³⁾	n. d. ³⁾	0.1	0.5	0.2	0.4	n. d. ³⁾	n. d. ³⁾
<i>Unknown 3 (54.5 min.)</i>	0.7	0.7	0.4	0.1	<0.1	0.1	0.3	n. d. ³⁾
<i>Unknown 4 (55.0 min.)</i>	n. d. ³⁾	0.1	0.2	n. d. ³⁾	n. d. ³⁾	n. d. ³⁾	0.2	n. d. ³⁾
<i>Unknown 5 (57.0 min.)</i>	n. d. ³⁾	n. d. ³⁾	0.1	0.1	n. d. ³⁾	n. d. ³⁾	n. d. ³⁾	n. d. ³⁾
Total²⁾	96.0	803	72.3	59.6	52.8	41.3	35.2	29.0

Footnotes to the table:

- 1) Values presented are the averages of triplicate repeated analysis for DAT 0 and of duplicate analysis for remaining time points;
- 2) The difference between the **Total** value reported here and the (**extracted as**): **ACN extracts** reported in the table B.8.1.1.1.1_CA-29 above, was postulated in the study report to be possibly due to the two following factors: rounding of figures (1), presence of other HPLC resolvable degradation products, individually not exceeding 0.1% AR (2);
- 3) n. d = not detected.

Table B.8.1.1.1.1_CA-31: The detailed results of the examination of acidic extracts.

Compound	Results obtained for sample collected at DAT ^{1,2)} :							
	0	7	14	32	90	181	270	368
<i>Flufenacet</i>	6.5	11.2	12.3	12.0	14.8	14.4	14.3	15.5
<i>FOE Thiadone</i>	n. d. ³⁾	0.8	0.4	0.2	0.2	0.2	0.4	0.3
<i>Unknown 1 (34.5 min.)</i>	n. d. ³⁾	n. d. ³⁾	n. d. ³⁾	n. d. ³⁾	n. d. ³⁾	n. d. ³⁾	n. d. ³⁾	<0.1
<i>Unknown 2 (54.0 min.)</i>	n. d. ³⁾	0.1	0.1	0.1	0.1	0.1	0.2	n. d. ³⁾
<i>Unknown 3 (54.5 min.)</i>	n. d. ³⁾	<0.1	<0.1	<0.1	<0.1	n. d. ³⁾	n. d. ³⁾	n. d. ³⁾
<i>Unknown 4 (55.0 min.)</i>	n. d. ³⁾	n. d. ³⁾	n. d. ³⁾	n. d. ³⁾	n. d. ³⁾	<0.1	n. d. ³⁾	n. d. ³⁾
Total^{3,4)}	6.5	12.1	12.8	12.3	15.1	14.7	14.9	15.8

Footnotes to the table:

- 1) Values presented are the averages of triplicate repeated analysis for DAT 0 and of duplicate analysis for remaining time points;
- 2) Represents 0.1N HCl in CH₃CN:H₂O (1:1 v/v) extract;
- 3) The difference between the **Total** value reported here and the (**extracted as**): **Acidic extracts** reported in the table B.8.1.1.1.1_CA-29 above, was postulated in the study report to be possibly due to the two following factors: rounding of figures (1), presence of other HPLC resolvable degradation products, individually not exceeding 0.1% AR (2);
- 4) Value corresponds to radiocarbon residues in organic acid extracts of soil. All aqueous extracts contained <0.9% AR and were not analysed by HPLC.
- 5) n. d = not detected.

The results of the additional TLC analysis were following:

- **NP-TLC** enabled the identification and quantitation of Flufenacet and following two fractions:
 - **Thiadone:** detected in extracts from all sampling points, in most of them in amounts <1.0% AR and in max. amount of 2.3% AR in DAT 7 sample;
 - **Origin:** not further characterised fraction having $R_f = 0.00$, detected in extracts from all sampling points, in none of them in amounts $\geq 2.0\%$ AR (the maximum amount quantified was 1.8% AR in DAT 270 sample).
- **RP-TLC** enabled the identification and quantitation of Flufenacet and following five fractions:
 - **Thiadone:** detected in extracts from all sampling points, in max. amount of 1.5% AR in DAT 14 sample;
 - **Metabolite 1:** not further identified fraction having $R_f = 0.00$, detected in almost all analysed sample extracts, with exception of DAT 0 sample, in amounts 0.2 – 0.3% AR;
 - **Metabolite 2:** not further identified fraction having $R_f = 0.64$, detected only in DAT 181 and DAT 368 samples in amounts of 0.1% AR;
 - **Metabolite 3:** not further identified fraction having $R_f = 0.75$, detected in almost all analysed sample extracts, with exception of DAT 0 and DAT 270 samples, usually not surpassing 0.4% AR and in one sample – DAT 7 detected in max. amount of 1.2% AR;
 - **Metabolite 4:** not further identified fraction having $R_f = 0.87$, detected in almost all analysed sample extracts, with exception of DAT 90, DAT 270 and DAT 360 samples, in amount 0.1% AR.

There were no further attempts to identify any of the detected Unknowns. That was due to the fact that none of them was detected in amounts $\geq 2.5\%$ AR throughout the study.

On the basis of the obtained results the possible transformation pathway of Flufenacet in soil was proposed. It was also stated that the degradation was predominantly, if not exclusively, biotically mediated.

In case of the degradation product Thiadone it was stated that when detected in DAT 0 samples it could possibly be the, at least partly, impurity of the treatment solution. At later time points it was solely a product of microbial transformation of Flufenacet.

Conclusions:

The obtained results showed that Flufenacet was extensively degraded in the experimental soil during 368 days of the experiment, reaching the level of 43.7% of the initial dose at the end of the study.

Also the level of mineralisation was high, comparing to the experiments with Flufenacet radiolabelled in phenyl ring, reaching ~52% AR at the study's end (DAT 368), while the formation of NER fraction was low.

One degradation product was identified – Thiadone, and 5 other, not further identified fractions detected, none of which reached individually the level of 2.5% AR.

The postulated mechanism for degradation of Flufenacet within Thiadiazole moiety was biologically mediated transformation. On the basis of the results obtained in this study the following transformation pathway of Flufenacet in aerobic soil, shown on the Fig B.8.1.1.1.1._CA-24, was proposed:

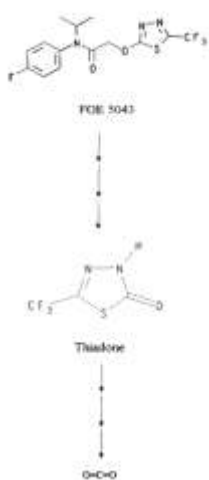


Figure B.8.1.1.1._CA-24: The transformation pathway of Flufenacet in aerobic soil, determined for the compound radiolabelled in thiadiazole moiety (scheme copied from the study report).

RMS's conclusions with regard to the validity of the study:

On the basis of the thorough examination of the study protocol RMS proposes to consider the study valid, despite the deficiencies it displays, as providing vital information in the area of the determination of the route of degradation of Flufenacet in soil.

The problem of the decline of soil microbial activity observed in the experimental soil, was thoroughly examined and satisfactorily explained in an independent study, summarised above as **Study 3**. In light of the findings of that study, the study summarised above can be considered acceptable and relevant for the purpose of the regulatory assessment of Flufenacet.

Two new studies specifically submitted for the purpose of this evaluation are summarised below.

Study 5:

Report: Hein E.-M., (2012): “[Thiadiazole-5-¹⁴C] Flufenacet: Aerobic Degradation/Metabolism in One European Soil.”; Bayer CropScience AG, BCS-D-EnSa-Testing, 40789 Monheim, Germany, Study M1251994-1; unpublished Study Report No. MEF-11/937; 2012. 09. 19, amended (Amendment No 1) 2013. 04. 10; study reference number: M-439105-02-1;

Guidelines: The study was performed to comply with the following Guidelines:

- Commission Directive 95/36/EC amending Council Directive 91/414/EEC (Annexes II and III, Fate and Behaviour in the Environment), 1995;
- OECD Guideline for the Testing of Chemicals, No. 307, Aerobic and Anaerobic Transformation in Soil, 2002;
- US. EPA OCSPP Fate, Transport and Transformation Test Guidelines, OPPTS 835.4100 and OPPTS 835.4200, Aerobic and Anaerobic Soil Metabolism, 2008.

No deviations were stated in the study report.

GLP: Yes

RMS comments: This is a new study submitted specifically for purpose of this assessment. It was verified by the RMS and found acceptable. No deviations from the declared Guidelines were stated. The study is summarised below.

Summary:

The aim of the study was to investigate the fate – route and rate of degradation, of Flufenacet in soil incubated under controlled (in the laboratory) aerobic conditions. The experiment was performed using one European test soil originating from Germany (Hoefchen am Hohenseh). Its characteristic is provided below in the table B.8.1.1.1.1_CA-32.

Table B.8.1.1.1.1_CA-32: The characteristic of soil used in the study.

Parameter		Soil:	
		<i>Hoefchen am Hohenseh 4a</i>	
Soil origin		<i>Burscheid/ North Rhine-Westphalia/ Germany</i>	
Soil type (USDA)		Silt loam	
Particle size distribution	Sand (50 µm – 2 mm) [%]	29	
	Silt (2 – 50 µm) [%]	56	
	Clay (< 2 µm) [%]	15	
pH value in water (soil:water ratio 1:1)		7.0	
pH value in 1N KCl		6.3	
pH value in 0.01M CaCl ₂ (soil:solution ratio 1:2)		6.7	
Organic carbon content (C _{org}) [%] ¹⁾		2.5	
Organic matter content (OM) [%] ²⁾		4.3	
Cation Exchange Capacity – CEC [mEq/100g]		12.9	
Bulk density (disturbed) [g/cm ³]		1.04	
Water holding capacity	Maximum [g H ₂ O/100 g soil d. w.]	61.1	
	at ½ bar (pF 2.5) [%]	23.7	
	at 0.1 bar (pF 2.0) [%]	29.8	
Soil biomass expressed in mg microbial C/kg soil in samples collected on DAT ³⁾ :	0 ⁵⁾	841 (BIO -) ⁶⁾	n. r. (BIO+) ⁷⁾
	60	693 (BIO -) ⁶⁾	638 (BIO+) ⁷⁾
	120	563 (BIO -) ⁶⁾	506 (BIO+) ⁷⁾
Soil biomass expressed as %OC ⁴⁾ in samples collected on DAT:	0 ⁵⁾	3.36 (BIO -) ⁶⁾	n. r. (BIO+) ⁷⁾
	60	2.77 (BIO -) ⁶⁾	2.55 (BIO+) ⁷⁾
	120	2.25 (BIO -) ⁶⁾	2.02 (BIO+) ⁷⁾

Footnotes to the table:

- 1) Measured value;
- 2) Value calculated by the Applicant using the following equation: OM = 1.724*OC;
- 3) Determined using the method by Anderson&Domsch;
- 4) Recalculated by the RMS, using the reported OC = 2.5%;
- 5) For that sampling point only the results for “BIO -” samples were available (please refer to the footnote 6) below);
- 6) “BIO -” stands for samples not treated with blank application solution - 358 µL of CH₃OH/H₂O 1:1 v/v solution;
- 7) “BIO +” stands for samples treated with blank application solution - 358 µL of CH₃OH/H₂O 1:1 v/v solution;

The test soil, representative for the agriculturally used area of the region of sampling, was taken from the field of the history of cropping system and Plant Protection Products use known for the 5 years before sampling. It was determined that during that period the plant cover of that designated field was grassland on which no pesticides were used. Soil used in the experiment was taken with shovel from the top 20-cm layer, placed in plastic container (bag or bucket) and transferred to the experimental facility, where it was sieved through 2-mm sieve.

The aliquots of the test soil were taken for the soil characterisation (soil texture, pH, CEC OC content and water holding capacity). Its results are reported above, in table B.8.1.1.1.1_CA-32. Soil moisture was determined in three 22 – 25g aliquots using an automated halogen moisture analyser.

Soil biomass was determined using Anderson & Domsch's method in the samples taken at the beginning of the incubation period – on DAT 0, on DAT 60 (in the middle of the incubation period) and on DAT 120 (the study's end).

The experiment was performed using the glass biometer flasks, presented below on figure B.8.1.1.1.1_CA-25.

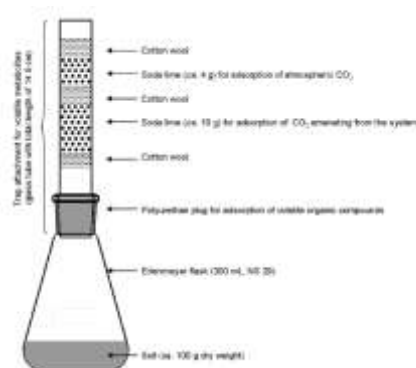


Figure B.8.1.1.1.1_CA-25: The biometer flask used in the experiment (copied from the study report).

They consisted of 300-mL Erlenmeyer flasks with wide-diameter glass tube adapters, sealed with traps for volatile compounds, permeable for oxygen. The traps contained polyurethane foam to absorb possible VOC and soda lime layer (~10 g.) to capture formed $^{14}\text{CO}_2$. The trapping system was capped with ~4-grams. layer of soda lime between two cotton-wool separators, placed to prevent soda-lime sorbent from being saturated with atmospheric CO_2 .

Each test vessel contained the equivalent of 100 grams of oven-dried test soil, adjusted to $55 \pm 5\%$ MWHC by addition of the appropriate amount of the distilled water. That level was maintained throughout of the incubation period, lasting up to 120 days. It was controlled on DAT 56 (prior to that time point it was assumed and then conformed that no significant losses in soil moisture were expected), when the remaining flasks were weighed, the loss of moisture from the system determined and the soil moisture in remaining incubation vessels adjusted to the pre-determined level by addition of the appropriate amount of distilled water.

So prepared incubation flasks were equilibrated to study conditions, in a temperature-controlled walk-in climatic chamber in the dark and at $T = 20 \pm 2^\circ\text{C}$, prior to the treatment of soil with the test compound.

The incubation flask were prepared for the following examinations: kinetic samples – in duplicate per each time point, samples for the determination of soil microbial biomass and those for the identification of transformation products.

The test compound used in the experiment was the ^{14}C -FOE 5043 radiolabelled in C5-thiadiazole position, as shown below on figure B.8.1.1.1.1_CA-26.

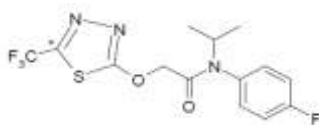


Figure B.8.1.1.1.1_CA-26.: The structural formula of the radiolabelled Flufenacet (FOE 5043) used in the experiment; the asterisk (*) indicates radiolabelling position (copied from the study report).

The specific radioactivity of the test compound used in the experiment was 1.54 MBq/mg and its radiochemical purity, determined using both HPLC and TLC, was > 99%. Also the chemical purity of the test compound, determined using HPLC equipped with UV detector, was > 99%.

It was used to prepare its stock solution by dissolving the total delivered amount in 12 mL of methanol. The so obtained solution had a nominal concentration of ~1 mg/mL (1540 kBq/mL). The exact concentration was verified by LSC, while the identity of the test compound and its purity was verified by means of ¹H-NMR and HPLC-MS(/MS).

It was stated that the exact concentration of the stock solution was 1423.08 kBq/mL and its radiochemical purity 100%.

Next two application solutions were prepared from the stock solution. One of them having the target nominal concentration of 616.0 kBq/mL was designated to be used in kinetic samples (further called **Application Solution 1**). The second one, having the same target nominal concentration – 616.0 mBq/mL was designated to treat samples for identification of transformation products (further called **Application Solution 2**).

Application Solution 1 was prepared by transferring 7.79 mL of the stock solution to a glass bottle and diluting it with 1.21 mL of methanol and 9.00 mL of deionised water to obtain the total volume of 18.00 mL. The so prepared solution had the experimentally determined (by LSC) concentration of 688.1 kBq/mL, corresponding to 446.8 µg Flufenacet/mL.

Application Solution 2 was prepared by transferring 3.64 mL of the stock solution to a glass bottle and diluting it with 0.04 mL of methanol and 3.675 mL of deionised water to obtain the total volume of 7.35 mL. The so prepared solution had the experimentally determined (by LSC) concentration of 748.8 kBq/mL, corresponding to 486.2 µg Flufenacet/mL.

The **Application Solution 1** was applied dropwise onto the soil surface in pre-equilibrated test vessels in amount of 358 µL/test vessel to obtain the application dose in the kinetic samples of 160 µg Flufenacet/100 g soil d. w. (1.6 mg Flufenacet/kg soil d. w.). According to the Applicant that corresponded to the application rate of 600 g Flufenacet/ha, assuming soil bulk density $d = 1.5 \text{ g/cm}^3$ and the thickness of the soil layer $l = 2.5 \text{ cm}$. RMS recalculated the assumed application rate using the standard assumptions: soil bulk density $d = 1.5 \text{ g/cm}^3$ and the thickness of the soil layer $l = 5.0 \text{ cm}$. The resulting application rate $A = 1200 \text{ g Flufenacet/ha}$, the application rate five times higher than that proposed in the EU-representative GAP prepared for the purpose of the current evaluation. When the measured soil bulk density - $d = 1.04 \text{ g/cm}^3$ was used the calculated application rate was $A = 832 \text{ g Flufenacet/ha}$.

The **Application Solution 2** was applied dropwise onto the soil surface in pre-equilibrated test vessels, in amount of 3290 µL/test vessel to obtain the application dose in the samples for identification of transformation products of 1600 µg Flufenacet/100 g soil d. w. (16 mg Flufenacet/kg soil d. w.). According to the Applicant that corresponded to the application rate of 6000 g Flufenacet/ha, assuming soil bulk density $d = 1.5 \text{ g/cm}^3$ and the thickness of the soil layer $l = 2.5 \text{ cm}$ – ten-fold the accepted field application rate of that compound. RMS recalculated the assumed application rate using the standard assumptions: soil bulk density $d = 1.5 \text{ g/cm}^3$ and the thickness of the soil layer $l = 5.0 \text{ cm}$. The resulting application rate $A = 12000 \text{ g Flufenacet/ha}$, the application rate fifty times higher than that proposed in the EU-representative GAP prepared for the purpose of the current evaluation. The justification for such high application dose was that it enabled the proper identification of the formed degradation products. When the measured soil bulk density - $d = 1.04 \text{ g/cm}^3$, was used, the calculated application rate was $A = 8320 \text{ g Flufenacet/ha}$.

After application of the test compound the kinetic samples, except DAT-0 samples were fitted with traps for volatile compounds and placed in the temperature-controlled walk-in climatic chamber to be incubated in the dark and at constant temperature $T = 20 \pm 2^\circ\text{C}$ for up to 120 days. The sampling points were designated on DATs (Days After Treatment) 0, 2, 4, 7, 10, 14, 35, 60, 87 and 120. On those specific time points duplicate samples were removed from the incubation chamber for the further examination.

The samples for identification of transformation products after application of the test compound were handled in the same way as described above for the kinetic samples.

The homogeneity of the application in these samples was determined before, during and after application, by pipetting 358 µL- aliquots of the **Application Solution 1** into 20-mL volumetric flasks filled to the volume with CH₃CN. The so prepared solutions were then tested for their radioactivity content using LSC method.

The exact application rate for kinetic samples was determined by measuring the amount of the radioactivity in DAT-0 samples by LSC before, during and after application. The determined level of radioactivity was considered to be 100% AR

The biomass samples were placed alongside the kinetic samples and those for identification of transformation products. They were prepared in the following way: the pre-equilibrated test vessels were divided into two groups: native soil biomass test systems – “BIO-”, and solvent control biomass test systems – “BIO+”. The “BIO-” samples were left untreated, while to the “BIO+” samples 358 μL aliquots of the blank application solution – 1:1 MeOH/H₂O solution not containing the test compound, were pipetted. So prepared samples, except DAT-0 “BIO-” samples, were then handled in the same manner as kinetic samples. On DAT 60 and DAT 120 “BIO-” and “BIO+” samples were taken for the determination of the soil biomass content using Anderson&Domsch’s method.

All samples were incubated under aerobic conditions in the dark, under the constant temperature $T = 20 \pm 2^\circ\text{C}$ and soil moisture $55 \pm 5\%$ MWHC. Soil moisture was controlled at the beginning of the study and on DAT 56 by weighing test systems and adjusting it, if necessary, to the designated level by adding the appropriate amount of deionised water.

The samples removed at the designated sample points were processed in the following way: prior to opening the incubation vessels all volatiles possibly present in the area between soil surface and the volatile trap filling were purged into the trap columns. Next the incubation vessels were dissected into Erlenmayer flasks containing soil and volatile traps, and further processed following the conceptual scheme presented below on Figure B.8.1.1.1._CA-27. The entire soil samples were taken for the analysis. They were quantitatively transferred, using the first extraction solvent, to centrifuge beakers used as the extraction vessels.

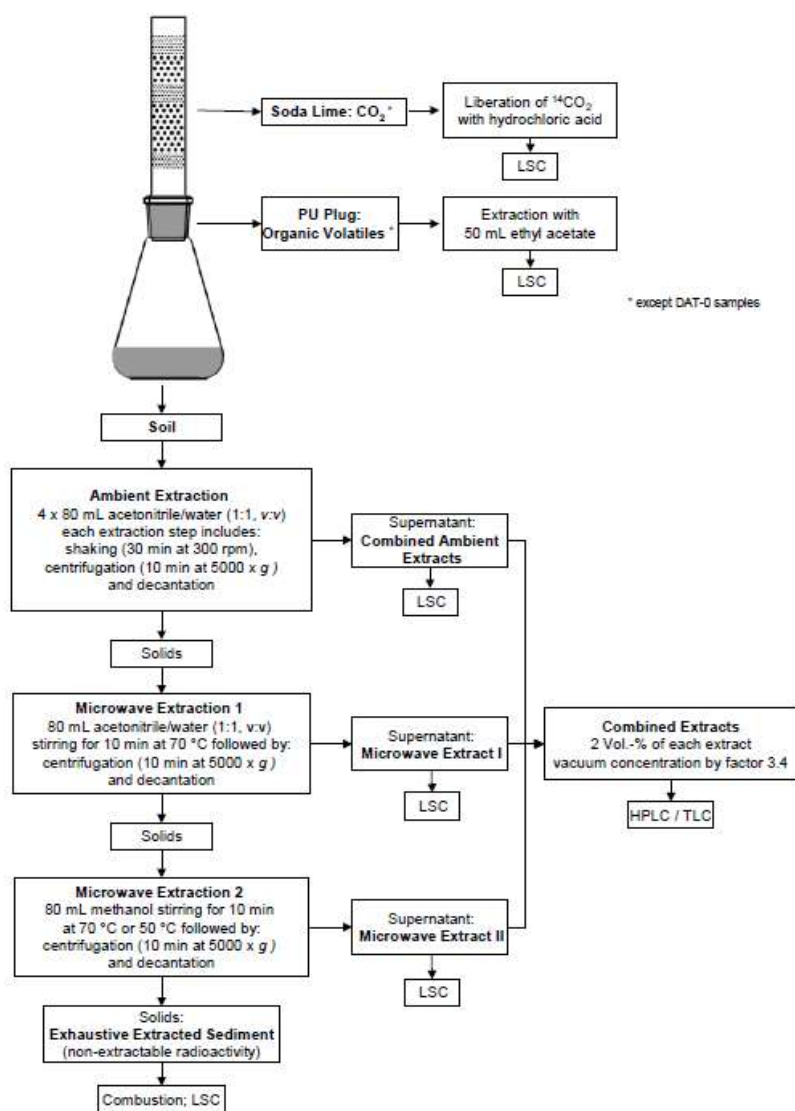


Figure B.8.1.1.1.-CA-27: The conceptual scheme of sample processing procedure (copied from the study report).

The extracted soil pellets were lyophilized, homogenised and three 1-g aliquots analysed for NER fraction, after combustion, using LSC.

That procedure was applied to kinetic samples. The samples for the identification of transformation products were not processed. Instead the isolation and identification of the transformation products was performed using concentrated combined extracts from DAT 35 samples, which were analysed by HPLC and the chromatographic eluates divided into six fractions which were further processed and analysed.

The extracted soil pellets were analysed for NER fraction. To do that each soil sample was allowed to air-dry overnight, after what its triplicate aliquots (50 – 100 mg) were oxidized by combustion. The formed $^{14}\text{CO}_2$ was trapped in alkaline solution which, after mixing with scintillation cocktail, was analysed by LSC. The further characterisation of NER fraction was not performed, because of its low content – max. 13.5% AR.

All samples were analysed for the content of radioactivity using LSC method. The LSC (Liquid Scintillation Counting) analysis was performed using LS6000 LL/6500 or LKB-Wallac 1219 Spectral counters.

The radioactivity in soil extracts and other liquid samples from HPLC analysis was determined in either:

- mini-vials, using the sample aliquots of up to 1 mL and 2 mL of Quicksafe[®] A solution containing 5% of water; the counting time was 10 min and the background 13 – 16 cpm;
- maxi-vials, using the sample aliquots of up to 5 mL and 7 mL of Quicksafe[®] A solution containing 5% of water; the counting time was 10 min and the background 22 – 23 cpm.

The $^{14}\text{CO}_2$ recovered from soda lime was absorbed in Oxysolve scintillation cocktail, in three vials per sample and radioactivity measured in each vial. The results were summed up. The counting time was 10 min and the background 17 – 20 cpm.

The radioactivity in extracts from PU plugs was determined in maxi-vials using the sample aliquots of up to 5 mL and 7 mL of Quicksafe[®] A solution containing 5% of water. The counting time was 10 min and the background 22 – 23 cpm.

The radioactivity in solid samples – extracted soil pellets, was determined after combustion of three 1-g aliquots of dried and homogenised material. The resulting $^{14}\text{CO}_2$ was absorbed in 15 mL of Oxysolve C400 liquid. The counting time was 10 min and the background 17 – 20 cpm.

The instrumental limit of detection – LOD_i was set to twice maximum instrument background count rate and instrumental limit of quantitation – LOQ_i to three times maximum instrument background count rate. Maximum instrument background count rate was determined to be 0.3 – 0.5 Bq. Therefore, for different types of liquid samples the instrumental LOD_i and LOQ_i were as follows:

- samples with scintillation cocktail of 2 mL Quicksafe A + 5% water, $\text{LOD}_i = 0.5$ Bq and $\text{LOQ}_i = 0.8$ Bq;
- samples with scintillation cocktail of 7 mL Quicksafe A + 5% water, $\text{LOD}_i = 0.8$ Bq and $\text{LOQ}_i = 1.2$ Bq;
- samples with scintillation cocktail of 15 mL Oxysolve C400, $\text{LOD}_i = 0.7$ Bq and $\text{LOQ}_i = 1.0$ Bq.

When calculated for different types of analysed samples, the determined LOD and LOQ values for LSC analysis were as presented below in the table B.8.1.1.1.1._CA-33:

Table B.8.1.1.1.1._CA-33: The LOD and LOQ values for different types of samples analysed using LSC.

Type of sample	max. total amount – volume or mass	min. aliquots analysed – volume or mass	LOD (worst case) expressed in:		LOQ (worst case) expressed in:	
			Bq	% AR	Bq	% AR
<i>Ambient extract</i>	380 mL	0.5 mL	405.3	0.2	608.0	0.2
<i>Microwave extract 1</i>	81 mL	0.5 mL	86.4	<0.1	129.6	<0.1
<i>Microwave extract 2</i>	78 mL	0.5 mL	83.2	<0.1	124.8	<0.1
<i>PU foam plug extract</i>	50 mL	5 mL	7.7	<0.1	11.5	<0.1
<i>Solid sample (combustion)</i>	101 g	0.9 g	75	<0.1	112.6	0.1
<i>$^{14}\text{CO}_2$ from soda lime traps</i>	Sample entirely used for LSC analysis		----	<0.1	----	<0.1

Sample extracts were analysed using the following analytical methods:

- HPLC – primary identification and quantitation method for parent compound and its degradation products;
- TLC – primary and conformatory quantitation method for the parent compound and its degradation products;
- LC-MS – identification method for parent compound and its degradation products;
- ^1H -NMR – supplementary identification method for parent compound in stock solution.

The RP-HPLC analysis was performed in a gradient mode. The system consisted of HP 1200 chromatograph equipped with a quaternary pump, autosampler, on-line degasser, column oven and a Variable Wavelength UV detector set at $\lambda = 254$ nm, coupled with Ramona 2000 radioactivity detector. Chromatographic separation was performed on and Purosphere Star C_{18e} 250 mm * 4.6 mm * 5 μ m chromatographic column, preceded by Purosphere Star C_{18e} 4 mm * 4 mm * 5 μ m guard column. It worked in the following gradient regime:

- **Mobile phase A:** 985 mL Water + 10 mL HCOOH + 5 mL NH₄COOH_(aq) (5 mM NH₄COOH/265 mM HCOOH);
- **Mobile phase B:** 985 mL CH₃CN + 10 mL HCOOH + 5 mL NH₄COOH_(aq) (5 mM NH₄COOH/265 mM HCOOH);
- **Gradient mode:** 0% B for the first 5 min., then linear gradient 95% B on 55th min., hold for next 5 min., linear gradient to 0% B at 62nd min. and hold until 65th min;
- Total run time was 65 minutes.

The flow rate was set to 1.0 mL/min. The chromatographic column was kept under the constant temperature T = 40°C.

The method had following performance parameters:

- mean recovery of 98.4%;
- good linearity – $R^2 > 0.9999$ for the injected amounts of the radiolabelled test compound ([Thiadiazole-5-¹⁴C] Flufenacet) in range 3.0 Bq – 504.0 Bq;
- LOD = 3.0 Bq, corresponding to LOD = 0.5% AR;
- LOQ = 3 * LOD – 9.0 Bq, corresponding to 1.5% AR.

The quantitative TLC analysis of polar fraction was performed as NP-TLC (Normal Phase TLC). It was carried out at ambient temperature, in saturated chamber, on silica gel Merck Si60, F₂₅₄, TLC plates. The solvent system used in the analysis was CH₃COOC₂H₅/CH₃CHOHCH₃/H₂O/CH₃COOH 65:24:11:1 (v/v/v/v) solution (CH₃CHOHCH₃ stands for 2-propanol).

Two detectors were used:

- UV cabinet (Camag) detector working at two wavelengths: $\lambda = 254$ nm or $\lambda = 366$ nm;
- Bio-Imaging Analyser “BAS-2000” for analysis of radioactivity.

The conformatory TLC method was also performed as NP-TLC (Normal Phase TLC). It was carried out at ambient temperature, in saturated chamber, on silica gel Merck Si60, F₂₅₄, TLC plates. Two detectors were used:

- UV cabinet (Camag) detector working at two wavelengths: $\lambda = 254$ nm or $\lambda = 366$ nm;
- Bio-Imaging Analyser “BAS-2000” for analysis of radioactivity.

Two solvent system were used in the analysis:

- eluent 1 (**Method D**) – CH₂Cl₂/CH₃COOC₂H₅ 8:2 (v/v) solution;
- eluent 2 (**Method A**) – CH₃COOC₂H₅/CH₃CHOHCH₃/H₂O/CH₃COOH 65:24:11:1 (v/v/v/v) solution (CH₃CHOHCH₃ stands for 2-propanol).

Method D was used to separate the non-polar compounds – Flufenacet and FOE Thiadone, while **Method A** for separation of the polar ones – FOE Trifluoroethanesulfonic acid and Trifluoroacetic acid (TFA).

The LC-MS analysis was performed using HP1000 HPLC system equipped with a Nucleodur Gravity C₁₈ chromatographic column (250 * 2 mm, 3 μ m), UV detector followed by the Ramona Star radiodetector and the LTQ Orbitrap XL mass spectrometer detector. The parameters of chromatographic analysis were following:

- column temperature: 40°C,
- flow rate: 0.2 mL/min,
- elution mode: gradient,
- mobile phase:
 - Solvent A: H₂O + 0.1% HCOOH,
 - Solvent B: CH₃CN + 0.1% HCOOH.
- two gradient programmes used, presented below in the table B.8.1.1.1.1._CA-34:
 - Gradient 1,
 - Gradient 2.

Table B.8.1.1.1.1._CA-34: Gradient programmes used in LC/MS analysis.

Gradient 1			Gradient 2		
Time [min]	% solvent A (H ₂ O + 0.1% HCOOH)	% solvent B (CH ₃ CN + 0.1% HCOOH)	Time [min]	% solvent A (H ₂ O + 0.1% HCOOH)	% solvent B (CH ₃ CN + 0.1% HCOOH)
0	95	5	0	100	0
1	95	5	5	100	0
25	5	95	25	5	95
35	5	95	35	5	95

Results and their discussion:

The monitoring of the experimental conditions demonstrated that the samples were incubated at the mean temperature 19.7⁰C, ranging from 19.4⁰C to 19.9⁰C. These values were within the limits of the assumed constant temperature T = 20 ± 2⁰C.

The soil moisture content was demonstrated to be within the assumed value of 55 ± 5% MWHC and no significant losses were observed throughout the study duration.

The change in soil biomass looked as follows:

- in soil not treated with blank application solution it decreased during the incubation period by 17.6% until the mid-point of the study (DAT60) and by 33.1% at its end – DAT 120;
- in soil treated with blank application solution it decreased during the incubation period by 24.1% until the mid-point of the study (DAT60) and by 39.8% at its end – DAT 120.

It shall be noted that the decrease in soil microbial activity was greater in soil treated with blank application solution. It was stated however, that it cannot be attributed to the influence of the application solution on the soil biomass, because of small difference in that parameter between treated and not treated samples. As a result, it can be stated that the decrease in soil microbial activity may be related predominantly to the natural phenomena. It was within the acceptability limits – the soil microbial biomass was throughout the study duration above the recommended level of 1% OC, making the obtained results reliable.

The LSC analysis of the homogeneity of application of the kinetic samples showed that it was homogenous, with RSD = 0.7%

The stability tests, performed using DAT-0 samples, demonstrated that the Flufenacet was stable during application and that the radiochemical purity of the application solution was 100%.

The application dose determined for DAT 0 samples was (average) 249885 Bq, equal to 162.3 µg Flufenacet/sample. That value was set as 100% AR for the kinetic samples.

The recovery of the applied radioactivity in experimental soil was generally good, in line with the recommendations of the relevant Guidelines: on average 99.5% AR with RSD = 1.2%, and range of 97.0% AR – 101.6% AR (values given as the means of two replicates).

The level of mineralization was not very high in comparison to the results obtained in another study with Flufenacet radiolabelled in thiadiazole moiety – it reached 5.6% AR at the end of the study (DAT 120).

The amount of NER fraction also increased with time from 0.5% AR on DAT 0 to max. 13.5% AR on DAT 60 (study's mid-point), to then slightly decrease to 12.5% AR at the study's end (DAT 120). It shall be noted that the fraction formed in higher amounts than in the earlier study with Flufenacet radiolabelled in thiadiazole moiety.

The amount of AR present as combined extractable fraction decreased with time from 99.7% at the beginning of the study – DAT 0 to 78.8% AR at its end (DAT 120). It was recovered predominantly in ambient extracts, while microwave extracts did not significantly contribute to the amounts of AR extracted.

The following compounds were identified in extracts:

- Flufenacet,
- FOE Thiadone - max. 5.8% AR on DAT 10,
- FOE 5043-Trifluoroethanesulfonic acid - max. 6.0% AR on DAT 14,
- Trifluoroacetic acid (TFA) – max. 77.7% AR on DAT 87.

The small fraction of unidentified radioactivity was detected, not surpassing 2% AR at any sampling point.

All identified degradation products listed above may be considered as major according to the criteria set by SANCO/211/2000 Guidance Document on the Assessment of the Relevance of Metabolites.

The detailed results are presented below, in table B.8.1.1.1.1._CA-35 (the means of the two replicates; values were rounded to one digit after the decimal point) and additionally in graphical form, on two figures - B.8.1.1.1.1._CA-28 for radioactivity distribution and B.8.1.1.1.1._CA-29 for identified compounds/fractions profiling.

Table B.8.1.1.1.1._CA-35: The detailed results obtained in the study.

% AR		Results obtained for sample collected at DAT ¹⁾ :									
		0	2	4	7	10	14	35	60	87	120
Extracted as:	Ambient extract	97.8	96.1	96.6	93.6	90.8	88.2	81.7	78.6	78.3	77.0
	Microwave extract 1	1.5	1.9	2.0	1.8	2.1	2.2	1.2	1.6	1.4	1.3
	Microwave extract 2	0.4	0.5	0.8	0.8	0.9	0.9	0.5	0.6	0.5	0.5
	Total extracted	99.7	98.4	99.3	96.2	93.8	91.4	83.4	80.8	80.2	78.8
In extracts identified as:	Flufenacet	99.7	92.2	87.8	75.6	64.1	54.8	13.8	3.7	1.6	0.9
	FOE Thiadone	n. d. ⁵⁾	3.4	4.5	5.5	5.8	3.4	1.6	0.6	<LOD	<LOD
	FOE 5043-Trifluoroethane-sulfonic acid	n. d. ⁵⁾	0.9	2.3	4.2	5.4	6.0	4.9	2.6	<LOD	<LOD
	Trifluoroacetic acid (TFA)	n. d. ⁵⁾	1.2	3.7	9.6	16.7	25.1	61.1	73.0	77.7	77.6
	Unidentified fraction ²⁾	n. d.	<LOD	0.9	0.9	1.5	1.8	1.8	1.8	<LOD	<LOD
	Total identified³⁾	99.7	98.2	99.3	95.8	93.4	91.1	83.2	80.7	79.6	78.5
Bound residues (NER fraction)		0.5	1.4	2.1	3.7	5.3	7.0	12.5	13.5	13.1	12.5
Volatile compounds	CO ₂	n. a. ⁶⁾	<0.1	0.1	0.3	0.7	1.1	3.2	4.5	5.2	5.6
	VOC	n. a. ⁶⁾	<0.1	<0.1	0.1	<0.1	<0.1	<0.1	0.1	0.1	0.1
	Total volatile compounds⁴⁾	n. a.⁶⁾	<0.1	0.1	0.4	0.7	1.1	3.2	4.6	5.3	5.7
Total recovered AR		100.2	99.9	101.6	100.2	99.8	99.5	99.1	98.9	98.6	97.0

Footnotes to the table:

- 1) Values presented are the means of two replicates for each sampling point;
- 2) A sum of all minor degradation products;
- 3) The difference between the Total Extracted AR and the Total identified AR was declared in the study report to be possibly due to the following factors: rounding of figures (1), cleanup and chromatographic losses (2);
- 4) Value calculated by adding the results obtained for VOC and those for CO₂
- 5) n. d. = not detected;
- 6) n. a. = not analysed, because of the assumption made that at that sampling point neither mineralisation nor formation of volatile degradation products is expected to occur.

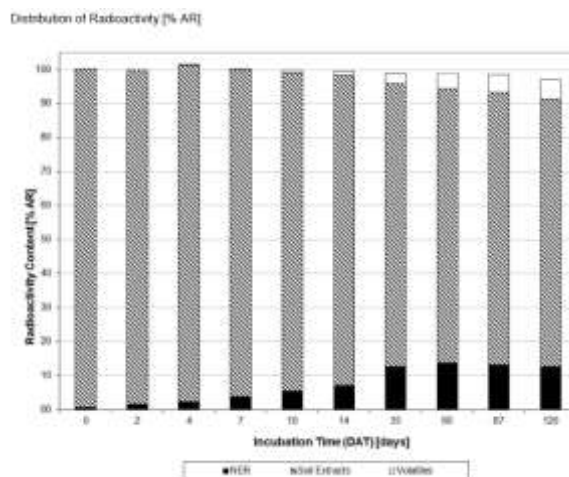


Figure B.8.1.1.1.1._CA-28: Graphical presentation of the obtained results - distribution of radioactivity (copied from the study report).

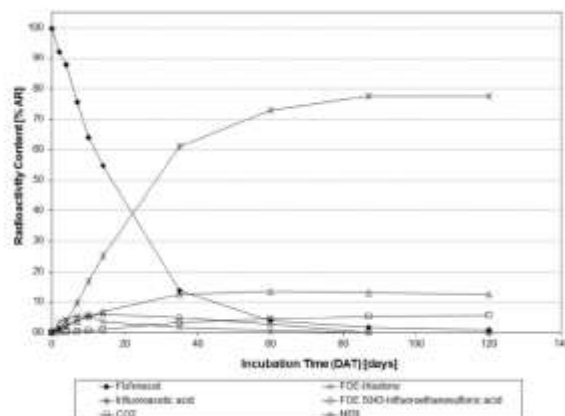


Figure B.8.1.1.1._CA-29: Graphical presentation of the obtained results – concentration profiles of identified degradation products (copied from the study report).

On the basis of the obtained results the Applicant proposed the transformation scheme presented below on figure B.8.1.1.1._CA-30. Mechanistically, it consisted of the following steps:

- cleavage of the test item on bridging oxygen of the thiadiazole heterocycle and tautomerisation of keto-enol functional group, resulting in formation of FOE Thiadone,
- hydrolytical opening of Thiadone ring and further oxidation resulting in formation of either FOE 5043-Trifluoroethanesulfonic acid or Trifluoroacetic acid (TFA), or else simple products of mineralisation and NER fraction – ultimate transformation products;
- further transformation of FOE 5043-Trifluoroethanesulfonic acid or Trifluoroacetic acid (TFA) to the simple products of mineralisation and NER fraction – ultimate transformation products.

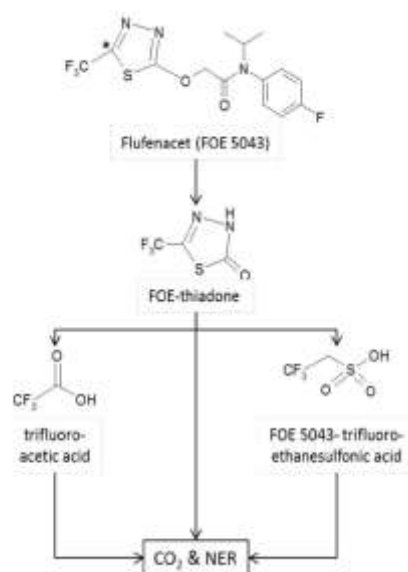


Figure B.8.1.1.1._CA-30: The conceptual scheme of the transformation of Flufenacet radiolabelled in thiadiazole moiety (copied from the study report).

The results obtained for Flufenacet were kinetically examined and the results of that examination presented as a part of the study report. The performed kinetic analysis complied with the current standards, set by FOCUS Kinetics Guidance Document [FOCUS, 2006]. It was however decided, in order to maintain the coherence of the Report, to present it under the relevant point of this document – B.8.1.1.2.1.1.

Study 6:

Report: Hein E.-M., (2012): “[Thiadiazole-5-¹⁴C] Flufenacet: Aerobic Degradation/Metabolism in Three European Soils.”; Bayer CropScience AG, BCS-D-EnSa-Testing, 40789 Monheim, Germany, Study M1252037-0; unpublished Study Report No. MEF-11/938; 2012. 10. 18, amended (Amendment No 1) 2013. 01. 28; study reference number: M-440348-02-1;

Guidelines: The study was performed to comply with the following Guidelines:

- OECD Guideline for the Testing of Chemicals, No. 307, Aerobic and Anaerobic Transformation in Soil, 2002;
- US. EPA OCSPP Fate, Transport and Transformation Test Guidelines, OPPTS 835.4100 and OPPTS 835.4200, Aerobic and Anaerobic Soil Metabolism, 2008.

GLP: Yes

RMS comments: This is a new study submitted specifically for purpose of this assessment. It was verified by the RMS and found acceptable. No deviations from the declared Guidelines were stated. The study is summarised below.

Summary:

The aim of the study was to investigate the fate – route and rate of degradation, of Flufenacet in soil incubated under controlled (in the laboratory) aerobic conditions. The experiment was performed using three European test soils. Their characteristic is provided below in the table B.8.1.1.1.1._CA-36.

Table B.8.1.1.1.1._CA-36: The characteristic of soils used in the study.

Parameter		Soil		
		<i>Laacherhof AXx</i> (AX)	<i>Dollendorf II</i> (DD)	<i>Laacherhof Wurmweise</i> (WW)
Soil origin		Monheim/North Rhine-Westphalia/Germany	Blankenheim/North Rhine-Westphalia/Germany	Monheim/North Rhine-Westphalia/Germany
Soil type (USDA)		Loamy sand	Clay Loam	Loam
Particle size distribution	Sand (50 µm – 2 mm) [%]	75	29	49
	Silt (2 – 50 µm) [%]	20	38	34
	Clay (< 2 µm) [%]	5	33	17
pH value in 0.01M CaCl ₂ (soil/solution ratio 1:2)		6.1	7.2	5.4
pH value in H ₂ O (soil/solution ratio 1:1)		6.4	7.4	5.7
pH value in 1N KCl		5.9	7.0	5.2
Organic carbon content (OC) [%]		2.4	5.3	2.2
Organic matter content (OM) [%] ¹⁾		4.1	9.1	3.8
Cation Exchange Capacity – CEC [mEq/100g]		9.9	20.9	10.8
Water holding capacity	Maximum [g H ₂ O/100 g soil]	49.1	79.8	59.9
	at 0.1 bar (pF 2.0) [%]	18.7	46.0	23.3
	at ½ bar (pF 2.5) [%]	12.0	35.9	16.3
Bulk density (disturbed) [g/cm ³]		1.19	0.95	1.12
Soil biomass expressed in mg microbial C/kg soil	“Bio - ” ³⁾	Initial (DAT 0)	1077	862
		Final (DAT 121)	451	341
	“Bio +” ⁴⁾	Initial (DAT 0)	n. d. ⁵⁾	n. d. ⁵⁾
		Final (DAT 121)	422	338
Soil biomass expressed as %OC ²⁾	“Bio - ” ³⁾	Initial (DAT 0)	4.49	3.92
		Final (DAT 121)	1.88	1.55
	“Bio +” ⁴⁾	Initial (DAT 0)	n. c. ⁶⁾	n. c. ⁶⁾
		Final (DAT 121)	1.76	1.54

Footnotes to the table:

- 1) Value calculated by the RMS using the following equation: OM = 1.724 * OC;
- 2) Values calculated by RMS;
- 3) “Bio - ” stands for samples not treated with blank application solution - 346 µL of CH₃OH/H₂O 1:1 v/v solution;
- 4) “Bio +” stands for samples treated with blank application solution - 346 µL of CH₃OH/H₂O 1:1 v/v solution;
- 5) Value not determined – at that time point the influence of application solution on soil biomass considered negligible;
- 6) Value not calculated due to the lack of the relevant experimental value;

The test soils, representative for the agriculturally used areas of the regions of sampling, were taken from the fields of the history of cropping system and Plant Protection Products use known for the 5 years before sampling. It was determined that during that period the plant cover of those designated fields was grassland on

which no pesticides were used. Soils used in the experiment were taken with shovel from the top 20-cm layer, placed in plastic containers (bag or bucket) and transferred to the experimental facility, where they were sieved through 2-mm sieve.

The aliquots of the test soils were taken for the soil characterisation (soil texture, pH, CEC OC content and water holding capacity), reported above in table B.8.1.1.1.1._CA-36. Soil moisture for each test soil was determined in three 10 – 20-g aliquots, using an automated halogen moisture analyser.

Soil biomass was determined using Anderson & Domsch's method in the samples taken at the beginning of the incubation period – on DAT 0 and at its end – on DAT 121.

The experiment was performed using the glass biometer flasks, presented below on figure B.8.1.1.1.1._CA-31.

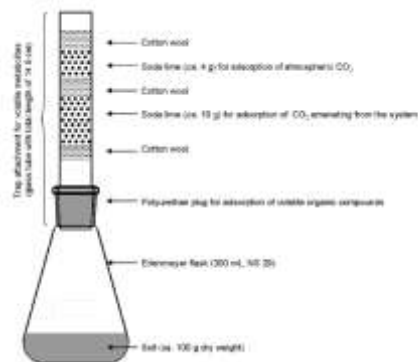


Figure B.8.1.1.1.1._CA-31: The biometer flask used in the experiment (scheme copied from the study report).

They consisted of 300-mL Erlenmeyer flasks with wide-diameter glass tube adapters, sealed with traps for volatile compounds, permeable for oxygen. The traps contained polyurethane foam to absorb possible VOC and soda lime layer (~10 g.) to capture formed $^{14}\text{CO}_2$. The trapping system was capped with ~4-grams. layer of soda lime between two cotton-wool separators, placed to prevent soda-lime sorbent from being saturated with atmospheric CO_2 .

Each test vessel contained the equivalent of 100 grams of oven-dried test soil, adjusted to $55 \pm 5\%$ MWHC bar by addition of the appropriate amount of the distilled water. That level was maintained throughout of the incubation period, lasting up to 121 days. It was controlled on DAT 67 (prior to that time point it was assumed, and then conformed, that no significant losses in soil moisture were expected), when the remaining flasks were weighed, the loss of moisture from the system determined and the soil moisture in remaining incubation vessels adjusted to the pre-determined level by addition of the appropriate amount of distilled water.

So prepared incubation flasks were equilibrated to study conditions, in a temperature-controlled walk-in climatic chamber in the dark and at $T = 20 \pm 2^\circ\text{C}$, prior to the treatment of soil with the test compound.

The incubation flask were prepared for the following examinations: kinetic samples – in duplicate per each time point, samples or the determination of soil microbial biomass and those for the identification of transformation products.

The test compound used in the experiment was the ^{14}C -FOE 5043 radiolabelled in C5-thiadiazole position, as shown below on figure B.8.1.1.1.1._CA-32.

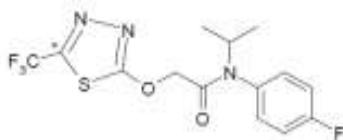


Figure B.8.1.1.1.1._CA-32: The structural formula of the radiolabelled Flufenacet (FOE 5043) used in the experiment; the asterisk (*) indicates radiolabelling position (copied from the study report).

The specific radioactivity of the test compound used in the experiment was 1.54 MBq/mg and its radiochemical purity, determined using both HPLC and TLC, was $> 99\%$. Also the chemical purity of the test compound, determined using HPLC equipped with UV detector, was $> 99\%$.

It was used to prepare its stock solution by dissolving the total delivered amount in 17 mL of methanol. The so obtained solution had a nominal concentration of ~2 mg/mL (3047 kBq/mL). The exact concentration was verified by LSC, while the identity of the test compound and its purity by means of ¹H-NMR and HPLC-MS/MS).

It was stated that the exact concentration of the stock solution was 3081.54 kBq/mL and radiochemical purity 100%.

Next two application solutions were prepared from the stock solution. One of them, having the target nominal concentration of 616.0 kBq/mL, was designated to for treating of the kinetic samples (further called **Application Solution 1**). The other one, having the target nominal concentration of 6160.0 mBq/mL, was designated to treat the samples for identification of transformation products (further called **Application Solution 2**)

Application Solution 1 was prepared by transferring 8.8 mL of the stock solution to a glass bottle and diluting it with 13.2 mL of methanol and 22.0 mL of deionised water to obtain the total volume of 44.0 mL. The so prepared solution had the experimentally determined (by LSC) concentration of 711.5 kBq/mL, corresponding to 462.0 µg Flufenacet/mL.

Application Solution 2 was prepared by transferring 5.60 mL of the stock solution to a glass bottle and evaporating it to dryness under the constant stream of nitrogen. The residue was reconstituted in 1.4 mL of methanol and 1.4 mL of deionised water to obtain the total volume of 2.8 mL. The so prepared solution had the experimentally determined (by LSC) concentration of 6445.8 kBq/mL, corresponding to 4185.6 µg Flufenacet/mL.

The **Application Solution 1** was applied dropwise onto the soil surface in pre-equilibrated test vessels, in amount of 346 µL/test vessel, to obtain the application dose in the kinetic samples of 160 µg Flufenacet/100 g soil d. w. (1.6 mg Flufenacet/kg soil d. w.). According to the Applicant that corresponded to the application rate of 600 g Flufenacet/ha, assuming soil bulk density $d = 1.5 \text{ g/cm}^3$ and the thickness of the soil layer $l = 2.5 \text{ cm}$. RMS recalculated the assumed application rate using the standard assumptions: soil bulk density $d = 1.5 \text{ g/cm}^3$ and the thickness of the soil layer $l = 5.0 \text{ cm}$. The resulting application rate $A = 1200 \text{ g Flufenacet/ha}$ – five times higher than that proposed in the EU-representative GAP prepared for the purpose of the current evaluation. When the measured soil bulk density, specific for each test soil was used, the calculated application rates were following:

- for **Laacherhof AXXa (AD)** soil, having the bulk density $d = 1.19 \text{ g/cm}^3$, calculated application rate was $A = 952 \text{ g Flufenacet/ha}$;
- for **Dollendorf II (DD)** soil, having the bulk density $d = 0.95 \text{ g/cm}^3$, calculated application rate was $A = 760 \text{ g Flufenacet/ha}$;
- for **Laacherhof Wurmweise (WW)** soil, having the bulk density $d = 1.12 \text{ g/cm}^3$, calculated application rate was $A = 896 \text{ g Flufenacet/ha}$.

The **Application Solution 2** was applied dropwise onto the soil surface in pre-equilibrated test vessels in amount of 382 µL/test vessel to obtain the application dose in the samples for identification of transformation products equal to 1600 µg Flufenacet/100 g soil d. w. (16 mg Flufenacet/kg soil d. w.). According to the Applicant that corresponded to the application rate of 6000 g Flufenacet/ha, assuming soil bulk density $d = 1.5 \text{ g/cm}^3$ and the thickness of the soil layer $l = 2.5 \text{ cm}$, ten-fold the accepted field application rate of that compound. RMS recalculated the assumed application rate using the standard assumptions: soil bulk density $d = 1.5 \text{ g/cm}^3$ and the thickness of the soil layer $l = 5.0 \text{ cm}$. The resulting application rate $A = 12000 \text{ g Flufenacet/ha}$ – fifty times higher than that proposed in the EU-representative GAP prepared for the purpose of the current evaluation. The justification for such high application dose was that it enabled the proper identification of the formed degradation products. When the measured soil bulk density, specific for each test soil was used, the calculated application rates were following:

- for **Laacherhof AXXa (AD)** soil, having the bulk density $d = 1.19 \text{ g/cm}^3$, calculated application rate was $A = 9520 \text{ g Flufenacet/ha}$;
- for **Dollendorf II (DD)** soil, having the bulk density $d = 0.95 \text{ g/cm}^3$, calculated application rate was $A = 7600 \text{ g Flufenacet/ha}$;
- for **Laacherhof Wurmweise (WW)** soil, having the bulk density $d = 1.12 \text{ g/cm}^3$, calculated application rate was $A = 8960 \text{ g Flufenacet/ha}$.

After application of the test compound the kinetic samples, except DAT-0 samples, were fitted with traps for volatile compounds and placed in the temperature-controlled walk-in climatic chamber to be incubated in the dark and at constant temperature $T = 20 \pm 2^\circ\text{C}$ for up to 121 days. The sampling points were designated on DATs (Days After Treatment) 0, 1, 2, 4, 7, 10, 14, 35, 63, 91 and 121. On those specific time points the duplicate samples were removed from the incubation chamber for the further examination.

The samples for identification of transformation products after application of the test compound were handled in the same way as described above for the kinetic samples.

The homogeneity of the application in kinetic samples was determined before, during and after application, by pipetting 346- μ L aliquots of the **Application Solution 1** into 20-mL volumetric flasks filled to the volume with CH₃CN. The so prepared solutions were then tested for their radioactivity content using LSC method.

The exact application rate of kinetic samples was determined by measuring the amount of the radioactivity in DAT-0 samples by LSC before, during and after application. The determined level of radioactivity was considered to be 100% AR

The biomass samples were placed alongside the kinetic samples those for identification of transformation products. They were prepared in the following way: the pre-equilibrated test samples were divided into two groups: native soil biomass test samples – “BIO-”, and solvent control biomass test samples – “BIO+”. The “BIO-” samples were left untreated, while “BIO+” samples received 346- μ L aliquots of the blank application solution – 1:1 MeOH/H₂O solution not containing the test compound. So prepared samples, except DAT-0 “BIO-” samples, were handled in the same manner as kinetic samples. On DAT 121 “BIO-” and “BIO+” samples were taken for the determination of the soil biomass content using Anderson&Domsch’s method.

All samples were incubated under aerobic conditions in the dark, under the constant temperature $T = 20 \pm 2^{\circ}\text{C}$ and soil moisture $55 \pm 5\%$ MWHC. Soil moisture was controlled at the beginning of the study and on DAT 67 by weighing test systems and, if necessary, adjusting it to the designated level by adding the appropriate amount of deionised water.

The samples removed at the designated sample points were processed in the following way: prior to opening the incubation vessels all volatiles, possibly present in the area between soil surface and the volatile trap filling, were purged into the trap columns. Next the incubation vessels were dissected into Erlenmeyer flasks containing soil and volatile traps and further processed following the conceptual scheme presented below on Figure B.8.1.1.1.1.-CA-33. The entire soil samples from the dissected incubation vessels were taken for the analysis and quantitatively transferred, using the first extraction solvent, to centrifuge beakers used as the extraction vessels.

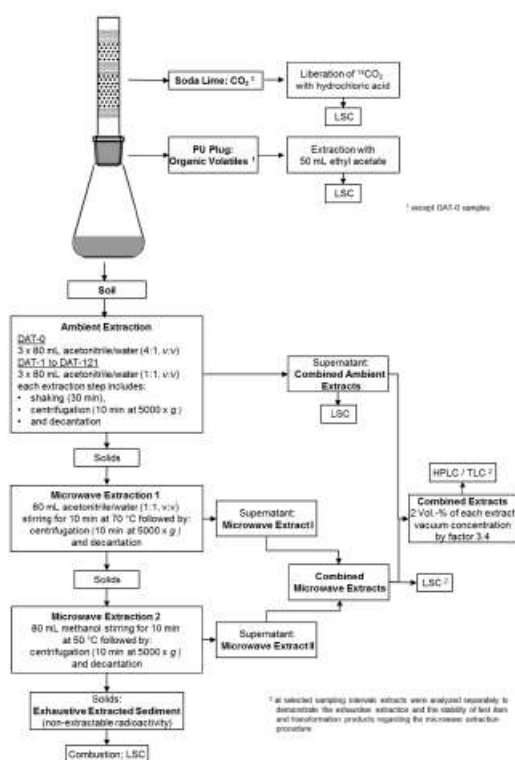


Figure B.8.1.1.1.-CA-33: The conceptual scheme of sample processing procedure (copied from the study report).

The extracted soil pellets were lyophilized, homogenised and three 1-g aliquots analysed for NER fraction after combustion using LSC.

The procedure was applied to kinetic samples, while the samples for identification of transformation products were not processed. Instead the isolation and identification of the transformation products was performed using concentrated combined extracts from DAT 10 samples, which were analysed by HPLC and the chromatographic eluates divided into three to four fractions which were further processed and analysed.

The extracted soil pellets were analysed for NER fraction. To do that each soil sample was allowed to air-dry overnight, after what its triplicate aliquots (50 – 100 mg) were oxidized by combustion. The formed $^{14}\text{CO}_2$ was trapped in alkaline solution which, after mixing with scintillation cocktail, was analysed by LSC. The further characterisation of NER fraction was not performed, because of its low content – max. 18.6% AR in Laacherhof AXXa (AX) soil, 11.5% AR in Dollendorf II (DD) soil and 18.6% AR in Laacherhof Wurmweise (WW) soil.

All samples were analysed for the content of radioactivity using LSC method. The LSC (Liquid Scintillation Counting) analysis was performed using a LS6000 LL/6500 or LKB-Wallac 1219 Spectral counters.

The radioactivity in soil extracts and other liquid samples from HPLC analysis was determined in either:

- mini-vials, using the sample aliquots of up to 1 mL and 2 mL of Quicksafe[®] A solution containing 5% of water; the counting time was 10 min and the background 12 – 16 cpm;
- maxi-vials, using the sample aliquots of up to 5 mL and 7 mL of Quicksafe[®] A solution containing 5% of water; the counting time was 10 min and the background 22 – 23 cpm.

The $^{14}\text{CO}_2$ recovered from soda lime was absorbed in Oxsolve scintillation cocktail, in three vials per sample, and radioactivity measured in each vial. The results were summed up. The counting time was 10 min and the background 17 – 20 cpm.

The radioactivity in extracts from PU plugs was determined in maxi-vials using the sample aliquots of up to 5 mL and 7 mL of Quicksafe[®] A solution containing 5% of water. The counting time was 10 min and the background 22 – 23 cpm.

The radioactivity in solid samples – extracted soil pellets, was determined after combustion of three 1-g aliquots of dried and homogenised material, the resulting $^{14}\text{CO}_2$ was absorbed in 15 mL of Oxsolve C400 liquid. The counting time was 10 min and the background 17 – 20 cpm.

The instrumental limit of detection – LOD_i was set to twice maximum instrument background count rate and instrumental limit of quantitation – LOQ_i to three times maximum instrument background count rate. The maximum instrument background count rate was determined to be 0.3 – 0.5 Bq. Therefore for different types of liquid samples the instrumental LOD_i and LOQ_i were as follows:

- samples with scintillation cocktail of 2 mL Quicksafe A + 5% water, $\text{LOD}_i = 0.5$ Bq and $\text{LOQ}_i = 0.8$ Bq;
- samples with scintillation cocktail of 7 mL Quicksafe A + 5% water, $\text{LOD}_i = 0.8$ Bq and $\text{LOQ}_i = 1.2$ Bq;
- samples with scintillation cocktail of 15 mL Oxsolve C400, $\text{LOD}_i = 0.7$ Bq and $\text{LOQ}_i = 1.0$ Bq.

When calculated for different types of analysed samples, the determined LOD and LOQ values for LSC analysis were as presented below in the table B.8.1.1.1.1_CA-37:

Table B.8.1.1.1.1_CA-37: The LOD and LOQ values for different types of samples analysed using LSC.

Type of sample	max. total amount – volume or mass	min. aliquots analysed – volume or mass	LOD (worst case) expressed in:		LOQ (worst case) expressed in:	
			Bq	% AR	Bq	% AR
<i>Ambient extract</i>	240 mL	0.5 mL	256.0	0.1	384.0	0.2
<i>Microwave extract 1</i>	233 mL	0.5 mL	248.5	0.1	372.8	0.2
<i>Microwave extract 2</i>	77 mL	0.5 mL	82.1	<0.1	123.2	<0.1
<i>PU foam plug extract</i>	50 mL	5 mL	7.7	<0.1	11.5	<0.1
<i>Solid sample (combustion)</i>	105 g	0.9 g	77.5	<0.1	116.2	0.1
<i>$^{14}\text{CO}_2$ from soda lime traps</i>	Sample entirely used for LSC analysis		----	<0.1	----	----

Sample extracts were analysed using the following analytical methods:

- HPLC – primary identification and quantitation method for parent compound and its degradation products;
- TLC – primary and conformatory quantitation method for the parent compound and its degradation products;
- LC-MS (either HPLC/MS or IEC/MS) – identification method for parent compound and its degradation products;
- ^1H -NMR – supplementary identification method for parent compound in stock solution.

The RP-HPLC analysis was performed in a gradient mode. The system consisted of HP 1100 chromatograph equipped with a binary pump, autosampler, on-line degasser, column oven and a Variable Wavelength UV detector set at $\lambda = 254$ nm, coupled with Ramona Star radioactivity detector. The chromatographic separation was performed on Purosphere Star RP 18e 250 mm * 4.6 mm * 5 μ m chromatographic column. It worked in the following gradient regime:

- **Mobile phase A:** 985 mL Water + 10 mL HCOOH + 5 mL $\text{NH}_4\text{COOH}_{(\text{aq})}$ (5 mM NH_4COOH /265 mM HCOOH),
- **Mobile phase B:** 985 mL CH_3CN + 10 mL HCOOH + 5 mL $\text{NH}_4\text{COOH}_{(\text{aq})}$ (5 mM NH_4COOH /265 mM HCOOH),
- **Gradient mode:** 0% B for first 5 min., then linear gradient to 95% B on 55th min., hold for next 5 min., linear gradient to 0% B on 62nd min. and hold until 75th min.,
- Total run time was 75 minutes.

The flow rate was set to 1.0 mL/min. The chromatographic column was kept under the constant temperature $T = 40^\circ\text{C}$.

The method had the following performance parameters:

- **mean recovery:** 99.7% for Laacherhof AXXa (AX) soil, 99.5% for Dollendorf II (DD) soil and 98.8% for Laacherhof Wurmweise (WW) soil;
- **good linearity** – $R^2 = 1.0$ for the injected amounts of the radiolabelled test compound ([Thiadiazole-5- ^{14}C] Flufenacet) in range 3.0 Bq – 490.8 Bq;
- **LOD** = 3.0 Bq, corresponding to LOD = 0.4% AR;
- **LOQ** = 3 * LOD – 1.3% AR.

The quantitative TLC analysis of polar fraction was performed as NP-TLC (Normal Phase TLC). It was carried out at ambient temperature, in saturated chamber, on silica gel Merck Si60, F_{254} , TLC plates. The solvent system used in the analysis was $\text{CH}_3\text{COOC}_2\text{H}_5/\text{CH}_3\text{CHOHCH}_3/\text{H}_2\text{O}/\text{CH}_3\text{COOH}$ 65:24:11:1 (v/v/v/v) solution ($\text{CH}_3\text{CHOHCH}_3$ stands for 2-propanol).

Two detectors were used:

- UV cabinet (Camag) detector working at two wavelengths: $\lambda = 254$ nm or $\lambda = 366$ nm;
- Bio-Imaging Analyser “BAS-2000” for analysis of radioactivity.

The conformatory TLC method was also performed as NP-TLC. It was carried out at ambient temperature, in saturated chamber, on silica gel Merck Si60, F_{254} , TLC plates. Two detectors were used:

- UV cabinet (Camag) detector working at two wavelengths: $\lambda = 254$ nm or $\lambda = 366$ nm;
- Bio-Imaging Analyser “BAS-2000” for analysis of radioactivity.

Two solvent system were used in the analysis:

- eluent 1 (**Method D**) – $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{COOC}_2\text{H}_5$ 8:2 (v/v) solution;
- eluent 2 (**Method A**) – $\text{CH}_3\text{COOC}_2\text{H}_5/\text{CH}_3\text{CHOHCH}_3/\text{H}_2\text{O}/\text{CH}_3\text{COOH}$ 65:24:11:1 (v/v/v/v) solution ($\text{CH}_3\text{CHOHCH}_3$ stands for 2-propanol).

Method D was used to separate the non-polar compounds – Flufenacet and FOE Thiadone, while **Method A** for separation of the polar ones – FOE Trifluoroethanesulfonic acid and Trifluoroacetic acid (TFA).

The LC-MS analysis was performed as either HPLC/MS or IEC/MS analysis.

HPLC/MS analysis was carried out using HP1000 HPLC system equipped with a Nucleodur Gravity C_{18} chromatographic column (250 * 2 mm, 3 μ m), UV detector followed by the Ramona Star radiodetector and one of the following two MS detectors:

- LTQ Orbitrap XL mass spectrometer,
- Q-Exactive mass spectrometer.

The parameters of chromatographic analysis were following:

- column temperature: 40°C ,
- flow rate: 0.2 mL/min,
- elution mode: gradient,
- mobile phase:
 - Solvent A: H_2O + 0.1% HCOOH,
 - Solvent B: CH_3CN + 0.1% HCOOH.
- two gradient programmes used, presented below in the table B.8.1.1.1.1_CA-38:
 - Gradient 1 – used in the system equipped with LTQ Orbitrap XL mass spectrometer,
 - Gradient 2 – used in the system equipped with Q-Exactive mass spectrometer.

Table B.8.1.1.1.1_CA-38: Gradient programmes used in HPLC/MS analysis.

Gradient 1			Gradient 2		
Time [min]	% solvent A (H ₂ O + 0.1% HCOOH)	% solvent B (CH ₃ CN + 0.1% HCOOH)	Time [min]	% solvent A (H ₂ O + 0.1% HCOOH)	% solvent B (CH ₃ CN + 0.1% HCOOH)
0	95	5	0	100	0
1	95	5	5	100	0
25	5	95	25	5	95
35	5	95	35	5	95

The IEC/MS (Ion Exchange Chromatography) analysis was performed using Dionex ICS-500 system equipped with AS20 column (250 * 2 mm), Ramona Star radiodetector and Q-Exactive mass spectrometer.

The parameters of chromatographic analysis were following:

- column temperature: 30⁰C,
- flow rate: 0.25 mL/min,
- elution mode: isocratic,
- mobile phase: 20mM KOH in water.

Results and their discussion:

The monitoring of the experimental conditions demonstrated that the samples were incubated at the mean temperature 19.8⁰C, ranging from 19.5⁰C to 20.2⁰C. The average incubation temperature and its range were within the limits of the assumed constant temperature T = 20 ± 2⁰C.

The soil moisture content was demonstrated to be within the assumed value of 55 ± 5% MWHC and no significant losses were observed throughout the study duration.

The determination of the soil biomass showed that:

- in **Laacherhof AXXa (AX)** it decreased during the incubation period by 58.1% in soil not treated with blank application solution ("BIO-") and by 60.8% in soil treated with blank application solution ("BIO+"), as determined at DAT 121;
- in **Dollendorf II (DD)** soil it decreased during the incubation period by 37.2% in soil not treated with blank application solution ("BIO-") and by 41.1% in soil treated with blank application solution ("BIO+"), as determined at DAT 121;
- in **Laacherhof Wurmwiess (WW)** soil it decreased during the incubation period by 60.4% in soil not treated with blank application solution ("BIO-") and by 60.8% in soil treated with blank application solution ("BIO+"), as determined at DAT 121.

It shall be noted that the decrease in soil microbial activity was greater in soil treated with blank application solution. It was stated however that it could not be attributed to the influence of the application solution on the soil biomass, because the difference between the decrease in "BIO-" and "BIO+" samples was not greater than 5%. As a result, it can be stated that the decrease in soil microbial activity may be related predominantly to the natural phenomena. It was within the acceptability limits - throughout the study duration it was above the recommended level of 1% OC in all test soils, so the obtained results may be considered reliable.

The LSC analysis of the homogeneity of application of the kinetic samples showed that it was homogenous, with RSD = 0.9%

The stability tests performed using DAT-0 samples demonstrated that Flufenacet was stable during application and the radiochemical purity of the application solution was 100%.

The application dose determined for DAT-0 samples was (average) 234072 Bq, equal to 152.0 µg Flufenacet/sample. That value was set as 100% AR for the kinetic samples.

The recovery of the applied radioactivity in the experimental soil was generally good, in line with the recommendations of the relevant Guidelines and looked as follows:

- in **Laacherhof AXXa (AX)** soil on average 99.1% AR with RSD = 0.9%, and range 97.1% AR – 100.9% AR (values given as the means of the two replicates);
- in **Dollendorf II (DD)** soil on average 99.7% AR with RSD = 1.8%, and range 95.7% AR – 103.0% AR (values given as the means of the two replicates);
- in **Laacherhof Wurmwiess (WW)** soil on average 98.7% AR with RSD = 1.2%, and range 96.2% AR – 99.8% AR (values given as the means of the two replicates).

The level of mineralization was not very high in comparison to the results obtained in another study with Flufenacet radiolabelled in thiadiazole moiety – at the end of the study (DAT 121) it reached 5.6% AR in Laacherhof AXXa (AA) soil, 6.5% AR in Dollendorf II (DD) soil and 4.5% AR in Laacherhof Wurmwielse (WW) soil.

The amount of NER fraction also increased with time and was as follows:

- in **Laacherhof AXXa (AX)** soil it increased from 0.4% AR on DAT 0 to max. 18.6% AR on DAT 63, to then slightly decrease to 17.2% AR at the study's end (DAT 121);
- in **Dollendorf II (DD)** soil it increased from 1.1% AR on DAT 0 to max. 11.5% AR on DAT 63, to then slightly decrease to 10.6% AR at the study's end (DAT 121);
- in **Laacherhof Wurmwielse (WW)** soil it increased from 0.7% AR on DAT 0 to max. 18.6% AR on DAT 35 and DAT 63, to then slightly decrease to 17.2% AR at the study's end (DAT 121).

NER fraction was not further characterised in any of the experimental soils.

The amount of AR present as combined extractable fraction decreased with time from 98.7% - 99.9% AR (depending on the test soil) at the beginning of the study – DAT 0, to 75.0 – 82.1% AR (depending on the test soil) at the study's end (DAT 121). It was recovered predominantly in ambient extracts, while microwave extracts contributed insignificantly to the amounts of radioactivity extracted.

The following compounds were identified in extracts:

- Flufenacet,
- FOE Thiadone,
- FOE 5043-Trifluoroethanesulfonic acid,
- Trifluoroacetic acid (TFA).

The small fraction of unidentified radioactivity, not surpassing 2.5% AR at any sampling point in any of the test soils, was also detected.

Of the identified degradation products listed above only TFA may be considered as major on the basis of the criteria set by SANCO/211/2000 Guidance Document on the Assessment of the Relevance of Metabolites.

The detailed results are presented below, individually for each test soil, in numerical (tabularised) and graphical forms.

The results obtained in Laacherhof AXXa (AX) soil are presented below in the table B.8.1.1.1.1_CA-39 (the means of the two replicates; values were rounded to one digit after the decimal point) and in graphical form on two figures - B.8.1.1.1.1_CA-33 for radioactivity distribution and B.8.1.1.1.1_CA-34 for identified compounds/fractions profiling.

Table B.8.1.1.1.1_CA-39: The detailed results obtained in the study with Laacherhof AXXa soil.

% AR		Results obtained for sample collected at DAT ¹⁾ :										
		0	1	2	4	7	10	14	35	63	91	121
Extracted as:	Ambient extract	93.6	93.6	89.0	90.8	88.5	85.9	81.9	73.8	71.1	70.6	71.3
	Microwave extract 1	5.1	5.2	6.2	5.8	6.2	5.8	6.0	6.2	5.5	3.6	4.7
	Microwave extract 2	n. a. ⁵⁾	n. a. ⁵⁾	n. a. ⁵⁾	n. a. ⁵⁾	n. a. ⁵⁾	n. a. ⁵⁾	n. a. ⁵⁾	n. a. ⁵⁾	n. a. ⁵⁾	1.1	n. a. ⁵⁾
	Total extracted	98.7	98.8	95.2	96.6	94.7	91.7	87.9	80.0	76.5	75.3	76.0
In extracts identified as:	Flufenacet	98.7	97.0	91.8	89.9	81.4	70.6	59.9	25.7	7.6	3.2	1.4
	FOE Thiadone	n. d. ⁶⁾	1.8	1.9	2.5	2.8	2.5	2.7	1.6	1.0	<LOD	<LOD
	FOE 5043-Trifluoroethane-sulfonic acid	n. d. ⁶⁾	n. d. ⁶⁾	<LOD	1.7	3.2	4.4	3.2	2.7	1.2	<LOD	0.5
	Trifluoroacetic acid (TFA)	n. d. ⁶⁾	n. d. ⁶⁾	1.6	2.7	7.2	13.9	22.1	48.2	65.9	71.5	74.1
	Unidentified fraction ²⁾	n. d. ⁶⁾	n. d. ⁶⁾	n. d. ⁶⁾	n. d. ⁶⁾	n. d. ⁶⁾	<LOD	n. d. ⁶⁾	1.8	1.0	n. d. ⁶⁾	n. d. ⁶⁾
	Total identified³⁾	98.7	98.8	95.2	96.6	94.7	91.7	87.9	80.0	76.5	75.0	76.0
Bound residues (NER fraction)		0.4	1.0	1.9	4.1	4.0	7.1	9.3	16.0	18.6	18.4	17.2
Volatile compounds	CO ₂	n. a. ⁷⁾	<0.1	<0.1	0.1	0.4	0.5	1.1	2.9	4.0	5.0	5.6
	VOC	n. a. ⁷⁾	<0.1	<0.1	<0.1	<0.1	0.1	0.1	0.1	0.1	0.1	0.1
	Total volatile compounds⁴⁾	n. a.⁷⁾	<0.1	0.1	0.2	0.4	0.6	1.2	3.0	4.2	5.1	5.6⁸⁾
Total recovered AR		99.1	99.9	97.1	100.9	99.1	99.3	98.4	99.0	99.3	98.8	98.8

Footnotes to the table:

- 1) Values presented are the means of two replicates for each sampling point;
- 2) A sum of all minor degradation products;
- 3) The difference between the Total Extracted AR and the Total identified AR was declared in the study report to be possibly due to the following factors: rounding of figures (1), cleanup and chromatographic losses (2);
- 4) Value calculated by adding the results obtained for VOC and those for CO₂
- 5) n. a. = not analysed ;
- 6) n. d. = not detected;
- 7) n. a. = not analysed, because of the assumption made that at that sampling point neither mineralisation nor formation of volatile degradation products is expected to occur;
- 8) Value reported by the Applicant.

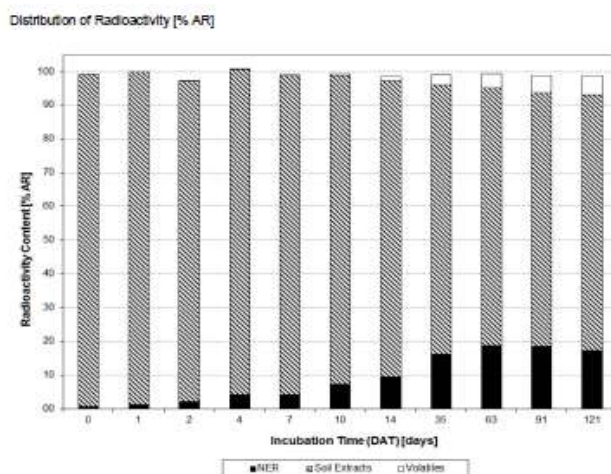


Figure B.8.1.1.1._CA-33: Graphical presentation of the results obtained for Laacherhof AXXa soil – distribution of radioactivity (copied from the study report).

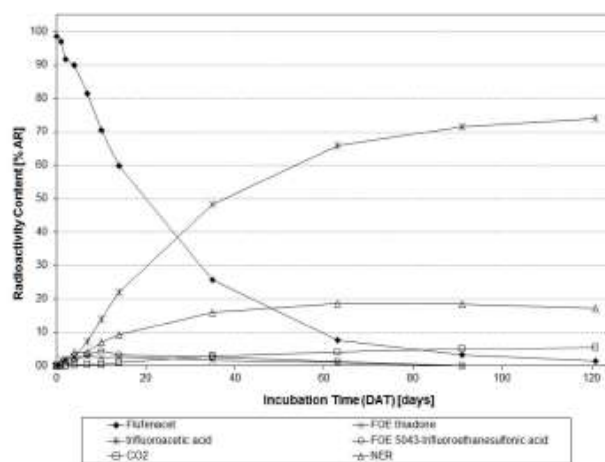


Figure B.8.1.1.1._CA-34: Graphical presentation of the results obtained for Laacherhof AXXa soil – concentration profiles of identified degradation products (copied from the study report).

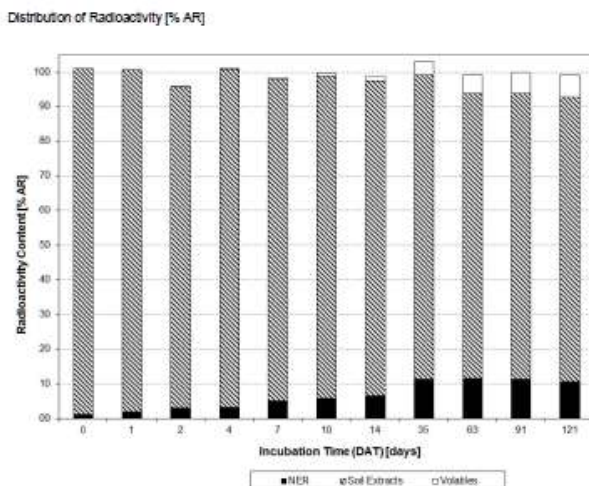
The results obtained in Dollendorf II (DD) soil are presented below in the table B.8.1.1.1._CA-40 (the means of the two replicates; values were rounded to one digit after the decimal point) and in graphical form on two figures - B.8.1.1.1._CA-35 for radioactivity distribution and B.8.1.1.1._CA-36 for identified compounds/fractions profiling.

Table B.8.1.1.1.1_CA-40: The detailed results obtained in the study with Dollendorf II soil.

% AR		Results obtained for sample collected at DAT ¹⁾ :										
		0	1	2	4	7	10	14	35	63	91	121
Extracted as:	Ambient extract	95.9	93.5	85.3	92.0	86.6	88.2	85.8	82.2	77.8	78.3	77.5
	Microwave extract 1	4.0	5.4	7.5	5.9	6.2	4.8	5.1	5.8	4.6	3.3	4.6
	Microwave extract 2	n. a. ⁵⁾	n. a. ⁵⁾	n. a. ⁵⁾	n. a. ⁵⁾	n. a. ⁵⁾	n. a. ⁵⁾	n. a. ⁵⁾	n. a. ⁵⁾	n. a. ⁵⁾	1.1	n. a. ⁵⁾
	Total extracted	99.9	98.9	92.8	97.9	92.8	93.1	91.0	88.0	82.4	82.7	82.1
In extracts identified as:	Flufenacet	99.9	96.8	88.2	87.7	77.0	65.1	55.9	15.3	2.5	1.2	0.9
	FOE Thiadone	n. d. ⁶⁾	2.1	2.5	3.9	4.0	5.6	4.8	3.2	0.7	n. d. ⁶⁾	n. d. ⁶⁾
	FOE 5043-Trifluoroethane-sulfonic acid	n. d. ⁶⁾	n. d. ⁶⁾	n. d. ⁶⁾	<LOD	2.2	3.4	1.7	1.6	0.6	n. d. ⁶⁾	<LOD
	Trifluoroacetic acid (TFA)	n. d. ⁶⁾	n. d. ⁶⁾	2.0	5.7	9.7	19.0	28.1	66.8	78.6	81.5	81.0
	Unidentified fraction ²⁾	n. d. ⁶⁾	n. d. ⁶⁾	n. d. ⁶⁾	n. d. ⁶⁾	n. d. ⁶⁾	n. d. ⁶⁾	<LOD		n. d. ⁶⁾	n. d. ⁶⁾	n. d. ⁶⁾
	Total identified³⁾	99.9	98.9	92.8	97.7	92.8	93.1	91.0	88.0	82.4	82.7	81.9
Bound residues (NER fraction)		1.1	1.8	2.9	3.0	4.9	5.7	6.5	11.2	11.5	11.2	10.6
Volatile compounds	CO ₂	n. a. ⁷⁾	<0.1	0.1	0.2	0.5	1.0	1.4	3.7	5.2	5.9	6.5
	VOC	n. a. ⁷⁾	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.2	0.1	<0.1
	Total volatile compounds⁴⁾	n. a.⁷⁾	<0.1	0.1	0.2	0.5	1.0	1.4	3.8⁸⁾	5.3⁸⁾	6.0	6.5
Total recovered AR		101.0	100.7	95.7	101.1	98.3	99.8	98.9	103.0	99.2	99.9	99.2

Footnotes to the table:

- 1) Values presented are the means of two replicates for each sampling point;
- 2) A sum of all minor degradation products;
- 3) The difference between the Total Extracted AR and the Total identified AR was declared in the study report to be possibly due to the following factors: rounding of figures (1), cleanup and chromatographic losses (2);
- 4) Value calculated by adding the results obtained for VOC and those for CO₂
- 5) n. a. = not analysed;
- 6) n. d. = not detected;
- 7) n. a. = not analysed, because of the assumption made that at that sampling point neither mineralisation nor formation of volatile degradation products is expected to occur;
- 8) Value reported by the Applicant.

**Figure B.8.1.1.1.1_CA-35:** Graphical presentation of the results obtained for Dollendorf II soil – distribution of radioactivity (copied from the study report).

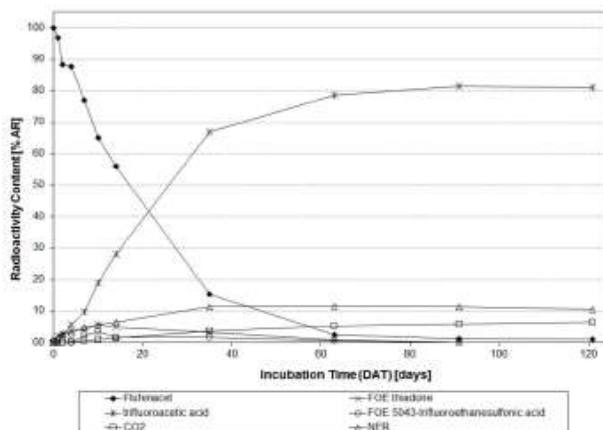


Figure B.8.1.1.1._CA-36: Graphical presentation of the results obtained for Dollendorf II soil – concentration profiles of identified degradation products (copied from the study report).

The results obtained in Laacherhof Wurmwiese (WW) soil are presented below in the table B.8.1.1.1._CA-41 (the means of the two replicates; values were rounded to one digit after the decimal point) and in graphical form on two figures - B.8.1.1.1._CA-37 for radioactivity distribution and B.8.1.1.1._CA-38 for identified compounds/fractions profiling.

Table B.8.1.1.1._CA-41: The detailed results obtained in the study with Laacherhof Wurmwiese soil.

% AR		Results obtained for sample collected at DAT ¹⁾ :										
		0	1	2	4	7	10	14	35	63	91	121
Extracted as:	Ambient extract	95.0	93.2	87.5	89.5	86.5	83.2	79.5	71.4	70.6	71.6	70.7
	Microwave extract 1	3.7	5.1	6.3	5.7	6.0	5.6	5.5	6.1	4.7	3.6	4.3
	Microwave extract 2	n. a. ⁵⁾	n. a. ⁵⁾	n. a. ⁵⁾	n. a. ⁵⁾	n. a. ⁵⁾	n. a. ⁵⁾	n. a. ⁵⁾	n. a. ⁵⁾	n. a. ⁵⁾	1.0	n. a. ⁵⁾
	Total extracted	98.7	98.3	93.8	95.2	92.5	88.8	85.0	77.5	75.3	76.2	75.0
In extracts identified as:	Flufenacet	98.7	96.8	90.5	86.2	74.4	63.4	47.4	13.3	3.6	1.3	1.0
	FOE Thiadone	n. d. ⁶⁾	1.5	2.0	3.1	4.6	3.3	3.1	1.7	0.7	n. d. ⁶⁾	n. d. ⁶⁾
	FOE 5043-Trifluoroethanesulfonic acid	n. d. ⁶⁾	n. d. ⁶⁾	<LOD	0.7	1.6	1.9	0.5	<LOD	<LOD	<LOD	<LOD
	Trifluoroacetic acid (TFA)	n. d. ⁶⁾	n. d. ⁶⁾	1.3	5.2	11.5	19.1	31.6	60.0	70.0	74.8	73.8
	Unidentified fraction ³⁾	n. d. ⁶⁾	n. d. ⁶⁾	n. d. ⁶⁾	n. d. ⁶⁾	0.5	1.0	2.4	2.3	<LOD	n. d. ⁶⁾	n. d. ⁶⁾
Total identified⁴⁾		98.7	98.3	93.8	95.2	92.5	88.8	85.0	77.3	75.1	76.1	74.8
Bound residues (NER fraction)		0.7	1.2	2.3	4.1	6.7	10.1	13.3	18.6	18.6	18.2	17.2
Volatile compounds	CO ₂	n. a. ⁷⁾	<0.1	<0.1	0.2	0.4	0.8	1.3	2.8	3.7	4.4	4.5
	VOC	n. a. ⁷⁾	<0.1	<0.1	<0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
	Total volatile compounds⁵⁾	n. a.⁷⁾	<0.1	0.1	0.2	0.5	0.8⁸⁾	1.3⁸⁾	2.8⁸⁾	3.8	4.5	4.6
Total recovered AR		99.3	99.5	96.2	99.5	99.7	99.8	99.7	98.9	97.7	98.8	96.7

Footnotes to the table:

- 1) Values presented are the means of two replicates for each sampling point;
- 2) A sum of all minor degradation products;
- 3) The difference between the Total Extracted AR and the Total identified AR was declared in the study report to be possibly due to the following factors: rounding of figures (1), cleanup and chromatographic losses (2);
- 4) Value calculated by adding the results obtained for VOC and those for CO₂
- 5) n. a. = not analysed;
- 6) n. d. = not detected;
- 7) n. a. = not analysed, because of the assumption made that at that sampling point neither mineralisation nor formation of volatile degradation products is expected to occur;
- 8) Value reported by the Applicant.

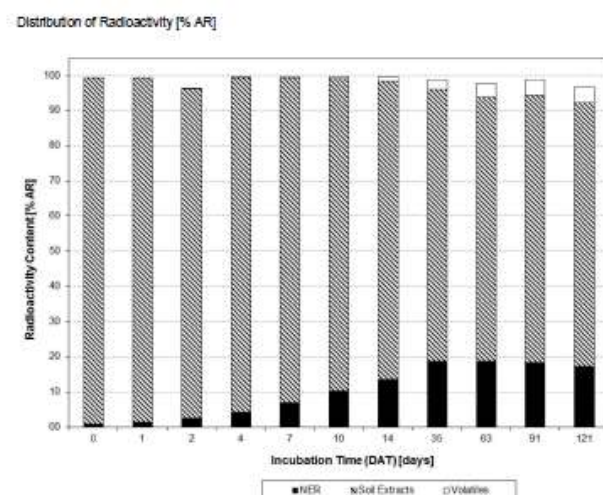


Figure B.8.1.1.1._CA-37: Graphical presentation of the results obtained in Laacherhof Wurmwiese soil – distribution of radioactivity (copied from the study report).

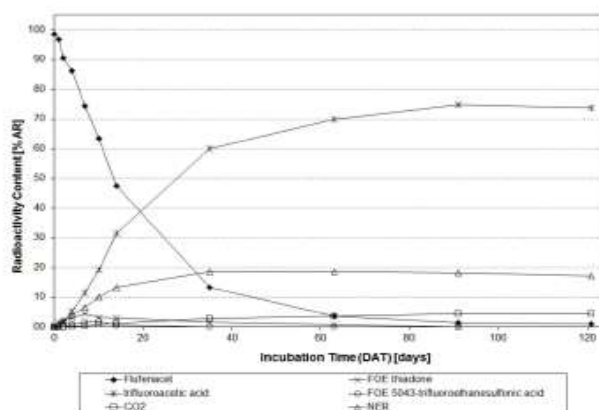


Figure B.8.1.1.1._CA-38: Graphical presentation of the results obtained in Laacherhof Wurmwiese soil – concentration profiles of identified degradation products (copied from the study report)..

On the basis of the obtained results the Applicant proposed the transformation scheme presented below on figure B.8.1.1.1._CA-39. It consisted of the following steps:

- cleavage of the test item on bridging oxygen of the thiadiazole heterocycle and tautomerisation of keto-enol functional group, resulting in formation of FOE Thiadone,
- hydrolytical opening of thiadiazole ring and further oxidation resulting in formation of either FOE 5043-Trifluoroethanesulfonic acid or Trifluoroacetic acid (TFA) or else simple products of mineralisation and NER fraction – ultimate transformation products;
- further transformation of FOE 5043-Trifluoroethanesulfonic acid or Trifluoroacetic acid (TFA) to the simple products of mineralisation and NER fraction – ultimate transformation products.

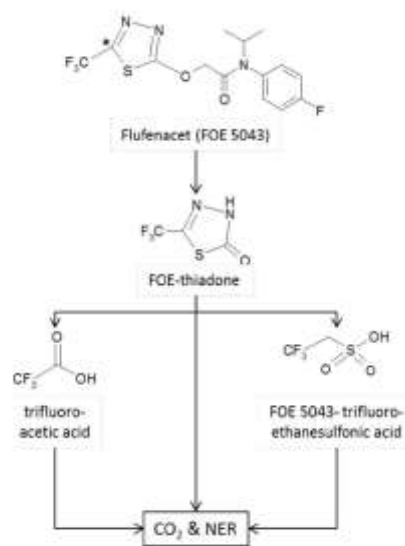


Figure B.8.1.1.1.1_CA-39: The conceptual scheme of the transformation of Flufenacet radiolabelled in thiadiazole moiety (copied from the study report).

The results obtained for Flufenacet were kinetically examined and the results of that examination presented as a part of the study report. The performed kinetic analysis complied with the current standards, set by FOCUS Kinetics Guidance Document [FOCUS, 2006]. It was however decided, in order to maintain the coherence of the Report, to present it under the relevant point of this document – B.8.1.1.2.1.1.

Additionally two publications relevant in the area of determination of the route and rate of degradation of flufenacet in soil under aerobic conditions were found. They are summarised below. To maintain the coherence of the document they are consecutively numbered as studies 7 and 8. The order in which the studies are reported reflects their relevance for the evaluation process. Also, in order to maintain the coherence of the Report, the numbering of the tables and figures follows the format and order of appearance adopted in this document.

Study 7:

Report: Bloomberg A. M., Shadrick B. A., Ellen A. L., Clay V. E. (2002): „Outdoor Soil Metabolism of [Phenyl- ^{14}C] Flufenacet on California Soils.”; Bayer Corporation, 17745 South Metcalf Avenue, Stilwell, KS, 66085, USA; published study – published in: *Phelps W. (ed.) “ACS Symposium Series, vol. 813: Pesticide Environmental Fate”, chapter 12, pp 167 – 182*; American Chemical Society, Washington, DC, 2002, publication date March 1, 2002;

Guidelines: None declared as this is an open-source study, therefore not submitted for the regulatory purposes. However, examination of the study protocol, also in cross-reference to other studies submitted by the Applicant, demonstrated that it complied with the following guidelines:

- US. EPA Guidelines for Pesticide Registration, Subdivision N, Section 162-1, Aerobic Soil Metabolism;

GLP: the study was declared to be a non-GLP study, but it followed the analytical protocol same as other, GLP studies, carried out in the same research facility.

RMS comments: The paper describes the study bridging the laboratory and field studies examining the fate and behaviour of Flufenacet in soil. Although not performed according to any specific Guidelines it was found to comply with the provisions of US EPA 162-1 Guideline. It was generally well documented, although only general information concerning test soil were presented, and it provides important information with regard to the route of degradation of Flufenacet in soil. Its results may be also used, as supplementary, in determination of the rate of degradation of that compound under realistic – field conditions. RMS considers the study valid for the regulatory purposes. Its extended summary is provided below.

Summary:

The abstract of the publication provided by the publisher – American Chemical Society, is presented below. It is reprinted with permission from: *Annette M. Bloomberg, Barbara A. Shadrick, Ellen L. Arthur et al. "Outdoor Soil Metabolism of [Phenyl U-¹⁴C]Flufenacet on California Soils.", ACS Symposium Series, 2002, vol 813: Pesticide Environmental Fate, chapter 12, pp. 167-182; Copyright 2002 American Chemical Society, reprinted with editor's permission.*

Abstract:

An outdoor soil metabolism study with [phenyl-U-¹⁴C] flufenacet was conducted on two sandy loams collected from Chualar and Fresno sites in California. This study involved more natural environmental conditions than a laboratory study and was conducted to obtain information on flufenacet residue identification and leaching potential. Vessels filled with approximately 13 cm of each soil were placed in an outdoor plot at Pan-Agricultural Laboratories in Madera, California, and treated with radioactive flufenacet at an equivalent rate of 0.89 lb a.i. per acre. Samples were collected in duplicate immediately after application and at 1, 4, 7, 11, 15, 19, 27, 35, 46, and 88 days after treatment. At each sampling interval, the top 3 cm (approximately) of soil was removed, extracted, and analyzed by high-pressure liquid chromatography for parent compound and metabolites. The total [¹⁴C]residues recovered from the vessels remained above 85.9% in the Fresno soil and 92.8% in the Chualar soil throughout the 88-day study with the greatest percentage of the radioactivity remaining in the top 0- to 3-cm layers. The extracted [¹⁴C]residues in the top layer decreased to 44.3% of the applied radioactivity in the Fresno soil and 62.6% in the Chualar soil at the 88-day interval, with 19.5% and 25.3% remaining bound to the soil, respectively. Residues of parent compound decreased to 17.8% and 29.0% at the 88-day interval in the Fresno and Chualar soils, respectively. The flufenacet alcohol and oxalate were the two major metabolites detected in this study. The flufenacet alcohol reached a maximum level of 21.2% in the Chualar 88-day sample, whereas the flufenacet oxalate reached a maximum of 13.0% in the Fresno 46-day sample. The half-lives for flufenacet in the Fresno and Chualar soil were calculated to be 36.1 days ($k = 0.0192 \text{ days}^{-1}$) and 49.9 days ($k = 0.0139 \text{ days}^{-1}$), respectively.

The extended summary of the publication, written by the RMS, is presented below.

The aims of the study were:

- to examine the rate of degradation of Flufenacet in soil by determining its half-life and first-order degradation rate constant k ;
- to identify the degradation products;
- to evaluate the leaching potential of Flufenacet and its soil degradation products under field conditions.

The study was conceived and performed as the outdoor metabolism study in order to bridge the results of laboratory and field studies and therefore conform that the results of the former are representative for what may be expected for Flufenacet with regard to its fate and behaviour in soil under realistic, field conditions.

The experiment was performed using two US soils collected on the fields on which soil dissipation studies had been performed, but from the untreated areas. The characteristic of the test soils is given in the table below in the table B.8.1.1.1.1._CA-42. It reproduces the data given in the source publication in the **Table 1. Pertinent characteristics of soils used in the ¹⁴C-flufenacet outdoor metabolite study.**

Table B.8.1.1.1.1._CA-42: The characteristic of the test soils used in the experiment.

Determined soil property		Test soil	
		<i>Chualar</i>	<i>Fresno</i>
Soil type ¹⁾		Sandy loam	Fine sandy loam
Soil type (USDA) ²⁾		Sandy loam	Sandy loam
Particle size distribution	Sand [%]	70.0	64.7
	Silt [%]	18.0	31.3
	Clay [%]	12.0	4.0
pH		6.4	7.5
Organic matter content (OM) [%]		1.3	0.5
Organic carbon content (OC) [%] ³⁾		0.75	0.29
Soil biomass [CFU/ g soil d. w.] ⁴⁾		1.08 E6	1.03 E6

Footnotes to the table:

- As given in the source paper;
- Verified by the RMS;
- Recalculated by the RMS using the following equation: $OM = 1.724 * OC$;
- [CFU/g soil d. w.] stands for Colony Forming Units per gram soil (dry weight), quantified on plate count agar.

The test soils were sieved through 2-mm sieve before the experiment started and placed in experimental vessels – jars having a volume of ~3.79 L (1 gallon), diameter of ~15.24 cm (6 inches), the same height and

closed bottom. They were brought to 50 – 90% MWHC, the level maintained throughout the study by daily irrigation. The test vessels were filled with ~12.7 – 13.97 cm (5 - 5½ inch) layer of the test soils and placed in the ground, on the experimental plot of Pan-Agricultural Laboratories, Inc, in Madera, California. The total amount of the test vessels was 44 – 22 per each test soil, placed two parallel double rows. Additionally between the rows two vessels containing a mixture of the test soils and three moisture sensors were placed. The scheme of the test plot is presented below on figure B.8.1.1.1.1. CA-40 (the figure is reproduced directly from: Annette M. Bloomberg, Barbara A. Shadrick, Ellen L. Arthur et al. "Outdoor Soil Metabolism of [Phenyl U-¹⁴C]Flufenacet on California Soils.", ACS Symposium Series, 2002, vol 813: Pesticide Environmental Fate, chapter 12, pp. 167-182; Copyright 2002 American Chemical Society, reprinted with editor's permission.).

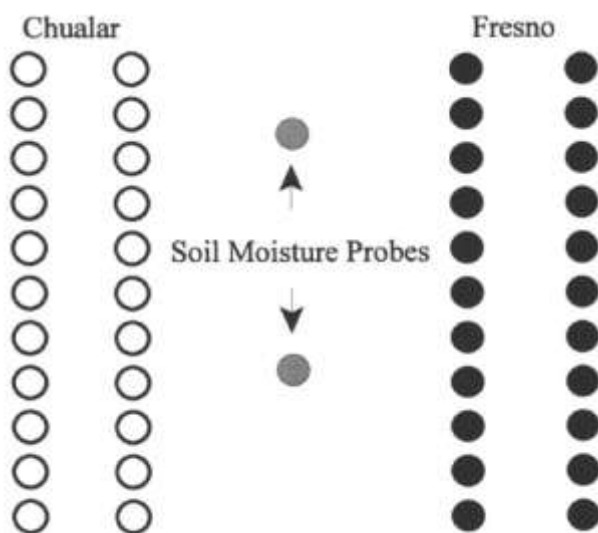


Figure 1. Test plot diagram for ¹⁴C-flufenacet outdoor metabolism study.

Figure B.8.1.1.1.1. CA-40: The scheme of the test plot (Reprinted with permission from Annette M. Bloomberg, Barbara A. Shadrick, Ellen L. Arthur et al. "Outdoor Soil Metabolism of [Phenyl U-¹⁴C]Flufenacet on California Soils.", ACS Symposium Series, 2002, vol 813: Pesticide Environmental Fate, chapter 12, pp. 167-182; Copyright 2002 American Chemical Society.

The test soils in each of the test vessels were treated with the radiolabelled test compound – [Phenyl U-¹⁴C] Flufenacet, applied to the soil surface in form of the application CH₃CN-solution by means of 2-mL syringe. The declared application rate was 0.89 lb a. s./acre, corresponding to 997.35 g a. s./ha.

The outdoor part of the experiment lasted from 16th July 1992 to 12th October 1992. The test vessels were kept open to the atmosphere. To avoid the overflow from excessive rainfall the plots were covered with a water-proof material when wet weather was forecasted. Also the experimental plot was maintained constantly bare by weeding it around the test vessels on DAT 29.

At the designated time points – on DATs (Days After Treatment) 0, 1, 4, 7, 11, 15, 19, 27, 35, 46 and 88 duplicate samples of each treated test soil were collected for further analysis. At these time points top layers of soil - 0-3 cm, were removed from the test vessels placed in 1-gallon (3.79-L) jars to which 700 mL of CH₃COOC₂H₅ was added immediately. Next they were freeze-dried and transported on dry ice to the laboratories of Bayer Corp. for further analysis.

In the laboratory the samples were extracted using the extraction procedure shown below on the figure B.8.1.1.1.1. CA-41 (the figure is reproduced directly from: Annette M. Bloomberg, Barbara A. Shadrick, Ellen L. Arthur et al. "Outdoor Soil Metabolism of [Phenyl U-¹⁴C]Flufenacet on California Soils.", ACS Symposium Series, 2002, vol 813: Pesticide Environmental Fate, chapter 12, pp. 167-182; Copyright 2002 American Chemical Society, reprinted with editor's permission.). It was indicated that the soil samples collected on DATs 0, 1, 4, 7, 11, 15 and 19 were subjected only to one step extraction – with ethyl acetate. For the samples collected at later time points – from DAT 27 onwards, the extraction with CH₃CN/H₂O 7:3 extracting solution at reflux was introduced as an additional step.

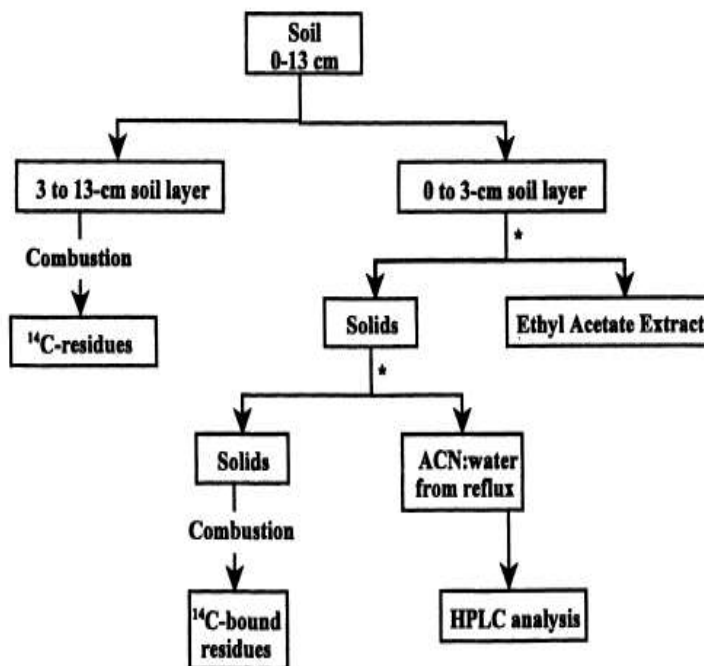


Figure 3. Analytical scheme for samples from the ^{14}C -flufenacet outdoor metabolism study (* denotes soil extraction occurring at this step).

Figure B.8.1.1.1._CA-41: The extraction procedure used in the experiment (Reprinted with permission from Annette M. Bloomberg, Barbara A. Shadrick, Ellen L. Arthur et al. "Outdoor Soil Metabolism of [Phenyl U- ^{14}C]Flufenacet on California Soils.", ACS Symposium Series, 2002, vol 813: Pesticide Environmental Fate, chapter 12, pp. 167-182; Copyright 2002 American Chemical Society.

The extracts and other liquid samples were analysed for their content of radioactivity using LSC method. Additionally they were analysed chromatographically, by TLC, HPLC and LC/MS in order to identify and quantify the extracted compounds.

The extracted soil pellets were air-dried and analysed for the content of the bound radioactivity (NER fraction) by LSC, after their oxidation.

Also in the samples collected on later time points – from DAT 15 onwards, the remaining 3 – 13 cm soil layers were analysed for the content of radioactivity – NER fraction, by LSC after combustion. In case of the samples collected at DATs 15 – 46 the whole 3-13-cm layers were taken for the analysis of NER, while for DAT-88 samples, the collected 3-13 cm layers were divided into 2-cm sections, each analysed separately for the radioactivity content.

The LSC analysis was performed using Packard Tricarb LS Counter Model 4640.

The TLC analysis was performed to determine the purity of the application solution. It was carried out using Merck Silica gel 60 F₂₅₄ plates, 0.25-mm thick, developed in $\text{CHCl}_3/\text{CH}_3\text{OH}$ 9:1 solvent system. The detection of radioactive zones was performed using Raytest Rita 6800 TLC radioactivity scanner.

HPLC was used to analyse qualitatively and quantitatively all extracts. It was performed using either Shimadzu SCL-6A liquid chromatograph or HP1090 liquid chromatograph, equipped with variable UV detector and Raytest Ramona 90 radioactivity monitor.

The chromatographic analysis was performed in a gradient mode on Hamilton PRP-1, 305*7 mm chromatographic column preceded by Hamilton PRP-1 guard column. The solvents were:

- **Solvent A:** 0.4% CH_3COOH in H_2O ,
- **Solvent B:** 0.4% CH_3COOH in CH_3CN .

The elution gradient used in the analysis is presented below in the table B.8.1.1.1._CA-43. The flow rate was 2 mL/min.

Table B.8.1.1.1.1_CA-43: The HPLC gradient modes used in the study.

Time [min]	Solvent ratio	
	<i>Solvent A – Water + 0.4% CH₃COOH</i>	<i>Solvent B – Acetonitrile + 0.4% CH₃COOH</i>
0	100	0
15	70	30
65	40	60
70	0	100
80	0	100
90	100	0

The LC/MS analysis was performed using Varian 5040 HPLC equipped with Hamilton PRP-1 (150 * 4.1 mm) chromatographic column, coupled with a Berthold LB 505 radioactivity monitor and Finnigan MAT 90 mass spectrometer with a thermospray interface. The chromatographic elution was performed in a linear gradient from 100% H₂O to 100% CH₃OH over 30 min at a flow rate of 0.8 mL/min. 0.2M CH₃COONH₄ solution was added post-column at a rate of 0.2 mL/min. MS analysis was performed in either positive-ion or negative-ion mode and the source temperature T = 210°C.

Results and their discussion:

It was stated that the radioactivity recovered from the test vessels was generally above the level of 85.9% of applied for Fresno soil and 92.8% of applied for Chualar soil. The volatile compounds were not collected, because the preliminary tests showed minimal volatility of the test compounds. Though such conclusion was not drawn by the authors, it may be assumed, on the basis of the other studies examining the fate and behaviour of Flufenacet in aerobic soil, that the losses in radioactivity may be attributed to mineralization of the test compound. It was also stated that the residues of Flufenacet were predominantly confined to the top 3 cm of soil and the migration down the soil profile was limited. That showed the results of the profiling of 3-13 cm layer of soil in samples collected on later time points. It was also noted that it was greater in case of Fresno soil, having lower OC and clay content and higher pH. However, in absence of more detailed results of soil characterization it may be difficult to draw more definitive conclusions.

The detailed results of the characterization of radioactivity in test soils is presented below in two tables – B.8.1.1.1.1_CA-44 for Fresno soil and B.8.1.1.1.1_CA-45 for Chualar soil.

Table B.8.1.1.1.1_CA-44: The results obtained in Fresno soil.

% AR		Results obtained for sample collected at DAT ¹⁾ :										
		0 ²⁾	1 ²⁾	4 ²⁾	7 ²⁾	11 ²⁾	15 ²⁾	19 ²⁾	27 ²⁾	35 ³⁾	46 ³⁾	88 ³⁾
in topsoil (0-3 cm)	Total extracted	99.1	95.8	93.2	79.9	77.2	67.1	62.9	68.5	65.1	63.1	44.3
	as Flufenacet	98.2	94.3	91.4	78.3	74.3	64.6	59.9	50.9	52.7	35.9	17.8
	as FOE Alcohol	0.3	0.7	1.5	1.4	2.5	2.0	2.7	5.2	6.1	7.8	8.1
	as FOE Oxalate	n. d. ⁵⁾	n. d. ⁵⁾	n. d. ⁵⁾	n. d. ⁵⁾	n. d. ⁵⁾	n. d. ⁵⁾	n. d. ⁵⁾	9.1	4.6	13.0	11.7
	as FOE Sulfonic acid	n. d. ⁵⁾	n. d. ⁵⁾	n. d. ⁵⁾	n. d. ⁵⁾	n. d. ⁵⁾	n. d. ⁵⁾	n. d. ⁵⁾	1.4	0.4	1.9	2.4
	as other degradates	0.2	0.8	0.3	0.2	0.4	0.5	0.3	1.9	1.3	4.5	4.3
	NER fraction⁴⁾	n. d. ⁵⁾	6.0	11.5	10.8	15.8	20.1	24.4	16.4	15.0	17.4	19.5
AR Recovered		99.1	102.0	105.0	90.7	93.0	87.2	87.3	84.9	80.1	80.5	63.8
in subsoil (3-13 cm)	NER fraction⁴⁾	n. a. ⁶⁾	n. a. ⁶⁾	n. a. ⁶⁾	n. a. ⁶⁾	n. a. ⁶⁾	8.9	6.6	11.6	15.6	6.9	22.1
Total AR recovered		99.1	102.0	105.0	90.7	93.0	96.1	93.9	96.5	95.7	87.4	85.9

Footnotes to the table:

- 1) Values reported as the mean of the two replicates, concentrations determined by HPLC;
- 2) Only CH₃COOC₂H₅ extracts analysed;
- 3) Results as a sum for the CH₃COOC₂H₅ and CH₃CN/H₂O (7:3) extracts;
- 4) In the original paper that fraction was called “bound residues”, it shall be noted however that it may comprise the extractable fraction, possible to be extracted e. g. by CH₃CN/H₂O (7:3) at reflux, were that extraction step applied (RMS comment);
- 5) n. d. = compound not detected;
- 6) n. a. = sample not analysed.

Table B.8.1.1.1.1_CA-45: The results obtained in Chualar soil.

% AR		Results obtained for sample collected at DAT ¹⁾ :										
		0 ²⁾	1 ²⁾	4 ²⁾	7 ²⁾	11 ²⁾	15 ²⁾	19 ²⁾	27 ³⁾	35 ³⁾	46 ³⁾	88 ³⁾
in topsoil (0-3 cm)	Total extracted	98.0	94.4	86.4	87.1	84.8	65.1	59.0	64.5	73.6	67.8	62.6
	as Flufenacet	97.0	92.9	84.5	84.5	79.8	62.6	56.8	51.5	51.3	42.3	29.0
	as FOE Alcohol	0.4	0.8	1.5	2.1	4.3	2.2	1.9	9.5	14.2	16.3	21.2
	as FOE Oxalate	n. d. ⁵⁾	n. d. ⁵⁾	n. d. ⁵⁾	n. d. ⁵⁾	0.1	n. d. ⁵⁾	n. d. ⁵⁾	1.7	5.2	6.1	7.6
	as FOE Sulfonic acid	n. d. ⁵⁾	0.1	n. d. ⁵⁾	n. d. ⁵⁾	n. d. ⁵⁾	n. d. ⁴⁾	n. d. ⁵⁾	0.5	0.8	0.9	1.3
	as other degradates	0.6	0.6	0.4	0.5	0.6	0.3	0.3	1.3	2.1	2.2	3.5
	NER fraction⁴⁾	n. d. ⁵⁾	4.2	11.1	13.7	12.9	19.0	23.7	22.3	24.2	22.3	25.3
AR Recovered		98.0	98.6	97.5	101.0	97.7	84.1	82.7	86.8	97.8	90.1	87.9
In subsoil (3-13 cm)	NER fraction⁴⁾	n. a. ⁶⁾	n. a. ⁶⁾	n. a. ⁶⁾	n. a. ⁶⁾	n. a. ⁶⁾	11.1	12.7	6.0	1.0	5.1	6.3
Total AR recovered		98.0	98.6	97.5	101.0	97.7	95.2	95.4	92.8	98.8	95.2	94.2

Footnotes to the table:

- 1) Values reported as the mean of the two replicates, concentrations determined by HPLC;
- 2) Only CH₃COOC₂H₅ extracts analysed;
- 3) Results as a sum for the CH₃COOC₂H₅ and CH₃CN/H₂O (7:3) extracts;
- 4) In the original paper that fraction was called "bound residues", it shall be noted however that it may comprise the extractable fraction, possible to be extracted e. g. by CH₃CN/H₂O (7:3) at reflux, were that extraction step applied (RMS comment)
- 5) n. d. = compound not detected;
- 6) n. a. = sample not analysed.

The results obtained for Flufenacet, presented in the tables above, were kinetically examined. The analysis was performed using first order kinetics (most probably SFO model). The obtained results were following:

- for Fresno soil: $k = 0.0192$ [days⁻¹] and half life = 36.1 days, with $r^2 = 0.99$;
- for Chualar soil: $k = 0.0139$ [days⁻¹] and half life = 49.9 days, with $r^2 = 0.96$.

The values were stated to be in range of kinetic parameters of degradation (lab studies) or dissipation (field studies) of Flufenacet in soil determined in other studies.

Three degradation products, considered major by the authors, were identified in the study:

- FOE Alcohol,
- FOE Oxalate,
- FOE Sulfonic Acid.

Finally, it was stated that residues of Flufenacet displayed low leaching potential in soil, what was in line with findings of performed subsequently field dissipation studies.

RMS comments to the study and its evaluation:

The paper reproduced the results presented in the following unpublished study:

Shadrick B. A., Kasper A. M., (1995): "Outdoor soil Metabolism of [Phenyl-U-¹⁴C] Thiafluamide (FOE 5043) on California Soils."; Pan-Agricultural Laboratories Inc., 32380 Avenue 10, Madera, California 93638, USA for Bayer Corporation (formerly Miles Inc.), Agriculture Division, Environmental Research, 17745 South Metcalf Avenue, Stilwell, Kansas 66085, USA; unpublished study No. MR 106210; 7 July 1995.

The study was declared to be a non-GLP study, performed to meet the criteria of the following Guidelines:

- US. EPA Guidelines for Pesticide Registration, Subdivision N, Section 162-1, Aerobic Soil Metabolism;
- US. EPA Guidelines for Pesticide Registration, Subdivision N, Section 164-1, Terrestrial Field Dissipation (supplemental).

That source study was not provided by the Applicant as a part of a dossier submitted for the completeness check. Instead it was placed on the negative list for the Flufenacet renewal approval. The Applicant, in course of the subsequent e-mail exchange with the RMS, provided the following rationale for that (text copied directly from the Applicant's explanatory e-mail):

The study design and sample processing used in this outdoor soil metabolism study is very special and the study itself has some deficiencies/ uncertainties. Thus, we do not believe that the results are representative for the aerobic metabolism of FFA in soil for the following reasons:

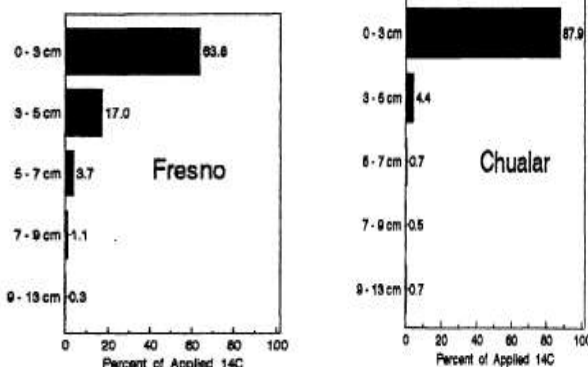
- RMS decided however to present the more detailed soil extraction procedure, provided by the source study. It is given below on figure B.8.1.1.1.1. CA-42.



Additionally copied from the report were numerical and graphical results of the determination of the distribution of the residues of Flufenacet in the whole soil profiles of DAT-88 samples. They are presented below on figure B.8.1.1.1.1. CA-43.

Graphical results

Soil Layer		Residues expressed as % of Applied Radioactivity	
Centimeters	Inches	Fresno Soil	Chualar Soil
0-3	0-1.2	63.8	87.9
3-5	1.2-2.0	17.0	4.4
5-7	2.0-2.8	3.7	0.7
7-9	2.8-3.5	1.1	0.5
9-13	3.5-5.0	0.3	0.7
TOTAL		85.9	94.2



80

As no significant differences between the unpublished report and its published open-literature version were stated, the RMS decided to base the following assessment on what was presented in the literature, peer-reviewed, study.

The thorough analysis of the analytical protocol of the study presented in the paper demonstrated that it followed the more general scheme also used in the studies by Pangilinan and Smith [1994] and Kelley et al [1995]. It shall be noted that, despite the fact that the volatile traps were not set, the recovery of AR was good, within the limits set by OECD 307 Guideline. The lower AR recovery at later time points may be attributed to two factors:

- 1) until DAT 15 only the top - 0-3 cm, layer of soil was examined;
- 2) the observed decrease of recovered AR with time may be due to increasing mineralization and resulting from it formation of (highly volatile) $^{14}\text{CO}_2$, the process not taken into account in the experiment.

The level of would-be mineralization, assuming minimal losses of AR during extraction and homogenous application, is estimated to be following:

- in Fresno soil the estimated mineralization level, on DAT 88, is 14.1% AR;
- in Chualar soil the estimated mineralization level on DAT 88 is 5.8% AR.

It is worth of noting that that mineralization level is in line with findings of the studies by Pangilinan and Smith [1994] and Kelley et al. [1995].

It was noted that the change in extraction procedure, by addition of a second extraction step, resulted in slight reduction of the non-extracted fraction in samples examined when/after that change occurred. That may indicate that in case of the DAT-11, DAT-15 and DAT- 19 samples extracted only with ethyl acetate, such extraction was not sufficient. It is also probable that introduction of that step from the beginning might have resulted in some change in metabolite profiling. Similar result might have given earlier analysis of the subsoil (3-13 cm layer), and extraction in particular.

The results obtained for FOE Sulfonic acid were comparable to those obtained in studies by Pangilinan and Smith [1994] and Kelley et al. [1995]. Different situation however was observed in case of two other identified degradation products – FOE Alcohol and FOE Oxalate. FOE Alcohol was formed early in the study and observed throughout it in significant amounts – up to 8.1% AR on DAT 88 (at increase) in Fresno soil and up to 21.2% AR on DAT 88 (at increase) in Chualar soil. That indicated the possibility of FOE Alcohol of becoming, under specific conditions, therefore requiring to be taken into consideration in the assessment. RMS also noted that the formation of FOE Alcohol was correlated with low OC content and lower microbial activity of the test soils, what may indicate that being in general transient, in weak, sandy soils, on which some cereals may be grown, it may become potentially relevant. That conclusion seems to be conformed by the results by other two studies – the **Study 1** [Kelley et al; 1995] and **Study 2** [Pangilinan and Smith; 1994].

FOE Oxalate was formed later in the study, but reached by its end levels enabling to classify this compound as a major degradate according to the criteria set by SANCO/221/2000 Guidance Document. It cannot be excluded that FOE Oxalate started to form earlier in both soils, but because of the extraction procedure applied, in the earlier sampling points it remained in the “bound fraction”. The relative sequence of formation of FOE Alcohol and FOE Oxalate seems to conform the degradation scheme proposed by the Applicant, according to which FOE Oxalate was formed as a product of further oxidation of FOE Alcohol, the process commonly observed during microbial fermentation of saccharides.

The kinetic examination of the data obtained for Flufenacet enabled to determine the SFO k and DT_{50} values. It shall be noted however that the analysis pre-dated the issuing FOCUS Kinetics Guidance document, therefore the kinetic analysis should be repeated in order to obtain kinetic endpoints fully complying with current standards. The open-literature publication does not provide the data enabling the running of the normalisation procedure leading to the derivation of modelling endpoints, the appropriate weather data, although requiring some processing, can be found in the source study report.

All that taken into account, in RMS opinion the study is of a sufficient quality to provide the data possible to be used for regulatory purposes, in particular in the area of the examination of the route of degradation of Flufenacet in soil and metabolite profiling.

Final conclusion: Study is fully reliable and its results in the area of metabolite profiling are proposed to be used for the regulatory purposes – to derive the regulatory endpoints.

Study 8:

Report: Lam C. K., McKinney M. K., Clay V. E., (2002): "Evaluation of Laboratory and Field Extraction Methods: Extraction of [Phenyl-U-¹⁴C] Flufenacet from Aged Soils."; Agriculture Division, Bayer Corporation, 17745 South Metcalf, Stilwell, KS 66085-9104, USA; published study – published in: *Phelps W. (ed.) "ACS Symposium Series, vol. 813: Pesticide Environmental Fate", chapter 11, pp 153 – 166*; American Chemical Society, Washington, DC, 2002, publication date March 1, 2002;

Guidelines: None declared as this is an open-source study, therefore not submitted for the regulatory purposes. However, examination of the study protocol, also in cross-reference to other studies submitted by the Applicant, demonstrated that it complied with the following guidelines:

- US. EPA Guidelines for Pesticide Registration, Subdivision N, Section 162-1, Aerobic Soil Metabolism;

GLP: the publication bears the declaration that the experiment it describes was a GLP study;

RMS comments: The study was performed on the same soil as used in two other studies submitted specifically for the regulatory purposes – by Pangilinan and Smith [1994] and Pangilinan and Smith [1994a]. It also follows the analytical protocol similar to that described in both studies listed above. Therefore it can be considered acceptable in the assessment of the fate and behaviour of Flufenacet in aerobic soil. Due however to the aim it had – the comparison of the performance of two extraction procedures developed for examining the fate and behaviour of Flufenacet in aerobic soil, it should be regarded as a supplementary and conformatory study, providing important information with regard to the acceptability of the results of other studies for Flufenacet in the same area, but not to be used to derive the regulatory endpoints.

Summary:

The abstract of the publication provided by the publisher – American Chemical Society, is presented below. It was reprinted with permission from: *Christopher K. Lam, Mary K. McKinney, Val E. Clay "Evaluation of Laboratory and Field Extraction Methods: Extraction of [Phenyl U-¹⁴C]Flufenacet from Aged Soils.", ACS Symposium Series, 2002, vol 813: Pesticide Environmental Fate, chapter 11, pp. 153-166; Copyright 2002 American Chemical Society.*

Abstract:

A study was conducted to compare the extraction efficiency of [phenyl-U-¹⁴C] flufenacet from aged soil using both laboratory and field extraction methods. Soil (sandy loam) was obtained from Howe, Indiana and treated with [phenyl-U-¹⁴C] flufenacet at the application rate of 0.9 ppm (equivalent to 0.8 lb. a.i./acre). After treatment, soils were aged aerobically in an environmental chamber at 21 ± 1 °C for 32 days. Extraction methods were compared. The laboratory extraction method employs a more aggressive procedure which involves three extraction steps while the field extraction method involves a single extraction step. At day 0, the laboratory method extracted 97.8% of applied radioactivity while the field method extracted 86%. At day 32, laboratory and field methods extracted 81.9% and 73.1% of applied radioactivity, respectively. The results demonstrated that the field extraction method could extract around 90% of the residues when compared with the laboratory extraction method. Degradates detected using both extraction methods were identical. The distribution of degradates in the extract when calculated based on the percent of analytes from the high-performance liquid chromatography (HPLC) instead of the percent of applied radioactivity were comparable with approximately 61% flufenacet, 27% flufenacet oxalate, and 5% flufenacet sulfonic acid.

The extended summary of the publication, written by the RMS, is presented below.

The aim of the study was to perform the comparative examination of the performance of two extraction methods used in the experiments examining the fate and behaviour of radiolabelled Flufenacet in aerobic soil performed under controlled – laboratory, conditions. The examined extraction methods were further called **laboratory extraction method** and **field extraction method**. The test soil used in this experiment was sandy loam soil obtained from Bayer Research Farm in Howe, Indiana, further called Howe soil. It was the same soil as used in the studies by Pangilinan and Smith [1994, 1994a]. Its characteristic is given below in the table B.8.1.1.1.1_CA-46.

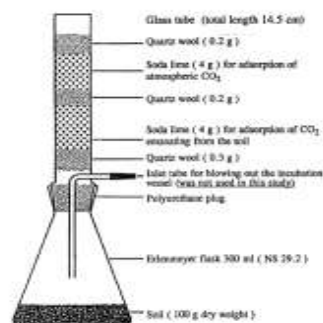
Table B.8.1.1.1.1_CA-46: The characteristic of soil used in the study.

Parameter	Soil:
Soil origin	Howe, Indiana, USA
Soil type (as reported in the study)	Sandy loam
Soil type (USDA, calculated by RMS)	US Sandy loam
Particle size distribution	Sand [%]
	Silt [%]
	Clay [%]
pH	6.2
Organic matter content (OM) [%]	1.6
Organic carbon content (C _{org}) [%] ¹⁾	0.93
Cation Exchange Capacity – CEC [mEq/100g]	12.1
Bulk density (disturbed) [g/cm ³]	1.35
Moisture holding capacity at ½ bar [%]	14.0
Moisture holding capacity at 15 bar [%]	6.2
Available nutrients [%]	Ca
	Mg
	Na
	K
	H
Total N [%]	0.094
Soluble Salts [mmhos/cm]	1.35

Footnotes to the table:

- 1) Value recalculated by the RMS from that reporting OM content given in the study report using the following equation: OM = 1.724 * OC;

The test soil was sieved through 2-mm sieve before being used, and its 100-g (d. w.) portions placed in incubation vessels – biometer flasks capped with traps for volatile compounds, very similar to those used in all studies examining the degradation of Flufenacet in aerobic soil. The example of such biometric flask system (closest to that used in this study) is presented in the summary of the study by Hellpointner [1995] as figure B.8.1.1.1.1_CA-14, reproduced below on figure B.8.1.1.1.1_CA-44. The differences consisted on higher volume of Erlenmeyer flask (500 mL), use of oil –covered glass wool instead of polyurethane plug for absorption of VOCs and the use of inlet tube for ventilating flask before opening it.

**Figure B.8.1.1.1.1_CA-44 (14):** The biometer flask used in the experiment (scheme copied from the study report by Hellpointner, 1995).

In total twenty biometer flask were prepared, six for testing **laboratory extraction method** and another six for examining **field extraction method**. The remaining flasks were spares.

The test soil in biometer flasks was treated with phenyl-¹⁴C Flufenacet applied in form of the application solution to the soil surface. The application dose was 0.9 ppm (0.9 mg/kg), corresponding to 0.8 lb Flufenacet/acre (896 g Flufenacet/ha). The test soil in each biometer flask was brought to the moisture content of 75% of ½ bar by adding the appropriate amount of water (~3.2 mL per flask). At the beginning of the experiment six biometer flasks were taken for the analysis. These samples were further called DAT-0 samples.

All remaining biometer flasks were incubated for 32 days in the dark, under aerobic conditions and at constant temperature $T = 21 \pm 1^{\circ}\text{C}$.

The biometer flasks, after being removed from the incubation chamber, were dissected and the volatile traps were analysed for the content of radioactivity it contained in the same manner as described in the summaries of the studies by Pangilinan and Smith [1994, 1994a].

Next whole portions of the test soil from the given biometric flask were extracted using one of the following tested extraction procedures:

- **laboratory extraction method:** three step extraction method consisting of the following steps:
 - extraction with 150 mL of CH₃CN,
 - extraction with 150 mL of CH₃CN/H₂O 7:3 solution,
 - extraction with 150 mL 0.2N HCl_{aq}/ CH₃CN 1:1 solution,
 each extract was filtered and analysed by LSC; the extraction procedure was identical to that used by Pangilinan and Smith [1994] and shown on figure B.8.1.1.1.1.-CA-11.
- **field extraction method:** a single-step extraction procedure in which 200 mL of 0.1N HCl_{aq}/ CH₃CN 1:1 solution was used; the extracts were evaporated and reconstituted in MeOH, then analysed by LSC and after filtration by HPLC.

The extracted soil pellets were dried, homogenised and analysed for radioactivity content by LSC, after being oxidised by combustion.

The LSC analysis was performed in a way identical to that used in other studies summarised above, e. g. in studies by Kelley et al. [1995] and by Pangilinan and Smith [1994, 1994a].

HPLC analysis for identification and quantitation of the constituents of obtained extracts was performed on HP 1090 HPLC equipped with autosampler and Hamilton PRP-1 (305* 7 mm, 10-µm) chromatographic column, coupled with Raytest Ramona 5-LS radioactivity detector. The elution was performed in a gradient mode, very similar to that used by Pangilinan and Smith [1994] and presented in the table B.8.1.1.1.1._CA-12 as Method A. It is presented below in the table B.8.1.1.1.1.-CA-47. The flow rate was set to 2 mL/min.

Table B.8.1.1.1.1._CA-47: The HPLC gradient mode used in the study.

Time [min]	Solvent ratio	
	<i>Solvent A – Water + 0.4% CH₃COOH</i>	<i>Solvent B – Acetonitrile + 0.4% CH₃COOH</i>
0	100	0
0-25	Linear gradient	
25	75	25
25 - 40	75	25
40 - 75	Linear gradient	
75	30	70
75 - 85	Linear gradient	
85	10	90
85 - 95	10	90

The DAT-0 samples were treated in the same way with exception that for them the traps for volatile radioactivity were not examined as they were not set. That was because it was assumed that no volatiles should be formed at that time point.

Results and their discussion:

The results of the analysis are presented below, separately for each extraction method, in two tables: B.8.1.1.1.1.-CA-48 for **laboratory extraction method** and B.8.1.1.1.1._CA-49 for **field extraction method**.

Table B.8.1.1.1.1._CA-48: The detailed results obtained for the **laboratory extraction method**.

% AR		Results obtained for sample collected at:	
		DAT 0	DAT 32
<i>Extracted in</i>	CH ₃ CN extract	90.2	45.8
	CH ₃ CN/H ₂ O 7:3 extract	6.4	25.6
	0.2N HCl _{aq} / CH ₃ CN 1:1 extract	1.2	1.2
Total extracted		97.8	81.9
<i>Identified in extracts as:</i>	Flufenacet	97.8	51.4
	FOE Oxalate	n. d.	22.7
	FOE Sulfonic acid	n. d.	4.0
	Unknown fraction	n. d.	3.8
Total identified in extracts		97.8	81.9
<i>Volatile compounds</i>	CO ₂	n. a.	n. d.
	VOC	n. a.	0.5
	Total volatiles	n. a.	0.5
Bound residues (NER Fraction)		0.1	10.5
Total AR recovered		97.9	92.9

Table B.8.1.1.1.1._CA-49: The detailed results obtained for the **field extraction method**.

% AR		Results obtained for sample collected at:	
		DAT 0	DAT 32
<i>Extracted in</i>	0.1N HCl _{aq} / CH ₃ CN 1:1 extract	86.0	73.1
Total extracted		86.0	73.1
<i>Identified in extracts as:</i>	Flufenacet	86.0	44.8
	FOE Oxalate	n. d.	19.5
	FOE Sulfonic acid	n. d.	4.3
	Unknown fraction	n. d.	4.5
Total identified in extracts		86.0	73.1
<i>Volatile compounds</i>	CO ₂	n. a.	n. d.
	VOC	n. a.	0.5
	Total volatiles	n. a.	0.5
Bound residues (NER Fraction)		11.4	28.0
Total AR recovered		97.4	101.6

The comparison of the efficiency of both extraction methods showed that the **field extraction method**, simpler, faster, cheaper and according to authors covering all three steps of the **laboratory extraction method**, was able to extract ~90% of AR extracted using more sophisticated **laboratory extraction method**. It had 87.9% relative efficiency for DAT-0 samples and 89.3% relative efficiency for DAT-32 samples. In addition, the amounts of degradation products extracted using each of the extraction method were comparable. It shall however be noted that in case of **field extraction method** the level of NER determined at the beginning of the study – on DAT 0, was relatively high – 11.4% AR, what may indicate that that fraction may be overestimated when this method is used.

Two degradation products were identified in the study:

- FOE Oxalate, reaching the level of 19.5 – 22.7% AR on DAT 32 (end of incubation period),
- FOE Sulfonic acid, reaching the level of 4.0 – 4.3% AR on DAT 32 (end of incubation period).

The level of mineralisation was very low, reaching 0.5% AR at the end of incubation period – on DAT 32. The amounts of NER fraction was 10.5% AR when **laboratory extraction method** was used. The almost triple that level of NER fraction determined with **field extraction method** may not fully reflect the actual situation in soil.

RMS comments to the study and its evaluation:

The thorough analysis of the analytical protocol of the study showed that it may be considered acceptable in line of the current standards. Its results indicate that the change of extraction procedure in the study by Pangilinan and Smith [1994a], made in order to limit losses related to high volatility of the detected compounds, had little impact on the overall results of the study. From that point of view it may be considered a conformatory study for that by Pangilinan and Smith [1994a] in the area of the analytical protocol adopted.

The results of the study, with regard to the identification and quantitation of the extracted compounds and the level of mineralisation are in line with the results obtained by Pangilinan and Smith [1994]. They are however not recommended to be used as regulatory endpoints.

Summary – Route of degradation of Flufenacet in aerobic soil:

The route of degradation of the acetanilide herbicide Flufenacet in aerobic soil was extensively examined in eight agricultural soils – seven originating from the EU and one from US. The test compound – Flufenacet, was radiolabelled in one of the following three following positions:

- uniformly in phenyl ring – compound tested on four soils,
- position C2 in thiadiazole moiety – test performed on one soil,
- position C5 in thiadiazole moiety – examined in four soils.

These data were presented in five unpublished studies submitted specifically for the purpose of this assessment. Additionally the data relevant for determining transformation pattern of Flufenacet in aerobic soil, relevant for regulatory purposes, were found in one scientific paper, examining the degradation of Flufenacet radiolabelled uniformly in phenyl ring in two US soils. That study was based on a non-GLP regulatory study, conceived as a bridging study for laboratory and field experiments on the degradation of Flufenacet in soil. That study was verified by RMS and found acceptable. Therefore the results of the literature study based on it were included into evaluation.

The key results of the examination of transformation of Flufenacet are presented in the tabularised form below (tables B.8.1.1.1.1_CA-50 – B.8.1.1.1.1_CA-53), separately for the compound radiolabelled in phenyl ring and in thiadiazole moiety.

Table B.8.1.1.1.1_CA-50: The levels of mineralisation and NER fraction formed, and identified degradation products in experiments with [Phenyl-U-¹⁴C] Flufenacet.

Study	Soil		Level of mineralisation [% AR]:		Level of NER [% AR]:			Identified degradation products
	Name	Type (USDA)	After ~100 days	at the study's end	Max.	After ~100 days	at the study's end	
Kelley <i>et al</i> ; 1995	BBA 2.2	Loamy sand	12.6 DAT 100	14.2 DAT 120	42.3 DAT 120	37.3 DAT 100	42.3 DAT 120	FOE Sulfonic acid; FOE Oxalate; FOE TGS; FOE Methylsulfoxide; FOE Methylsulfone
	Laacherhof	Silt loam	20.8 DAT 100	23.8 DAT 120	37.1 DAT 120	29.9 DAT 100	37.1 DAT 120	FOE Sulfonic acid; FOE Oxalate; FOE TGS; FOE Methylsulfoxide; FOE Methylsulfone
	Hofchen im Tal	Silt loam	10.2 DAT 100	12.0 DAT 120	58.0 DAT 120	56.2 DAT 100	58.0 DAT 120	FOE Sulfonic acid; FOE Oxalate; FOE TGS; FOE Methylsulfoxide; FOE Methylsulfone
Pangi-linan & Smith; 1994	Howe	Sandy loam	2.7 DAT 91	5.9 DAT 365	17.7 DAT 271	16.3 DAT 91	16.5 DAT 365	FOE Sulfonic acid; FOE Oxalate; FOE Alcohol; FOE TGS; FOE Methylsulfoxide; FOE Chloroacetanilide;
Bloom-berg <i>et al</i> ; 2002	Fresno	Sandy loam	14.1 ¹⁾ DAT 88	14.1 ¹⁾ DAT 88	41.6 ²⁾ DAT 88	41.6 ²⁾ DAT 88	41.6 ²⁾ DAT 88	FOE Sulfonic acid; FOE Oxalate; FOE Alcohol;
	Chualar	Sandy loam	5.8 ¹⁾ DAT 88	5.8 ¹⁾ DAT 88	46.4 ²⁾ DAT 19	31.6 ²⁾ DAT 88	31.6 ²⁾ DAT 88	FOE Sulfonic acid; FOE Oxalate; FOE Alcohol;

Footnotes to the table:

- 1) Value estimated as a difference between the reported “total AR recovered” and the theoretical 100% AR;
- 2) The value is the sum of NER fraction in topsoil (0-3 cm) and subsoil (3-13 cm) for the given time point; in the subsoil the detected radioactivity was not further examined, but considered to represent NER fraction, so that value may be an overestimate;

Table B.8.1.1.1.1_CA-51: Concentrations and classification of soil degradation products identified in experiments with [Phenyl-U-¹⁴C] Flufenacet

Degradation product	Maximum [% AR] in soil, detected on:						Classification according to SANCO/221/2000	Justification ¹⁾
	BBA 2.2	Laacherhof	Hofchen im Tal	Howe	Fresno	Chualar		
FOE Sulfonic acid	25.4 DAT 100	26.3 DAT 100	13.5 DAT 100	7.7 DAT 180	2.4 DAT 88	1.3 DAT 88	major/relevant for GW assessment	> 10% AR
FOE Oxalate	6.6 DAT 28	15.6 DAT 28	10.0 DAT 28	26.5 DAT 365	13.0 DAT 46	7.6 DAT 88	major/relevant for GW assessment	>10% AR
FOE Alcohol	n. d.	n. d.	n. d.	2.1 DAT 44, DAT 65	8.1 DAT 88	21.2 DAT 88	major/relevant for GW assessment	>10% AR
FOE TGS	3.3 DAT 56	5.5 DAT 28	1.9 DAT 28	3.7 DAT 180	n. d. ²⁾	n. d. ²⁾	minor/not relevant for GW assessment	Not meeting any of the criteria
FOE Methyl-sulfoxide	1.1 DAT 28, DAT 56	3.5 DAT 56	1.5 DAT 56	0.6 DAT 28	n. d. ²⁾	n. d. ²⁾	minor/not relevant for GW assessment	Not meeting any of the criteria
FOE Methyl-sulfone	6.6 DAT 100	4.3 DAT 120	5.6 DAT 120	n. d.	n. d. ²⁾	n. d. ²⁾	major/relevant for GW assessment	>5% AR at study end, increasing
FOE Chloroacet-anilide	n. d. ²⁾	n. d. ²⁾	n. d. ²⁾	5.1 DAT 44	n. d. ²⁾	n. d. ²⁾	minor/not relevant for GW assessment	Not meeting any of the criteria

Footnotes to the table:

- 1) Justification based on the criteria set by the Guideline SANCO/221/2000, listed under the point 4 on page 6:
“As a minimum, degradation products must be characterized and identified by the notifiers to the extent that it is technically feasible and their relevance must be assessed, if one of the following conditions applies:
a) *Metabolites, which account for more than 10% of the amount of active substance added in soil at any time during the studies; or*
b) *which account for more than 5% of the amount of active substance added in soil in at least two sequential measurements during the studies; or*
c) *for which at the end of soil degradation studies the maximum of formation is not yet reached.*
- 2) Compound not detected in that soil.

Table B.8.1.1.1.1_CA-52: The levels of mineralisation and NER fraction formed, and identified degradation products in experiments with [Thiadiazole-¹⁴C] Flufenacet.

Study/ radiolabelling position	Soil		Level of mineralisation [% AR]:		Level of NER [% AR]:			Identified degradation products
	Name	Type (USDA)	after ~100 days	at the study's end	Max.	after ~100 days	at the study's end	
Pangilinan & Smith; 1994a [Thiadiazole-2- ¹⁴ C]	Howe	Sandy loam	31.9 DAT 90	50.9 DAT 368	6.9 DAT 270	6.2 DAT 90	6.5 DAT 368	FOE Thiadone
Hein; 2012 [Thiadiazole-5- ¹⁴ C]	Hoefchen am Hohenseh 4a	Silt loam	5.7 DAT 120	5.7 DAT 120	13.5 DAT 60	12.5 DAT 120	12.5 DAT 120	FOE Thiadone; FOE 5043- Trifluoroethanesulfonic acid; Trifluoroacetic acid (TFA)
Hein; 2012a [Thiadiazole-5- ¹⁴ C]	Laacherhof AXXa	Loamy sand	5.6 DAT 121	5.6 DAT 121	18.6 DAT 63	17.2 DAT 121	17.2 DAT 121	FOE Thiadone; FOE 5043- Trifluoroethanesulfonic acid; Trifluoroacetic acid (TFA)
	Dollendorf II	Clay loam	6.5 DAT 121	6.5 DAT 121	11.5 DAT 63	10.6 DAT 121	10.6 DAT 121	FOE Thiadone; FOE 5043- Trifluoroethanesulfonic acid; Trifluoroacetic acid (TFA)
	Laacherhof Wurmwiess	Loam	4.6 DAT 121	4.6 DAT 121	18.6 DAT 35, DAT 63	17.2 DAT 121	17.2 DAT 121	FOE Thiadone; FOE 5043- Trifluoroethanesulfonic acid; Trifluoroacetic acid (TFA)

Table B.8.1.1.1.1_CA-53: Concentrations and classification of soil degradation products identified in experiments with [Thiadiazole-¹⁴C] Flufenacet

Degradation product	Maximum [% AR] in soil, detected on:					Classification according to SANCO/221/2000	Justification ¹⁾
	Howe	Hoefchen am Hohenseh 4a	Laacherhof AXxa	Dollendorf II	Laacherhof Wurmweise		
FOE Thiadone	3.9 DAT 7	5.8 DAT 10	2.8 DAT 7	5.6 DAT 10	4.6 DAT	major/relevant for GW assessment	> 5% AR at two consecutive time points
FOE Trifluoroethanesulfonic acid	n. d. ²⁾	6.0 DAT 14	4.4 DAT 10	3.4 DAT 10	1.9 DAT 10	major/relevant for GW assessment	> 5% AR at two consecutive time points
TFA (Trifluoroacetic acid)	n. d. ²⁾	77.7 DAT 87	74.1 DAT 121	81.5 DAT 91	74.8 DAT 91	major/relevant for GW assessment	> 10% AR

Footnotes to the table:

1) Justification based on the criteria set by the Guideline SANCO/221/2000, listed under the point 4 on page 6:

“As a minimum, degradation products must be characterized and identified by the notifiers to the extent that it is technically feasible and their relevance must be assessed, if one of the following conditions applies:

- Metabolites, which account for more than 10% of the amount of active substance added in soil at any time during the studies; or*
- which account for more than 5% of the amount of active substance added in soil in at least two sequential measurements during the studies; or*
- for which at the end of soil degradation studies the maximum of formation is not yet reached.*

2) Compound not detected in that soil.

The transformation pattern of Flufenacet in soil was examined only on biologically viable soil. That was due to the fact that, on the basis of available results it was assumed that all transformation processes were predominantly or solely biologically-mediated. It was postulated that the initial step of the degradation was the cleavage of the test item on bridging oxygen of the thiadiazole heterocycle. The further sequence for the thiadiazole moiety is presented below:

- tautomerisation of keto-enol functional group, resulting in formation of FOE Thiadone,
- hydrolytical opening of thiadone ring and further oxidation resulting in formation of either FOE 5043-Trifluoroethanesulfonic acid or Trifluoroacetic acid (TFA), or else simple products of mineralisation and NER fraction – ultimate transformation products;
- further transformation of FOE 5043-Trifluoroethanesulfonic acid or Trifluoroacetic acid (TFA) to the simple products of mineralisation and NER fraction – ultimate transformation products.

In case of the moiety containing fluorophenyl ring next postulated step was the formation of the transient FOE Cysteine- or FOE Glutathione conjugates, undergoing subsequent quick transformation to FOE Methylsulfoxide, FOE Alcohol and FOE Chloroacetanilide. As possible side-processes were postulated direct formation of FOE Chloroacetanilide and FOE Alcohol. It shall be noted that FOE Chloroacetanilide may be not only a genuine degradation product, but also, and possibly to greater extent, analytical artefact. However, as the issue was not satisfactorily clarified, the RMS's proposal is to consider FOE Chloroacetanilide a genuine degradation product.

The proposed transformation pathway of Flufenacet in aerobic soil, resulting from the data presented above, is presented on figure B.8.1.1.1.1_CA-45.

Additionally, as in course of evaluation FOE Alcohol was identified to be a potentially major degradation product, the additional assessment was performed to determine whether, in absence of data for that compound, the exposure assessment for FOE Alcohol may be considered to be covered by that for its immediate degradate – FOE Oxalate.

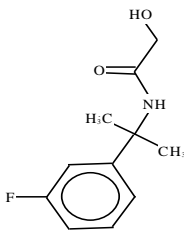
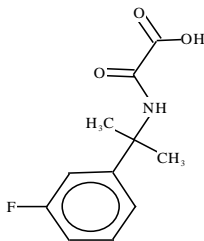
The Applicant in course of the discussion on the nature of FOE Alcohol made a following statement (the text is copied directly from the Applicant's e-mail; the “outdoor soil metabolism study” refers to the cited study by Shadrick and Kasper [1995]):

We cannot reconstruct what the reason for the accumulation or artificial formation of FOE alcohol (aka FOE hydroxy) was in that outdoor soil metabolism study, but we have several other laboratory studies, as well as EU and US field studies, which demonstrate, that FOE alcohol is a minor, transient metabolite, not accumulating at all, but rather being further oxidized quickly to FOE oxalate.

RMS having analysed the results provided by the study by Shadrick and Kasper [1995], reproduced in the publication by Bloomberg et al. [2002], noted that the compound was formed in greater amounts in Chualar soil, having lower OC content and slightly lower microbial activity of the two soils used in the experiment. Taking into account the fact that FOE Alcohol was also detected only in the study by Pangilinan and Smith [1994], performed on another soil having low OC content and microbial activity, but not in the study by Kelley et al [1995], all that may indicate that FOE Alcohol is indeed a transient, fast degrading compound, that would appear in higher amounts and for longer only in weak soils.

To further demonstrate that it was possible to cover the exposure assessment for FOE Alcohol with that for its immediate degradate – FOE Oxalate, RMS performed the comparative analysis by means of QSAR calculations, carried out with EPI Suite ver. 4.10 (September 2010) tool. The detailed results of the calculations are presented in the Appendix 3 of this report, while the summary output for both compounds is presented below in the table B.8.1.1.1.1._CA-54.

Table B.8.1.1.1.1._CA-54: Results of the QSAR analysis for FOE Alcohol and FOE Oxalate

Compound: FOE Alcohol	Compound: FOE Oxalate
<p><i>Structural formula (drawn by the tool):</i></p> 	<p><i>Structural formula (drawn by the tool):</i></p> 
<p><i>Numerical results:</i></p> <p>SMILES : <chem>c1ccc(F)cc1C(C)(C)NC(=O)CO</chem> CHEM : MOL FOR: C11 H14 F1 N1 O2 MOL WT : 211.24</p> <p>----- EPI SUMMARY (v4.10) -----</p> <p>Physical Property Inputs: Water Solubility (mg/L): ----- Vapor Pressure (mm Hg) : ----- Henry LC (atm-m3/mole) : ----- Log Kow (octanol-water): ----- Boiling Point (deg C) : ----- Melting Point (deg C) : -----</p> <p>Log Octanol-Water Partition Coef (SRC): Log Kow (KOWWIN v1.68 estimate) = 1.52</p> <p>Boiling Pt, Melting Pt, Vapor Pressure Estimations (MPBPWIN v1.43): Boiling Pt (deg C): 369.94 (Adapted Stein & Brown method) Melting Pt (deg C): 133.29 (Mean or Weighted MP) VP(mm Hg,25 deg C): 1.14E-007 (Modified Grain method) VP (Pa, 25 deg C) : 1.52E-005 (Modified Grain method) Subcooled liquid VP: 1.39E-006 mm Hg (25 deg C, Mod-Grain method) : 0.000186 Pa (25 deg C, Mod-Grain method)</p> <p>Water Solubility Estimate from Log Kow (WSKOW v1.42): Water Solubility at 25 deg C (mg/L): 1933 log Kow used: 1.52 (estimated) no-melting pt equation used</p> <p>Water Sol Estimate from Fragments: Wat Sol (v1.01 est) = 2.5837e+005 mg/L</p> <p>ECOSAR Class Program (ECOSAR v1.11): Class(es) found: Amides</p> <p>Henrys Law Constant (25 deg C) [HENRYWIN v3.20]: Bond Method : 6.36E-010 atm-m3/mole (6.44E-005 Pa-m3/mole) Group Method: Incomplete For Henry LC Comparison Purposes: User-Entered Henry LC: not entered Henrys LC [via VP/WSol estimate using User-Entered or Estimated values]: HLC: 1.639E-011 atm-m3/mole (1.661E-006 Pa-m3/mole) VP: 1.14E-007 mm Hg (source: MPBPVP)</p>	<p><i>Numerical results:</i></p> <p>SMILES : <chem>c1ccc(F)cc1C(C)(C)NC(=O)C(=O)O</chem> CHEM : MOL FOR: C11 H12 F1 N1 O3 MOL WT : 225.22</p> <p>----- EPI SUMMARY (v4.10) -----</p> <p>Physical Property Inputs: Water Solubility (mg/L): ----- Vapor Pressure (mm Hg) : ----- Henry LC (atm-m3/mole) : ----- Log Kow (octanol-water): ----- Boiling Point (deg C) : ----- Melting Point (deg C) : -----</p> <p>Log Octanol-Water Partition Coef (SRC): Log Kow (KOWWIN v1.68 estimate) = 0.85</p> <p>Boiling Pt, Melting Pt, Vapor Pressure Estimations (MPBPWIN v1.43): Boiling Pt (deg C): 397.32 (Adapted Stein & Brown method) Melting Pt (deg C): 164.63 (Mean or Weighted MP) VP(mm Hg,25 deg C): 3.53E-007 (Modified Grain method) VP (Pa, 25 deg C) : 4.71E-005 (Modified Grain method) Subcooled liquid VP: 9.66E-006 mm Hg (25 deg C, Mod-Grain method) : 0.00129 Pa (25 deg C, Mod-Grain method)</p> <p>Water Solubility Estimate from Log Kow (WSKOW v1.42): Water Solubility at 25 deg C (mg/L): 6113 log Kow used: 0.85 (estimated) no-melting pt equation used</p> <p>Water Sol Estimate from Fragments: Wat Sol (v1.01 est) = 1.4972e+005 mg/L</p> <p>ECOSAR Class Program (ECOSAR v1.11): Class(es) found: Neutral Organics</p> <p>Henrys Law Constant (25 deg C) [HENRYWIN v3.20]: Bond Method : 1.79E-013 atm-m3/mole (1.82E-008 Pa-m3/mole) Group Method: Incomplete For Henry LC Comparison Purposes: User-Entered Henry LC: not entered Henrys LC [via VP/WSol estimate using User-Entered or Estimated values]: HLC: 1.711E-011 atm-m3/mole (1.734E-006 Pa-m3/mole) VP: 3.53E-007 mm Hg (source: MPBPVP)</p>

Compound: FOE Alcohol	Compound: FOE Oxalate
WS: 1.93E+003 mg/L (source: WSKOWWIN)	WS: 6.11E+003 mg/L (source: WSKOWWIN)
Log Octanol-Air Partition Coefficient (25 deg C) [KOAWIN v1.10]: Log Kow used: 1.52 (KowWin est) Log Kaw used: -7.585 (HenryWin est) Log Koa (KOAWIN v1.10 estimate): 9.105 Log Koa (experimental database): None	Log Octanol-Air Partition Coefficient (25 deg C) [KOAWIN v1.10]: Log Kow used: 0.85 (KowWin est) Log Kaw used: -11.136 (HenryWin est) Log Koa (KOAWIN v1.10 estimate): 11.986 Log Koa (experimental database): None
Probability of Rapid Biodegradation (BIOWIN v4.10): Biowin1 (Linear Model) : 0.0219 Biowin2 (Non-Linear Model) : 0.0002 Expert Survey Biodegradation Results: Biowin3 (Ultimate Survey Model): 2.2191 (months) Biowin4 (Primary Survey Model) : 3.7379 (days-weeks) MITI Biodegradation Probability: Biowin5 (MITI Linear Model) : 0.5396 Biowin6 (MITI Non-Linear Model): 0.0131 Anaerobic Biodegradation Probability: Biowin7 (Anaerobic Linear Model): -0.4481 Ready Biodegradability Prediction: NO	Probability of Rapid Biodegradation (BIOWIN v4.10): Biowin1 (Linear Model) : -0.0708 Biowin2 (Non-Linear Model) : 0.0001 Expert Survey Biodegradation Results: Biowin3 (Ultimate Survey Model): 2.3928 (weeks-months) Biowin4 (Primary Survey Model) : 3.9738 (days) MITI Biodegradation Probability: Biowin5 (MITI Linear Model) : 0.4686 Biowin6 (MITI Non-Linear Model): 0.0065 Anaerobic Biodegradation Probability: Biowin7 (Anaerobic Linear Model): -0.4201 Ready Biodegradability Prediction: NO
Hydrocarbon Biodegradation (BioHCwin v1.01): Structure incompatible with current estimation method!	Hydrocarbon Biodegradation (BioHCwin v1.01): Structure incompatible with current estimation method!
Sorption to aerosols (25 Dec C)[AEROWIN v1.00]: Vapor pressure (liquid/subcooled): 0.000185 Pa (1.39E-006 mm Hg) Log Koa (Koawin est): 9.105 Kp (particle/gas partition coef. (m3/ug)): Mackay model : 0.0162 Octanol/air (Koa) model: 0.000313 Fraction sorbed to airborne particulates (phi): Junge-Pankow model : 0.369 Mackay model : 0.564 Octanol/air (Koa) model: 0.0244	Sorption to aerosols (25 Dec C)[AEROWIN v1.00]: Vapor pressure (liquid/subcooled): 0.00129 Pa (9.66E-006 mm Hg) Log Koa (Koawin est): 11.986 Kp (particle/gas partition coef. (m3/ug)): Mackay model : 0.00233 Octanol/air (Koa) model: 0.238 Fraction sorbed to airborne particulates (phi): Junge-Pankow model : 0.0776 Mackay model : 0.157 Octanol/air (Koa) model: 0.95
Atmospheric Oxidation (25 deg C) [AopWin v1.92]: Hydroxyl Radicals Reaction: OVERALL OH Rate Constant = 13.8073 E-12 cm3/molecule-sec Half-Life = 0.775 Days (12-hr day; 1.5E6 OH/cm3) Half-Life = 9.296 Hrs Ozone Reaction: No Ozone Reaction Estimation Fraction sorbed to airborne particulates (phi): 0.467 (Junge-Pankow, Mackay avg) 0.0244 (Koa method) Note: the sorbed fraction may be resistant to atmospheric oxidation	Atmospheric Oxidation (25 deg C) [AopWin v1.92]: Hydroxyl Radicals Reaction: OVERALL OH Rate Constant = 11.7355 E-12 cm3/molecule-sec Half-Life = 0.911 Days (12-hr day; 1.5E6 OH/cm3) Half-Life = 10.937 Hrs Ozone Reaction: No Ozone Reaction Estimation Fraction sorbed to airborne particulates (phi): 0.117 (Junge-Pankow, Mackay avg) 0.95 (Koa method) Note: the sorbed fraction may be resistant to atmospheric oxidation
Soil Adsorption Coefficient (KOCWIN v2.00): Koc : 46.38 L/kg (MCI method) Log Koc: 1.666 (MCI method) Koc : 21.32 L/kg (Kow method) Log Koc: 1.329 (Kow method)	Soil Adsorption Coefficient (KOCWIN v2.00): Koc : 10 L/kg (MCI method) Log Koc: 1.000 (MCI method) Koc : 2.37 L/kg (Kow method) Log Koc: 0.375 (Kow method)
Aqueous Base/Acid-Catalyzed Hydrolysis (25 deg C) [HYDROWIN v2.00]: Rate constants can NOT be estimated for this structure!	Aqueous Base/Acid-Catalyzed Hydrolysis (25 deg C) [HYDROWIN v2.00]: Rate constants can NOT be estimated for this structure!
Bioaccumulation Estimates (BCFBAF v3.01): Log BCF from regression-based method = 0.413 (BCF = 2.589 L/kg wet-wt) Log Biotransformation Half-life (HL) = -1.1393 days (HL = 0.07257 days) Log BCF Arnot-Gobas method (upper trophic) = 0.520 (BCF = 3.313) Log BAF Arnot-Gobas method (upper trophic) = 0.520 (BAF = 3.313) log Kow used: 1.52 (estimated)	Bioaccumulation Estimates (BCFBAF v3.01): Log BCF from regression-based method = 0.500 (BCF = 3.162 L/kg wet-wt) Log Biotransformation Half-life (HL) = -0.9640 days (HL = 0.1086 days) Log BCF Arnot-Gobas method (upper trophic) = 0.175 (BCF = 1.496) Log BAF Arnot-Gobas method (upper trophic) = 0.175 (BAF = 1.496) log Kow used: 0.85 (estimated)
Volatilization from Water: Henry LC: 6.36E-010 atm-m3/mole (estimated by Bond SAR)	Volatilization from Water: Henry LC: 1.79E-013 atm-m3/mole (estimated by Bond SAR)

Compound: FOE Alcohol	Compound: FOE Oxalate
Method) Half-Life from Model River: 1.338E+006 hours (5.575E+004 days) Half-Life from Model Lake : 1.46E+007 hours (6.082E+005 days)	Method) Half-Life from Model River: 4.909E+009 hours (2.045E+008 days) Half-Life from Model Lake : 5.355E+010 hours (2.231E+009 days)
Removal In Wastewater Treatment: Total removal: 1.98 percent Total biodegradation: 0.09 percent Total sludge adsorption: 1.89 percent Total to Air: 0.00 percent (using 10000 hr Bio P,A,S)	Removal In Wastewater Treatment: Total removal: 1.87 percent Total biodegradation: 0.09 percent Total sludge adsorption: 1.78 percent Total to Air: 0.00 percent (using 10000 hr Bio P,A,S)
Level III Fugacity Model: Mass Amount Half-Life Emissions (percent) (hr) (kg/hr) Air 0.00733 18.6 1000 Water 22.1 1.44e+003 1000 Soil 77.8 2.88e+003 1000 Sediment 0.0932 1.3e+004 0 Persistence Time: 1.93e+003 hr	Level III Fugacity Model: Mass Amount Half-Life Emissions (percent) (hr) (kg/hr) Air 2.35e-006 21.9 1000 Water 35 900 1000 Soil 64.9 1.8e+003 1000 Sediment 0.0835 8.1e+003 0 Persistence Time: 1.15e+003 hr

The presented results indicate that the properties of both compounds relevant for their environmental fate and behaviour are comparable. Therefore the exposure assessment performed for FOE Oxalate may be considered as covering that for FOE Alcohol. The Applicant also indicated that, according to the results of toxicological and ecotoxicological studies, submitted for the purpose of the current evaluation, Foe Alcohol was demonstrated not to be toxicologically or ecotoxicologically relevant degradation product.

The proposed transformation pathway of Flufenacet in aerobic soil, resulting from the data presented above, is presented below on figure B.8.1.1.1.1_CA-45.

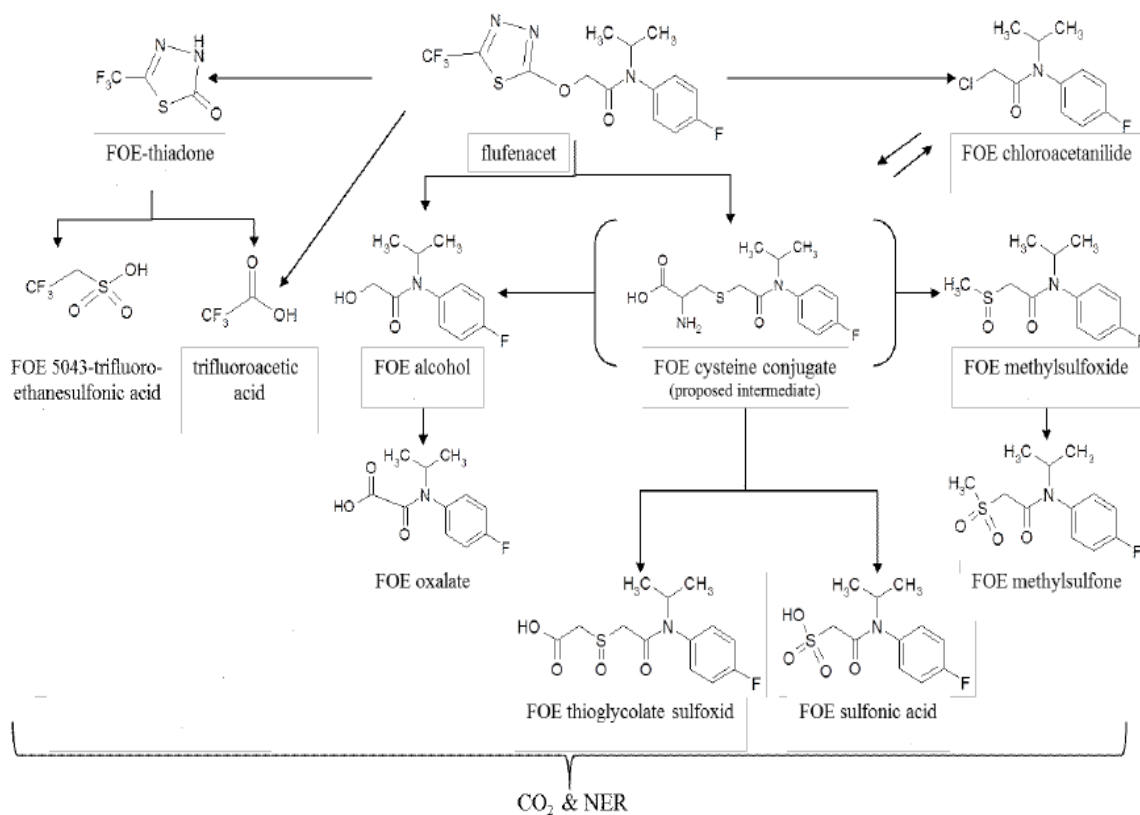


Figure B.8.1.1.1.1_CA-45: Postulated transformation pathway of Flufenacet in soil as proposed by the Applicant (modified by the RMS).

The proposed final set of endpoints is presented below, in format recommended for the EU-agreed endpoints (SANCO/12483/2014-rev.2; 12 December 2014).

Route of degradation (aerobic) in soil (Regulation (EU) N° 283/2013, Annex Part A, point 7.1.1.1)

Mineralisation after 100 days	<p>2.7% after 91 d, [¹⁴C-<i>U-Phenyl</i>]-label (n= 1) 10.2 – 20.8% after 100 d, [¹⁴C-<i>U-Phenyl</i>]-label (n= 3) 31.9% after 90 d, [¹⁴C-<i>2-Thiadiazole</i>]-label (n= 1) 4.5 – 6.5% after 120-121 d, [¹⁴C-<i>5-Thiadiazole</i>]-label (n= 4)</p>
Non-extractable residues after 100 days	<p>16.3% after 91 d, [¹⁴C-<i>U-Phenyl</i>]-label (n= 1) 29.9 – 56.2% after 100 d, [¹⁴C-<i>U-Phenyl</i>]-label (n= 3) 6.2% after 90 d, [¹⁴C-<i>2-Thiadiazole</i>]-label (n= 1) 10.6 – 17.2% after 120-121 d, [¹⁴C-<i>5-Thiadiazole</i>]-label (n= 4)</p>
Metabolites requiring further consideration - name and/or code, % of applied (range and maximum)	<p><i>FOE Sulfonic acid</i> – max. 26.3% at 100 d (n= 6); [¹⁴C-<i>U-Phenyl</i>] label; <i>FOE Alcohol</i> – max. 21.2% at 88 d (n= 3); [¹⁴C-<i>U-Phenyl</i>] label; <i>FOE Oxalate</i> – max. 26.5% at 365 d (n= 6); [¹⁴C-<i>U-Phenyl</i>] label; <i>FOE Methylsulfone</i> – max. 6.6% at 100 d (n= 3); [¹⁴C-<i>U-Phenyl</i>] label; <i>FOE Thiadone</i> – max. 5.8% at 10 d (n= 5); [¹⁴C-<i>2-Thiadiazole</i>] & [¹⁴C-<i>5-Thiadiazole</i>] labels <i>FOE 5043-Trifluoroethanesulfonic acid</i> – max. 6.0% at 14 d (n= 4); [¹⁴C-<i>5-Thiadiazole</i>] label <i>Trifluoroacetic acid (TFA)</i> – max. 81.5% at 91 d (n= 4); [¹⁴C-<i>5-Thiaiazole</i>] label Sterile conditions: <i>not examined</i></p>

B.8.1.1.1.2. – Anaerobic degradation

In the previous evaluation of Flufenacet for its authorisation in the EU it was stated that the studies on the degradation in anaerobic soil were not supplied. The following statement was given in the DAR as a justification of that: *“Due to the proposed patterns (application as pre- or early post-emergence herbicide in maize and cereals) it can be justified that FOE 5043 will not be exposed to anaerobic conditions. Therefore, a study on anaerobic degradation is considered as being not relevant.”*

However, for the purposes of the present evaluation the proposed EU-representative GAP was substantially changed. The proposed use pattern was limited to those in winter and spring cereals. On the other hand the application timing was extended to cover both autumn- and spring uses. As a result, the occurrence of anaerobic conditions, especially for the autumn applications, cannot be ruled out. For that reason the Applicant submitted two studies covering the issue of the degradation of Flufenacet in soil under anaerobic conditions. These studies are summarised below.

Study 1:

Report: Pangilinan N. C., Smith D. M., (1995): “Anaerobic Soil Metabolism of [Phenyl-U-¹⁴C] FOE 5043”; Bayer Corporation (formerly Miles Inc.), Agriculture Division, P. O. Box 4913, Kansas City, Missouri 64120-0013, USA; study No. F3042106; unpublished Miles Report No. MR 106645; 20 June 1995; study reference number: M-002162-01-1;

Guidelines: The study was performed to comply with the following Guidelines:

- US. EPA Guidelines for Pesticide Registration, Subdivision N, Section 162-2, Anaerobic Soil Metabolism (Expanded).

GLP: Yes

RMS comments: From the point of view of evaluation of Flufenacet in the EU this is a new study. It was submitted specifically for the purpose of the renewal of authorisation. In the study report it was declared that it was carried out to address the requirements set forth in the EPA Guidelines for Pesticide Registration, Subdivision N, Section 162-2 as required by 40 CFR, 158.130, despite the fact that at the time of submission two valid anaerobic aquatic metabolism studies for Flufenacet were provided. However, as indicated in US EPA Rejection Rate Criteria (*“the aerobic preincubation would certainly be indicated for those compounds, which degrade somewhat rapidly under aerobic conditions”*) the study had to be submitted, because Flufenacet displayed short half-life under aerobic conditions, so the fate of its aerobic metabolites under anaerobic conditions had to be addressed. It shall be therefore assumed that, although the study is newly submitted for the purpose of the registration in the EU, it could already have been evaluated for the registration purposes elsewhere, e.g. in the US, and found acceptable.

RMS evaluated the study for its validity and compliance with the following Guidelines:

- US. EPA Guidelines for Pesticide Registration, Subdivision N, Section 162-2, Anaerobic Soil Metabolism;
- OECD 307 Guideline – Aerobic and Anaerobic Transformation in Soil;
- US EPA OPPTS Guideline 835.4100 – Aerobic Soil Metabolism/835.4200 – Anaerobic Soil Metabolism.

The study was found to be fully compliant with these three Guidelines. As such it may be considered fully valid. It is summarised below in its part related to the examination of the route of degradation in soil under anaerobic conditions. The assessment of the degradation kinetics is provided under the point B.8.1.1.2.1.

Summary:

The aim of the study was to examine the degradation of Flufenacet and its aerobic soil degradation products in anaerobic soil system (waterlogged soil) established after 30-days aerobic preincubation of the treated test soil. The experiment was performed with one test soil – Howe Sandy loam soil, used in two other experiments aimed on the examination of the transformation of Flufenacet in aerobic soil - [Pangilinan and Smith; 1994] and [Pangilinan and Smith; 1994a], summarised above, under the point B.8.1.1.1.1. as **Study 2** and **Study 4**. The characteristic of the test soil used in the experiment is presented below in the table B.8.1.1.1.2._CA-1.

Table B.8.1.1.1.2._CA-1: The characteristic of soil used in the study.

Parameter		Soil:			
		395			
Soil origin		Howe, Indiana, USA			
Batch analysed		A ¹⁾	B ²⁾	C ³⁾	Average
Soil type (USDA)		Sandy loam	Sandy loam	Sandy loam	Sandy loam
Particle size distribution	Sand [%]	72.5	77.5	70.4	73.5
	Silt [%]	20.0	17.2	20.0	19.1
	Clay [%]	7.5	5.3	9.6	7.5
pH value (in water, 1:1)		6.1	6.4	6.2	6.2
pH value in CaCl ₂ ⁴⁾		5.5	5.9	5.6	5.6 ⁵⁾
Organic matter content (OM) [%]		0.2	0.4	1.2	0.6
Organic carbon content (C _{org}) [%] ⁶⁾		0.12	0.23	0.70	0.35
Cation Exchange Capacity – CEC [mEq/100g]		6.9	7.4	5.1	6.5
Bulk density (disturbed) [g/cm ³]		1.31	1.33	1.47	1.37
Moisture holding capacity at ½ bar [%]		14.8	13.1	11.4	13.1
Soil biomass expressed in mg microbial C/kg soil in samples collected on DAT ⁷⁾ :	0	-----	-----	-----	83
	30	-----	-----	-----	101
Soil biomass expressed as %OC ⁸⁾ in samples collected on DAT:	0	-----	-----	-----	2.37
	30	-----	-----	-----	2.89
Soil biomass expressed in Cells/g soil ⁹⁾	DAT 0 ¹⁰⁾	-----	-----	-----	2.9 E8
	DAT 30 ¹¹⁾	-----	-----	-----	2.6 E8
	DAF 7 ¹²⁾	-----	-----	-----	8.4 E8 ¹³⁾
	DAF 95 ¹²⁾	-----	-----	-----	5.2 E8 ¹³⁾
	DAF 180 ¹²⁾	-----	-----	-----	3.5 E8 ¹⁴⁾
	DAF 203 ¹²⁾	-----	-----	-----	3.2 E8 ¹⁵⁾
		-----	-----	-----	2.6 E8 ¹⁶⁾
		-----	-----	-----	1.9 E8 ¹⁵⁾

Footnotes to the table:

- 1) Analysis performed by Agvise Inc. on 13 August 1991;
- 2) Analysis performed by Agvise Inc. on 4 February 1992;
- 3) Analysis performed by A&L Great Lakes Laboratories Inc. on 29 March 1993;
- 4) Value recalculated by the RMS using the following equation: $pH_{H_2O} = 0.982 pH_{CaCl_2} + 0.648$;
- 5) Value calculated from the corresponding pH in water;
- 6) Value calculated by RMS using the following relationship: OC = OM/1.724.
- 7) The soil microbial biomass was determined in soil samples incubated under aerobic conditions using Anderson&Domsch's method;
- 8) Values calculated using the average OC content – 0.35%;
- 9) Determined using PLFA method, assuming that 1 g d. w. of microbial cells = 1 E8 pmols PLFA and 1 g d. w. microbial cells = 2.0 E12 microbial cells, therefore 1 pmol PLFA = 3 E4 microbial cells ;
- 10) DAT = Days After Treatment, aerobic phase
- 11) DAT = Days After Treatment, aerobic phase, last day of aerobic phase and first day of anaerobic phase;
- 12) DAF = Days After Flooding, determining the duration of anaerobic phase;
- 13) Analysed in samples set specifically for microbial evaluation, incubated during anaerobic phase in a flow-through system;
- 14) Analysed in sample set specifically for microbial control, incubated during anaerobic phase in a static system;
- 15) Analysed in a sample set as a non-sterile control, incubated during anaerobic phase in a static system;
- 16) Analysed in a sample set as a non-sterile control, incubated during anaerobic phase in a flow-through system.

The test soil was taken from a Miles Research Farm in Howe, Indiana, USA, and placed in two 5-gallon (~19L) buckets in the greenhouse. In order to maintain its microbiological viability soil was planted with soybean prior to the conduct of the study.

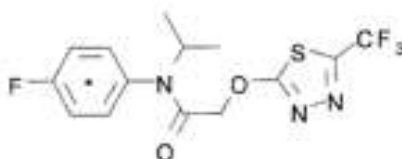
Immediately before the experiment began, 10-kg portion of soil from the top 5-6 inch (corresponding to 12-15 cm) layer was taken to the laboratory, where soybean plants were removed and moist soil sieved through 2-mm sieve. Then the test soil was air-dried for 2 hours to the level of 75% of ½ bar (the soil moisture level kept throughout the experiment) and placed in the test vessels.

Water used in anaerobic phase to waterlog soil was rainwater collected at Bayer Research Farm in Stillwell, KS in June and July 1994. It was collected in five 5-gallon (~19L) buckets, placed on the field located in some distance from research buildings to avoid water contamination with material possibly emitted from them. The collected water was stored frozen until the beginning the anaerobic phase of the study. Just before initialisation of that phase water was thawed, filtered through 250-µm sieve and its aliquots shipped for characterisation. The characteristic of water used in the experiment is presented below in the table B.8.1.1.1.2._CA-2.

Table B.8.1.1.1.2._CA-2: The characteristic of water used in the study.

Parameter	Measured value
<i>pH</i>	7.7
<i>Conductivity [mS/cm]</i>	0.06
<i>Total Suspended Solids [mg/mL]</i>	3
<i>Alkalinity [mg CaCO₃/L]</i>	28
<i>Hardness [mg CaCO₃/L]</i>	28
<i>COD [mg O₂/L]</i>	16

The test substance used in the experiment was the ¹⁴C-FOE 5043 radiolabelled uniformly in phenyl ring, as shown below on figure B.8.1.1.1.2._CA-1.

**Figure B.8.1.1.1.2._CA-1.:** The structural formula of the radiolabelled Flufenacet (FOE 5043) used in the experiment (copied from the study report).

The specific radioactivity of the test compound used in the experiment was 66.5 mCi/mmol (4.064 E5 dpm/μg) and its radiochemical purity, determined with TLC, was 99.2%. It was prepared as a benzene solution having a concentration 0.837 mg Flufenacet/mL.

The test compound was applied to the test soil in incubation vessels in form of the application solution prepared in a following way: 4.6 mL of benzene solution of [phenyl-U-¹⁴C]-Flufenacet in was evaporated to dryness under gentle stream of nitrogen and then redissolved in 7.6 mL of CH₃CN (acetonitrile), to which 30.4 mL of distilled water was added next. The so prepared solution was stirred and its concentration measured. It was determined to contain 103 μg Flufenacet/mL. That application solution, further called **Application solution 1**, was used to treat the kinetic samples.

Additionally, for samples prepared for metabolite profiling (identification), another application solution was prepared, having three times higher concentration of Flufenacet. It was prepared by first evaporating to dryness, under the gentle stream of nitrogen, 2.2 mL of benzene solution of [phenyl-U-¹⁴C]-Flufenacet. The residue was reconstituted in 24 μL of non-radiolabelled Flufenacet ([isopropyl-1,3-¹³C] Flufenacet) in CH₃CN, to which 1.6 mL of CH₃CN was added next, to give a 3:1 mixture of [¹⁴C]-Flufenacet/[¹³C]-Flufenacet. The solution was thoroughly mixed and 6.4 mL of distilled water was added to it. After that the solution was once again mixed and analysed by LSC and LC/MS. The concentration of Flufenacet in so prepared solution was determined to be 303 μg/mL and the solution's specific activity was 304637 dpm/μL. That application solution is further referred to as **Application solution 2**.

The experiment consisted of two phases:

- aerobic incubation phase, which was the first phase of the experiment;
- anaerobic incubation phase, following the aerobic phase.

For both phases 100-g (d. w.) portions of the test soil were weighed into 250-mL Erlenmeyer flask. In total 71 flasks were prepared, of which 35 as kinetic samples, 6 for metabolite isolation (further in the text that number was changed to 8), 25 as non-sterile controls and 5 for microbial evaluation.

For the aerobic phase of the experiment the incubation was performed in biometric flasks, presented below on figure B.8.1.1.1.2._CA-2. For the incubation under anaerobic conditions the setup of the incubation vessels was changed, by replacing the traps for volatile compounds with glass stoppers having inlet and outlet branch, as shown on the figure B.8.1.1.1.2._CA-3. The samples were then incubated in either flow-through incubation system, presented on figure B.8.1.1.1.2._CA-4, or in a static system.

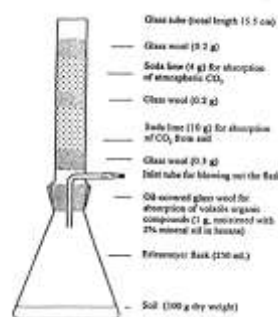


Figure B.8.1.1.2._CA-2: The biometer flask used in the aerobic phase of the experiment (scheme copied from the study report).

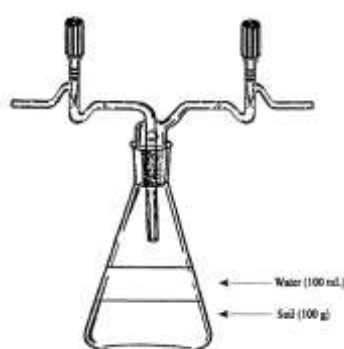


Figure B.8.1.1.2._CA-3: The incubation vessel used in the anaerobic phase of the experiment (scheme copied from the study report).

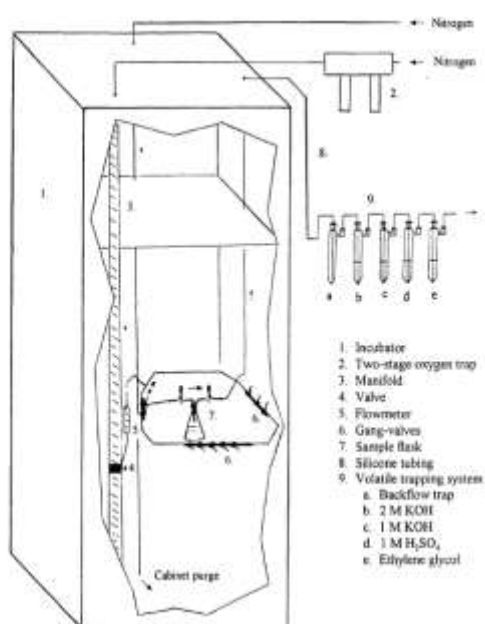


Figure B.8.1.1.2._CA-4: The flow-through incubation system used in the anaerobic phase of the experiment (scheme copied from the study report).

Kinetic samples were treated with the test substance, applied to the soil surface in form of the **Application solution 1**, at rate of 1.03 mg Flufenacet /kg. Applicant declared that it corresponded to approximately field application rate of 0.8 lbs a. i./acre, assuming soil depth of 3 inches and soil bulk density of 1.33 g/cm³. When recalculated by the RMS as expressed in g/ha, assuming soil depth of 5 cm and soil bulk density of 1.5 g/cm³, the exact application rate was **772.5** g Flufenacet/ha. The use of the measured average soil bulk density – $d = 1.37 \text{ g/cm}^3$, resulted in the application rate of **705.55** g Flufenacet/ha.

Samples for metabolite identification were treated with the **Application solution 2** at rate of 3 ppm, corresponding to the application rate, calculated by RMS assuming soil depth of 5 cm and soil bulk density of 1.5 g/cm³, of **2250** g Flufenacet/ha. The use of the measured average soil bulk density – $d = 1.37 \text{ g/cm}^3$, resulted in application rate of **2055** g Flufenacet/ha. These samples were further called **Metabolite ID** samples.

The amount of the **Application solution 1** introduced into each test vessel for kinetic samples and **Application solution 2** introduced into each test vessel for **Metabolite ID** samples, was 1 mL. It was applied dropwise to the soil surface using Hamilton 500 μL syringe. The treated flask was shaken after introducing each 500 μL -portion of the application solution to grant the even distribution of the test compound in soil.

Control and microbial-biomass flasks were treated with 2-mL portions of blank solvent carrier ($\text{CH}_3\text{CN}:\text{H}_2\text{O}$ 1:4 v/v).

After treatment the appropriate amount of distilled water was added to each test vessel to establish a soil moisture of 75% of $\frac{1}{3}$ bar. For that purpose 80 μL of water was added to each flask.

After treatment the Erlenmeyer incubation flask were sealed with traps for volatile compounds, weighed and covered with aluminium foil to exclude light. They were placed in the dark in a controlled environmental chamber and incubated for 30 days under aerobic conditions at constant temperature $T = 21 \pm 1^\circ\text{C}$. The soil moisture during that period was controlled in 7-days intervals and adjusted, if needed to the fixed level of 75% of $\frac{1}{3}$ bar. That phase of the experiment was called **aerobic phase**, during which samples were taken for the analysis at the following time-points DAT 0, DAT 7, DAT 15 and DAT 30 (DAT stands for Days After Treatment). At these time points, with exception of DAT 0 point, duplicate samples were taken for the analysis. The initial processing procedure was identical to that used in the examination of the aerobic degradation of [Phenyl- $\text{U-}^{14}\text{C}$] Flufenacet performed by Pangilinan and Smith [1994] and described under the point B.8.1.1.1.1. of this Report, in the summary of the **Study 2**. DAT 0 samples were analysed in triplicate and the traps for volatile compounds were not set, as for that time point no volatile compounds were expected to be formed.

On DAT 30 the **anaerobic phase** of the experiment begun. All remaining test vessels were dissected in a way identical to that used for aerobic phase samples, volatile traps collected for further analysis of the radioactivity they contained and each flask waterlogged with 100 mL of rain water characterised above in the table B.8.1.1.1.2_CA-2. Water was enriched with glucose (5 mg/mL) to enhance soil microbial growth and facilitate the attainment of anaerobic conditions. The amount of so prepared water added to each flask was such to give ~2-cm water layer above the soil surface. After waterlogging flask were capped with stoppers shown above on figure B.8.1.1.1.1_CA-3, the joints sealed with lubricant and additionally with parafilm. So prepared incubation vessels were purged with N_2 for ~5 minutes to remove the oxygen and induce the anaerobic conditions, after what the stopcocks on inlet and outlet branches were closed tight. Incubation vessels were then wrapped with aluminium foil to exclude light, and returned to incubator. The anaerobic incubation phase lasted for 6 months.

The samples were incubated during that phase in two separate incubation systems:

- **Flow-through system**, presented above on figure B.8.1.1.1.2_CA-4. The samples in the incubator's chamber were placed on four shelves, each containing at least 10 flasks. Anaerobic conditions were maintained by constant passing of the oxygen-free N_2 gas through the headspace of each flask to the trapping solutions for volatile compounds at initial rate 10 mL/min, but from 15th day of anaerobic incubation onwards reduced, to avoid a build-up of gasses in the headspace; the loss of mass, presumably water, resulting from constant purging was monitored by weighing the flask at sampling points and comparing their current weight with the initial;
- **Static system** set, in separate incubation chamber, for eight treated samples and six non-sterile control samples to provide the data for material balance in case the losses in the flow-through system, mainly related to not capturing the formed methane, were observed. The incubation vessels in that system, after being purged with nitrogen to induce anaerobic conditions, were kept sealed and the gasses formed during the incubation were removed by purging and trapped in the special sample bags. The purging took place weekly during first month of anaerobic incubation, then from 2nd to 6th months in 1-month intervals; the scheme of purging device used in a static incubation system is shown below on figure B.8.1.1.1.1_CA-5.

All samples were incubated in the dark at constant, monitored temperature $T = 21 \pm 1^\circ\text{C}$. To maintain anaerobic conditions in both incubation chambers they were continuously flushed with N_2 at rate 500 mL/min for the first 4 months of incubation and afterwards until the end of the 6th month of incubation, at rate 1 mL/min. At designated sampling points – DAFs 15, 30, 67, 123 and 180 (DAF stands for Days After Flooding), triplicate

(DAF 15) or duplicate (remaining time points) samples were taken for the analysis from the flow-through system. In case of the static system duplicate samples were taken for the analysis on DAFs 62, 123 and 180.

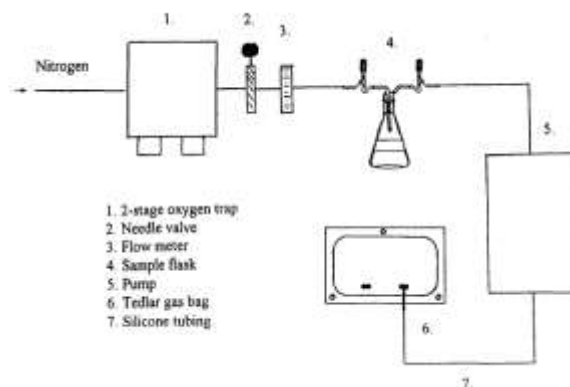


Figure B.8.1.1.2 CA-5: The purging device used to collect the volatile compounds formed in test vessels incubated in a static incubation system (scheme copied from the study report).

The maintenance of anaerobic conditions was monitored by measuring pH, redox potential and dissolved oxygen (DO) content in non-sterile controls, incubated in a flow-through system, on DAF's 0, 7, 15, 30, 67, 123 and 180.

Volatile compounds produced in flasks incubated in the flow-through system were captured in a following sequence of trapping solutions (each having volume of 30 mL): 2M KOH_{aq} (1), 1M KOH_{aq} (2), 1M H₂SO₄ (3), ethylene glycol (4). The traps were filled with fresh portions of trapping solutions after 4 months of incubation and the collected solutions analysed for content of radioactivity by LSC (triplicate aliquots analysis).

In case of static incubation system, volatile compounds collected in Tedlar gas bag were transferred to the set of trapping solutions identical to those used for capturing volatiles in a flow-through system. The trapping solutions were next radioassayed by LSC for their radioactivity content. The volatiles not captured by any of the solutions were passed through a quartz tube containing CuO, placed inside the furnace heated to ~700°C, where they were combusted and the combustion product (¹⁴CO₂) trapped in three 10-mL portions of scintillation cocktail (CarboSorbE/Permafluor-E⁺ 2:5) set in a sequence. The solutions were then radioassayed. The same method was used to remove and collect the volatile compounds directly (not using Tedlar bag) from vessels head-space at sampling points.

After the dissection of incubation vessels the content of the Erlenmeyer flasks – soil for **aerobic phase** and soil and water overlying it for **anaerobic phase**, was analysed qualitatively and quantitatively for the radioactivity it contained.

In case of soil from **aerobic phase** whole 100-g portions of test soil were extracted in three-step sequential extraction procedure, identical to that used by Pangilinan and Smith in the **Study 2**, which examined the transformation of Flufenacet in soil under aerobic conditions.

Samples collected during **anaerobic phase** of the experiment were treated in the following way:

- Water was separated from soil using Buchner funnel and Whatman #42 filter paper, collected and its volume measured, then triplicate aliquots were radioassayed by LSC. Next 10-mL aliquots were filtered through 0.45 µm Nylon acrodics and analysed by HPLC. Finally at least 50-mL portions of water were processed before being analysed by TLC.
- Remaining soil was processed and analysed in a way identical to that used for **aerobic-phase** samples.

The whole procedure of processing water and soil samples prior to their LSC and chromatographic analysis is presented below on figure B.8.1.1.2.-CA-6.

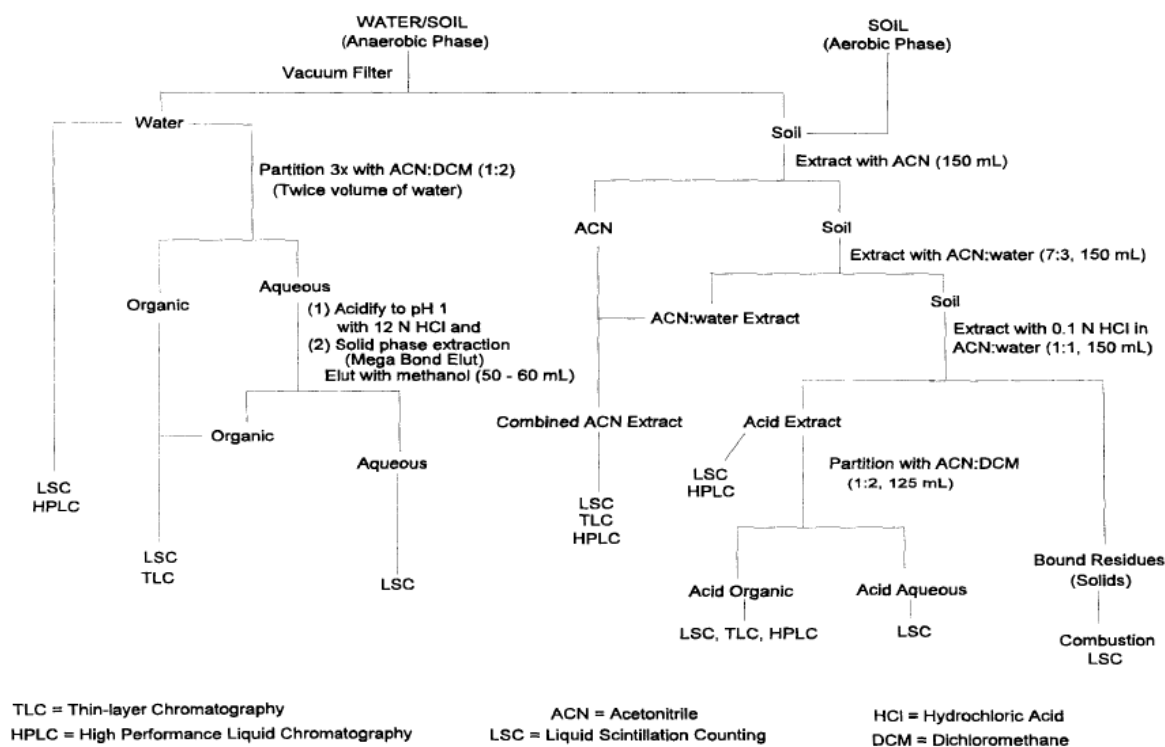


Figure B.8.1.1.2._CA-6: The schematic presentation of sample-processing procedure used in the study (scheme copied from the study report).

The obtained acetonitrile extracts were combined, concentrated under vacuum and analysed by LSC, HPLC and TLC. Acid extracts were halved. One part was radioassayed by LSC and analysed by HPLC. The remaining one was partitioned with three portions of $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$ 1:2. Organic fractions were combined, their aliquots radioassayed by LSC, then concentrated and analysed by HPLC and TLC. Aqueous fractions were radioassayed by LSC.

The extracted soil pellets were analysed for NER fraction. To do that each soil sample was allowed to air-dry overnight, after what its triplicate aliquots (50 – 100 mg) were oxidized by combustion. The formed $^{14}\text{CO}_2$ was trapped in alkaline solution which, after mixing with scintillation cocktail, was analysed by LSC.

All samples were analysed for the content of radioactivity using LSC method. The LSC (Liquid Scintillation Counting) analysis was performed using a Packard Tri-Carb Model 4640 counter equipped with automatic external standardisation.

Liquid samples were radioassayed in triplicate, after addition of 15 mL of Ultima Gold scintillation cocktail. The minimum sensitivity of LSC analysis for those samples was 2.488 E-4 ppm , corresponding to $0.02416 \% \text{AR}$. When expressed as Lowest Acceptable Gross Count Rate (LAGC) it was 64 cpm, while as Lowest Acceptable Net Count Rate (LANC) – 32 cpm, assuming average background (BCGK) of 32 cpm ($\text{LAGC} = 2 \times \text{BCGK}$ and $\text{LANC} = \text{LAGC} - \text{BCGK}$). The greatest probable error $\text{GPE} = 9.24\%$.

Solid samples were oxidised using Packard Model 306 sample oxidizer (50 – 200 mg aliquots were used) and generated $^{14}\text{CO}_2$ trapped on 6 mL Carbo-sorb E and 15 mL Perma Fluor E, to be quantified by LSC. The minimum sensitivity of LSC analysis for those samples was 8.735 E-6 ppm , corresponding to 8.498 E-4 \%AR . When expressed as Lowest Acceptable Gross Count Rate (LAGC) it was 64 cpm, while as Lowest Acceptable Net Count Rate (LANC) – 32 cpm, assuming average background (BCGK) of 32 cpm ($\text{LAGC} = 2 \times \text{BCGK}$ and $\text{LANC} = \text{LAGC} - \text{BCGK}$). The greatest probable error $\text{GPE} = 9.24\%$.

Sample extracts were analysed using the following techniques:

- HPLC – major identification and quantitation method for parent compound and its degradation products;
- TLC – secondary quantitation method for the parent compound and its degradation products;
- LC-MS – identification method for parent compound and its degradation products;
- GC/MS – supplementary identification method for parent compound and its degradation products.

The HPLC analysis was performed using a Hewlett Packard Model 1090 chromatograph equipped with UV detector set at the wavelength $\lambda = 254$ nm, coupled to Ramona 5-LS radioactivity monitor. Three following HPLC methods were used:

- **Method A:** gradient mode analysis performed using PRP-1, 5 μm , 150 x 4.1 mm chromatographic column (Hamilton Co., Reno) and PRP-1 cartridge as a guard column. The mobile phase consisted of water + 0.4% CH_3COOH as **Solvent A** and CH_3CN + 0.4% CH_3COOH as **Solvent B**. Gradient elution lasted 95 minutes. Its parameters are shown in the table B.8.1.1.1.2._CA-2. The flow rate was set to 2 mL/min. The method was used as a main method for identification and quantitation of ^{14}C residues in analysed extracts and was able to detect and radioactive residues >1.0% AR.
- **Method B:** gradient mode analysis performed using PRP-1, 5 μm , 150 x 4.1 mm chromatographic column (Hamilton Co., Reno) and PRP-1 cartridge as a guard column. The mobile phase consisted of water + 0.4% CH_3COOH as **Solvent A** and CH_3CN + 0.4% CH_3COOH as **Solvent B**. Gradient elution lasted 95 minutes. Its parameters are shown in the table B.8.1.1.1.2._CA-2. The flow rate was set to 2 mL/min. The method was used to isolate and purify degradation products formed in the experiment, in **Metabolite ID** samples.
- **Method C:** gradient mode analysis performed using Selectosil 5, C-18, 5 μm , 250 x 4.6 mm chromatographic column (Phenomenex, California) and RP-18 Spheri-5, 5 μm , guard column. The mobile phase consisted of water as **Solvent A** and CH_3OH as **Solvent B**. Gradient elution lasted 60 minutes. Its parameters are shown in the table B.8.1.1.1.2._CA-2. The flow rate was set to 1 mL/min. Method was used for further purification of the degradation products isolated using **Method B**.
- **Method D:** gradient mode analysis performed using Selectosil 5, C-18, 5 μm , 250 x 4.6 mm chromatographic column (Phenomenex, California) and RP-18 Spheri-5, 5 μm , guard column. The mobile phase consisted of water as **Solvent A** and CH_3CN as **Solvent B**. Gradient elution lasted 25 minutes. Its parameters are shown in the table B.8.1.1.1.2._CA-2. The flow rate was set to 1 mL/min. Method was used for further purification of the degradation products isolated using **Method B**.
- **Method E:** gradient mode analysis performed using Selectosil 5, C-18, 5 μm , 250 x 4.6 mm chromatographic column (Phenomenex, California) and RP-18 Spheri-5, 5 μm , guard column. The mobile phase consisted of water as **Solvent A** and CH_3CN as **Solvent B**. Gradient elution lasted 35 minutes. Its parameters are shown in the table B.8.1.1.1.2._CA-2. The flow rate was set to 1 mL/min. Method was used for further purification of the degradation products isolated using **Method B**.

The LOD for the listed above chromatographic methods, in reference to the performance of the used radioactivity detector, was determined to be 1000 dpm, what corresponded to 1.0% AR. The value was determined experimentally on the basis of the comparison of radioactivity injected and eluted (expressed in dpm, as determined by LSC). The results of that examination, aimed on the determination of both LOD and the linearity of HPLC analysis, are presented in the table B.8.1.1.1.2._CA-3. The linearity of the analysis, expressed as r^2 , was: $r^2 = 0.999983$.

The identification of the chromatographic peaks was performed by means of the comparison of their retention times R_t with those of the standards. The retention times of each of the examined compounds for the HPLC **Method A** and **Method B** are presented in the table B.8.1.1.1.2._CA-4.

Table B.8.1.1.1.2._CA-2: The HPLC gradient modes used in the study.

Method A:		
Time [min]	Solvent ratio	
	<i>Solvent A – Water + 0.4% CH₃COOH</i>	<i>Solvent B – Acetonitrile + 0.4% CH₃COOH</i>
0	100	0
0-25	Linear gradient	
25	75	25
25 - 40	75	25
40 - 75	Linear gradient	
75	30	70
75 - 85	Linear gradient	
85	0	100
85 - 95	0	100
Method B:		
Time [min]	Solvent ratio	
	<i>Solvent A – Water + 0.4% CH₃COOH</i>	<i>Solvent B – Acetonitrile + 0.4% CH₃COOH</i>
0	100	0
0-20	Linear gradient	
20	75	25
20 - 25	75	25
25 - 75	Linear gradient	
75	30	70
75 - 85	Linear gradient	
85	0	100
85 - 95	0	100
Method C:		
Time [min]	Solvent ratio	
	<i>Solvent A – Water</i>	<i>Solvent B – MeOH</i>
0	85	15
0 – 5	85	15
5 – 25	Linear gradient	
25	75	25
25 – 30	75	25
30 - 60	Linear gradient	
60	0	100
Method D:		
Time [min]	Solvent ratio	
	<i>Solvent A – Water</i>	<i>Solvent B – Acetonitrile</i>
0	65	35
0 – 10	Linear gradient	
10	60	40
10 – 15	60	40
15 – 25	Linear gradient	
25	55	45
Method E:		
Time [min]	Solvent ratio	
	<i>Solvent A – Water</i>	<i>Solvent B – Acetonitrile</i>
0	65	35
0 – 10	Linear gradient	
10	60	40
10 – 15	60	40
15 – 30	Linear gradient	
30	0	100
30 – 35	0	100

Table B.8.1.1.1.2._CA-3: The results of the determination of linearity and LOD of the HPLC analysis.

Sample No.	Radioactivity in [dpm]:		Integration ^{3, 4)}
	Injected ¹⁾	Eluted ²⁾	
1	1080734	1037270	86167
2	212100	203520	17118
3	106050	101760	8415
4	35350	33920	2592
5	7734	7422	628
6	2062	1979	184
7 ⁵⁾	1031	990	102

Footnotes to the table (for 1,2,3, as given in the study report):

- 1) Values determined by LSC analysis of the aliquots of the [¹⁴C]-Flufenacet standard solution injected, radioassayed prior to HPLC analysis;
- 2) Values determined by LSC analysis of the aliquots of HPLC eluates;
- 3) Regions of interest were integrated with background correction, determined at the beginning and the end of analysis;
- 4) Linearity of the analysis, expressed as r² value, was determined to be r² = **0.999983**;
- 5) The value corresponding to LOD (by averaging the amount of injected and eluted it was set to LOD = 1000 dpm)

Table B.8.1.1.1.2._CA-4: Chromatographic – HPLC, identification of Flufenacet and its degradation products in the study.

Compound	HPLC identification – retention time (R _t) [min] determined for:	
	HPLC Method A	HPLC Method B
<i>Flufenacet (FOE 5043)</i>	78	76
<i>FOE Oxalate</i>	24	29
<i>FOE Alcohol</i>	52.5	51.5
<i>FOE Sulfonic acid</i>	26.5	33
<i>FOE Methylsulfide</i>	71	68
<i>FOE Methylsulfoxide</i>	35.5	n. a. ¹⁾
<i>FOE Methylsulfone</i>	57	55.5
<i>FOE Amine acetate</i>	60	56.5
<i>FOE Thioglycolate sulfoxide</i>	32	39.5
<i>FOE Amine</i>	27	n. a. ¹⁾
<i>FOE Thiol acetate</i>	70	n. a. ¹⁾
<i>Hydroxy FOE Alcohol</i>	29.5	n. a. ¹⁾
<i>FOE Cysteine conjugate</i>	30	n. a. ¹⁾
<i>FOE N-Acetyl conjugate</i>	48	n. a. ¹⁾
<i>des-Fluoro FOE Alcohol</i>	50	n. a. ¹⁾
<i>4-FluoroAcetanilide</i>	36	n. a. ¹⁾
<i>FOE 5043 N-isomer</i>	80	n. a. ¹⁾
<i>des-Isopropyl FOE Oxalate</i>	23.5	25.5
<i>FOE Thioglycolate</i>	56	56

Footnotes to the table:

- 1) n. a. = not analysed using that method;

The TLC analysis of the extracts was performed in two modes:

- as RP-TLC (reversed phase TLC);
- as NP-TLC (normal phase TLC).

The RP-TLC analysis was carried out using Whatman KC₁₈F TLC plates, having a dimensions 20x20 cm and 200-μm thick, with a fluorescent indicator. The solvent system used in the analysis was CH₃CN:CH₃OH:0.5N NaCl_{aq} 2:2:1 (v/v) solution.

The NP-TLC analysis was carried out using silica gel TLC plates, having a dimensions 20x20 cm and 250-μm thick, with a fluorescent indicator. The solvent system used in the analysis was CHCl₃:CH₃COOC₂H₅:CH₃COOH 75:25:1 (v/v) solution.

The LOD was set to 1.0% AR for each individual compound detected. The quantitative analysis was performed using RITA 68000 Radio-TLC analyser. The LOD for this detector was determined to be 150 dpm. The complete results of the determination of linearity and LOD of the detector are presented in the table B.8.1.1.1.2._CA-5.

The identification was performed by means of the comparison of R_f values of the detected fractions with those of the known standards. These values are provided below in the table B.8.1.1.1.2._CA-6.

Table B.8.1.1.1.2._CA-5: The results of the determination of linearity and LOD of the TLC analysis.

Sample No.	LSC Counts Total dpm/band	Scanner Counts	
		dpm/ 600 sec	dpm/ 1200 sec
1	145	23	32
2	329	43	58
3	512	57	131
4	1033	103	224
5	1919	158	366
6	5594	549	1099
7	8788	962	1871
Background	----	9	15
Correlation coefficient	----	0.994	0.997

Table B.8.1.1.1.2._CA-6: Chromatographic – TLC, identification of Flufenacet and its degradation products in the study.

Compound	TLC identification – R _f value determined for:	
	RP-TLC	NP-TLC
Flufenacet (FOE 5043)	0.48	0.50
FOE Oxalate	0.85	0.00
FOE Alcohol	0.68	0.17
FOE Sulfonic acid	0.85	0.00
FOE Methylsulfide	0.55	0.47
FOE Methylsulfoxide	0.76	0.03
FOE Methylsulfone	0.72	0.22
FOE Amine acetate	0.61	0.28
FOE Thioglycolate sulfoxide	0.88	0.00
FOE Amine	0.52	0.50
FOE Thiol acetate	0.56	0.47
Hydroxy FOE Alcohol	0.82	0.10
FOE Cysteine conjugate	0.74	0.00
FOE N-Acetyl conjugate	0.83	0.00
des-Fluoro FOE Alcohol	0.71	0.29
4-FluoroAcetanilide	0.76	0.16
Hydroxy Isopropyl FOE Sulfone	0.83	0.03
Hydroxy Isopropyl FOE Sulfoxide	0.84	0.01
FOE 5043 N-isomer	0.41	0.66

The LC-MS analysis was performed using Varian 5040 HPLC equipped with a Regis Spherisorb S5 ODS column working in a gradient mode and Berthold LB 505-HPLC Radioactivity Monitor, coupled with Finnigan MAT 90 MS detector. The parameters of gradient were following:

- **Mobile phase A:** Water,
- **Mobile phase B:** CH₃OH,
- **Gradient mode:** linear from 0% B at 0 min to 100% B at 30 min.

The flow rate in the system was set to 0.8 mL/min.

The reported parameters of MS detector were following:

- Spectrometer operated in either positive or negative mode,
- aerosol temperature: 210⁰C,
- 0.2 M ammonium acetate added post column at rate of 0.2 mL/min.

The identification of Flufenacet and its degradation products in LC/MS analysis was performed by comparison of mass spectra of each chromatographic peaks with those obtained for the standards, for which base peaks and protonated molecular ion peaks were identified. These are presented in the table B.8.1.1.1.2._CA-7.

Table B.8.1.1.2._CA-7: LC/MS identification of Flufenacet and its degradation products in the study.

Compound	Representative signals used in identification	
	Position – m/z	Description
Flufenacet	364	Protonated molecular ion [M+H] ⁺
	381	Ammonia adduct [M + NH ₄] ⁺
FOE Sulfonic acid	274	Peak for [M – H] ⁻ (negative-ion mode)
FOE Oxalate	226	Protonated molecular ion [M+H] ⁺
	243	Ammonia adduct [M + NH ₄] ⁺
FOE Methylsulfoxide	258	Protonated molecular ion [M+H] ⁺
	275	Ammonia adduct [M + NH ₄] ⁺
FOE Alcohol	212	Protonated molecular ion [M+H] ⁺
FOE Thioglycolate sulfoxide	316	Protonated molecular ion [M+H] ⁺ for methylated derivative

GC/MS analysis was performed to conform the identity of Flufenacet and its degradation products. It was carried out with HP Model 5890A Gas Chromatograph/Finnigan Incos 50 Mass Spectrometer. GC was equipped with DB5-MS column (152 m * 0.25 mm x 0.25 µm film thickness).

The oven programme used was following:

- GC oven was programmed to start at T = 80⁰C and it was held at that level for t = 1 min. Then the temperature increased linearly at rate of 20⁰C/min up to T = 250⁰C and held at that level for t = 1 min. The injector's temperature was T = 250⁰C. MS detector operated in the electron impact mode with a mass range 50 – 400 amu.

To facilitate MS identification the degradation products were methylated. That was accomplished by direct addition of 0.3 M (0.5 mL) of diazomethane or 2.0 M (0.05 mL) of (trimethylsilyl)diazomethane to at least 0.1mL of MeOH solution of HPLC-purified degradation products. The solution was left for ~1 hour at room temperature to allow the reaction to complete. Before being analysed by LC/MS methylated degradation products were purified using HPLC Method E.

Results and their discussion:

The results of the determination of soil microbial biomass has been presented in the table B.8.1.1.2._CA-1. It can be stated that it was within the recommended limits throughout the study and no significant decrease was observed during either aerobic or anaerobic incubation period.

The results of the monitoring of anaerobic conditions in the test vessels during anaerobic incubation phase are presented in the table B.8.1.1.2._CA-8. All reported values are those measured in soil layer. The presented values clearly indicate that the anaerobic conditions were maintained during whole that phase.

Table B.8.1.1.1.2_CA-8: The results of monitoring of anaerobic conditions in incubation vessels during anaerobic incubation phase.

Time point (DAF) ¹⁾	Incubation system ²⁾	Replicate	Measured value for:				
			pH	Redox potential [mV]		Dissolved oxygen (DO) [ppm]	
				Method A ³⁾	Method B ⁴⁾	Method A ⁵⁾	Method B ⁶⁾
0	Flow-through	1	6.0	+321	+351	5.1	6.0
		2	5.9	+334	+346	4.4	4.9
7	Flow-through	1	5.1	-263	-230	0.3	0.2
		2	5.4	-317	-355	0.3	0.2
15	Flow-through	1	5.6	-205	-212	0.3	0.2
		2	5.4	-272	-312	0.2	0.2
30	Flow-through	1	6.5	-365	-368	0.2	0.0
		2	6.4	-401	-410	0.2	0.0
67	Flow-through	1	6.9	-412	-425	0.2	0.2
		2	6.8	-427	-439	0.2	0.2
	Static	1	6.3	-406	-413	0.2	0.3
		2	6.1	-405	-413	0.2	0.2
123	Flow-through	1	7.0	-314	-325	0.5	0.5
		2	7.1	-300	-313	0.5	0.6
	Static	1	6.5	-306	-312	0.4	0.6
		2	6.5	-302	-305	0.4	0.6
180	Flow-through	1	7.3	-365	-345	0.6	0.3
		2	7.3	-377	-386	0.6	0.4
	Static	1	6.7	-216	-230	0.7	0.5
		2	6.8	-366	-312	0.7	0.3

Footnotes to the table:

- 1) DAF – Days After Flooding;
- 2) The measurements performed either solely in Flow-through system (DAFs 0 – 30) or in both Flow-through and Static systems; both systems described in detail on p.96 of the report;
- 3) Measured using Cole-Parmer combination electrode;
- 4) Measured using Corning redox combination electrode;
- 5) Measured using YSI Model 58 DO-Meter;
- 6) Measured using Orion Model 820 DO-Meter ;

The examination of the stability of test compound demonstrated that Flufenacet was stable throughout application, extraction and chromatographic analysis.

The recovery of applied radioactivity at application (DAT 0) was 97% AR and throughout the aerobic incubation phase (DAT 0 – DAT 30) it was in range of 96 – 105% AR. For anaerobic incubation phase the average recovery of radioactivity was 93% AR, with range of 91 – 94% AR. As in samples incubated in Flow-through system around DAF 60 the recover decreased to 88.9% AR, what suggested losses due to probable leakage in the system, both samples from Flow-through system and Static system were analysed for the incubation period between DAF 60 – 180 (last three sampling points). The comparative analysis of the results showed that recoveries of radioactivity in samples from both systems were comparable (same reduction level). Therefore the theory about the possible loss of volatile compounds due to the leakage was discounted.

The level of mineralisation and of formation of other volatile compounds was low during both aerobic and anaerobic phases. The formation of NER fraction was low during aerobic incubation phase, reaching the level of 8.4% AR on DAT 30 (end of incubation period). It increased significantly during anaerobic incubation period to reach the level of 32.6% AR at the end of that incubation phase – DAF 180 (the termination of the whole study).

During the aerobic incubation phase the radioactivity in the system remained mainly in extractable form – as Flufenacet and its degradation products. The concentration of Flufenacet declined steadily to reach the level of 69.0% AR on DAT 30 (end of aerobic incubation phase). The following degradates were identified in soil during aerobic incubation period:

- FOE Oxalate – max. 11.2% AR on DAT 30,
- FOE Sulfonic acid – max 6.6% AR on DAT 30,
- FOE Thioglycolate sulfoxide – max 2.7% AR on DAT 15,
- FOE Alcohol – max 0.4% AR on DAT 0.

Additionally a small fraction of other metabolites, comprising up to 12 compounds, was detected, not surpassing the level of 0.2% AR at any sampling point.

During anaerobic incubation phase the amount of extractable radioactivity (sum of that recovered in water phase and extracted from soil) decreased from 89.7% AR at the beginning of that phase to 56.8% AR at its end. It shall be noted that the distribution of radioactivity between water and soil was at relatively constant ratio: 3:4 – 3:5, throughout the whole incubation period.

Concentration of Flufenacet steadily decreased during anaerobic phase from the level of 69.0% AR at its beginning to 39.0% AR at the end. One new degradation product was identified – FOE Thioglycolate. In case of other degradates, already identified during aerobic incubation phase the metabolite profiles looked as follows:

- The amounts of FOE Oxalate initially increased up to 30th day of anaerobic incubation, to steadily decrease afterwards;
- Also increase in concentration was observed for FOE Alcohol, although in that case the formation-decline pattern was not very clear;
- The remaining two degradation products – FOE Sulfonic acid and FOE Thioglycolate sulfoxide were on the decline phase.

The detailed results of the experiment are presented in the table B.8.1.1.1.2._CA-9. RMS decided to present the results for aerobic and anaerobic phases together in one table, differentiating them by delicately shading grey the cells containing the results obtained for aerobic phase. The concentrations of identified compounds are those obtained using HPLC. The quantitative results of TLC are not presented as they did not differ significantly from HPLC results. Additionally the results are presented in graphical form on figure B.8.1.1.1.2_CA-7. The graphs present: the distribution of radioactivity in the test system (top left-hand), the concentrations of the identified compounds in function of time recorded in aerobic phase (top, right-hand) and the concentrations of the identified compounds in function of time recorded in anaerobic phase (bottom graph).

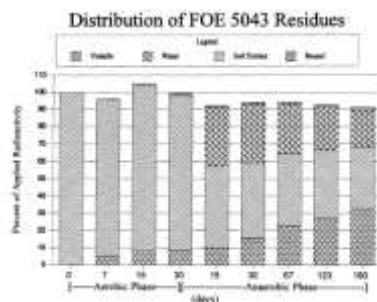
Table B.8.1.1.1.2._CA-9: The detailed results of the experiment.

AR			Results [%AR] obtained for:								
			Aerobic incubation phase				Anaerobic incubation phase ¹⁾				
			DAT 0	DAT 7	DAT 15	DAT 30 ²⁾	DAT 45	DAT 60	DAT 97	DAT 153	DAT 210
						DAF 0	DAF 15	DAF 30	DAF 67	DAF 123	DAF 180
Extracted	Total extracted		99.9	90.6	91.6	89.7	80.7	77.0	70.0	64.0	56.8
	Water phase		n. a. ⁸⁾	n. a. ⁸⁾	n. a. ⁸⁾	n. a. ⁸⁾	33.6	33.4	28.5	24.8	21.1
	Soil phase	Combined ACN extracts ³⁾	99.0	83.9	87.9	81.2	38.2	31.0	29.8	25.7	22.0
		Acid organic extract	0.9	6.2	6.8	6.7	8.1	n. r. ¹¹⁾	n. r. ¹¹⁾	n. r. ¹¹⁾	n. r. ¹¹⁾
		Acid aqueous extract	<0.1	0.5	1.4	1.8	0.8	n. r. ¹¹⁾	n. r. ¹¹⁾	n. r. ¹¹⁾	n. r. ¹¹⁾
		total Acid extract	0.9	6.7	8.2	8.5	8.9	12.6	11.7	13.5	13.7
		Total soil extract	99.9	90.6	91.6	89.7	41.7	43.6	41.5	39.2	35.7
In extract identified as	Flufenacet		99.4	82.2	78.7	69.0	60.3	55.6	52.0	44.2	39.0
	FOE Oxalate		n. f. ¹⁰⁾	4.9	9.8	11.2	12.2	14.5	10.9	11.4	9.9
	FOE Sulfonic acid		n. f. ¹⁰⁾	2.1	4.7	6.6	6.1	5.3	4.7	5.0	4.5
	FOE Alcohol		0.4	0.3	n. f. ¹⁰⁾	n. f. ¹⁰⁾	0.3	n. f. ¹⁰⁾	0.6	1.4	0.9
	FOE TGS ⁴⁾		n. f. ¹⁰⁾	0.9	2.7	2.6	0.5	n. f. ¹⁰⁾	n. f. ¹⁰⁾	n. f. ¹⁰⁾	n. f. ¹⁰⁾
	FOE Thioglycolate		n. a. ⁸⁾	n. a. ⁸⁾	n. a. ⁸⁾	n. a. ⁸⁾	1.1	1.7	1.5	1.3	1.4
	Others		0.0	0.2	0.1	0.2	0.2	0.0	0.2	0.7	1.1
Total identified			99.8	90.6	96.0	89.6	89.6	77.1	69.9	64.0	56.8
Bound residues (NER fraction)			0.1	5.0	8.0	8.4	10.2	15.8	22.9	27.2	32.6
Volatile compounds	Aerobic phase	CO ₂ ⁵⁾	n. d. ⁹⁾	0.3	0.9	1.4	1.3	1.3	1.4	1.4	1.3
		VOC	n. d. ⁹⁾	n. f. ¹⁰⁾	n. f. ¹⁰⁾	n. f. ¹⁰⁾	n. r. ¹¹⁾	n. r. ¹¹⁾	n. r. ¹¹⁾	n. r. ¹¹⁾	n. r. ¹¹⁾
	Anaerobic phase	CO ₂ ⁶⁾	n. a. ⁸⁾	n. a. ⁸⁾	n. a. ⁸⁾	n. a. ⁸⁾	<0.1	<0.1	<0.1	<0.1	0.5
		VOC	n. a. ⁸⁾	n. a. ⁸⁾	n. a. ⁸⁾	n. a. ⁸⁾	n. d. ⁹⁾	n. d. ⁹⁾	n. d. ⁹⁾	<0.1	<0.1
	Total volatiles ⁷⁾		n. d. ⁹⁾	0.3	0.9	1.4	1.3	1.3	1.4	1.5	1.8
Total recovered			100	95.9	105.0	99.5	92.2	94.1	94.3	92.7	91.3

Footnotes to the table:

- 1) For anaerobic phase the data points are presented as both Days After Treatment (DAT) – continuous numbering of data points, and Days After Flooding (DAF) to present the duration of anaerobic phase;
- 2) The time point DAT 30/DAF0 is the last time point for aerobic phase and first point for anaerobic phase. The data were presented for aerobic system as it was assumed that no significant changes would occur in the system immediately after setting of anaerobic conditions;
- 3) Represents CH₃CN and CH₃CN/H₂O 7:3 extracts;
- 4) FOE TGS = FOE Thioglycolate sulfoxide;
- 5) Amounts found in soda lime traps, for anaerobic phase samples in traps set for 30-days aerobic preincubation;
- 6) Amounts found in KOH traps;
- 7) Sum of all volatiles
- 8) Not applicable - fraction not present in aerobic incubation samples;
- 9) Not determined – it was assumed that at the time point no volatiles would form;
- 10) n. f. = not found (not determined);
- 11) n. r. = not reported;

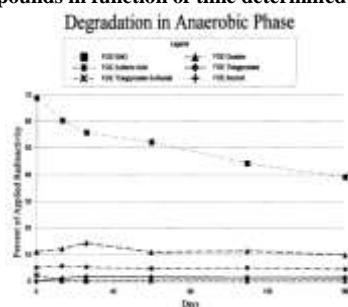
Distribution of the radioactivity in the test system



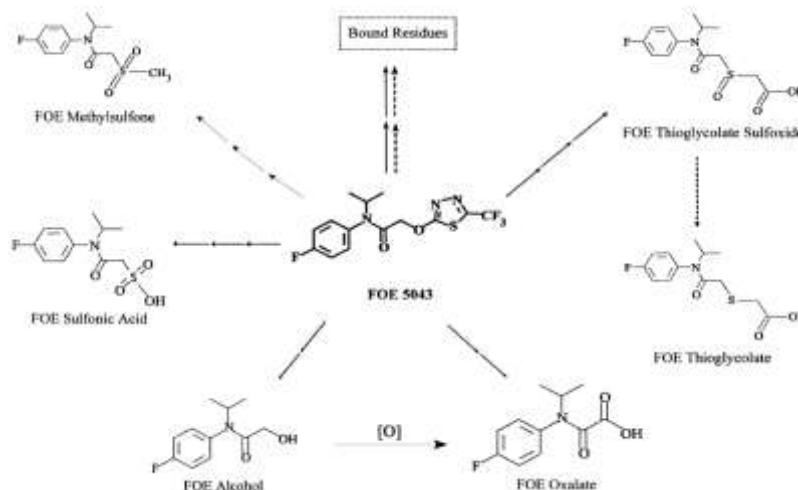
Concentrations of identified compounds in function of time determined during aerobic incubation phase



Concentrations of identified compounds in function of time determined during anaerobic incubation phase

**Figure B.8.1.1.2.CA-7:** The graphical results of the experiment (schemes copied from the study report).

On the basis of the results obtained in this experiment the following transformation scheme for [Phenyl- ^{14}C] Flufenacet was proposed by the Applicant – Figure B.8.1.1.2._CA-8. The scheme comprises processes that occur during both aerobic phase (solid lines) and anaerobic phase (dashed lines).

**Figure B.8.1.1.2._CA-8:** The proposed transformation scheme of Phenyl- ^{14}C] Flufenacet in aerobic/anaerobic soil. Solid lines represent processes occurring in aerobic soil, dashed lines those observed in anaerobic soil (scheme copied from the study report).

The kinetic analysis of the results of this study will be presented under the relevant point, further down this report – please refer to the point B.8.1.1.2.1.2.

Study 2:

Report: Heinemann O., (2012): “[Thiadiazole-5-¹⁴C] FOE 5043: Anaerobic Degradation/Metabolism in Two European Soils.”; Bayer CropScience AG, Development Environmental Safety-Testing, Alfred-Nobel-Str. 50, D-40789 Monheim am Rhein, Germany; Study M1262057-3; unpublished Study Report No. MEF-11/908; 2012. 08. 16; amended by: Amendment No. 1 on 2013. 02. 28 and Amendment No. 2 on 2013. 11. 27; study reference number: M-437443-03-1;

Guidelines: The study was performed to comply with the following Guidelines:

- OECD Guideline for the Testing of Chemicals, No. 307, Aerobic and Anaerobic Transformation in Soil, 2002;
- US. EPA OCSPP Fate, Transport and Transformation Test Guidelines, OPPTS 835.4100 and OPPTS 835.4200, Aerobic and Anaerobic Soil Metabolism, 2008.

GLP: Yes.

RMS comments: This is a new study submitted specifically for purpose of this assessment. It was verified by the RMS and found acceptable. No deviations from the declared Guidelines were stated. The study is summarised below.

Summary:

The aim of the study was to examine the transformation of [Thiadiazole-5-¹⁴C] Flufenacet in soil under anaerobic conditions, in order to establish a transformation pathway of so radiolabelled compound under these conditions, including the identification and quantitation of the degradation products, and to determine the kinetics of the degradation of Flufenacet in anaerobic soil.

The experiment was performed on two soils, used also to examine the transformation of [Thiadiazole-5-¹⁴C] Flufenacet in aerobic soil. Their characteristic is provided, in two tables – table B.8.1.1.2._CA-10 for physicochemical properties, and table B.8.1.1.2._CA-11 for soil microbial activity. It shall be noted that microbiological activity of the test soils was determined independently for aerobic and anaerobic phases of the experiment, using two different methods – SIR method for aerobic phase and Plate Account Assay method for anaerobic phase.

Table B.8.1.1.2._CA-10: The characteristic of soils used in the study.

Parameter		Soil	
		<i>Hoefchen am Hohenseh 4a</i>	<i>Dollendorf II</i>
Soil origin		Burscheid/ North Rhine-Westphalia/ Germany	Blankenheim/North Rhine-Westphalia/ Germany
Soil type (USDA)		Silt loam	Loam
Particle size distribution	Sand (50 µm – 2 mm) [%]	22	48
	Silt (2 – 50 µm) [%]	62	28
	Clay (< 2 µm) [%]	16	42
pH value in 0.01M CaCl ₂ (soil/solution ratio 1:2)		6.1	7.0
pH value in H ₂ O (soil/solution ratio 1:1)		6.3	7.1
pH value in 1N KCl		5.8	6.7
Organic carbon content (OC) [%]		2.0	4.6
Organic matter content (OM) [%] ¹⁾		3.4	7.9
Cation Exchange Capacity – CEC [mEq/100g]		11.1	19.5
Water holding capacity	Maximum [g H ₂ O/100 g soil]	54.8	79.1
	at 0.33 bar (½ bar WHC - pF2.5)	20.9	35.1
	[g H ₂ O/100 g soil]		
Bulk density (disturbed) [g/cm ³]		1.09	1.03

Footnotes to the table:

1) Value calculated by the RMS using the following equation: OM = 1.724 * OC.

Table B.8.1.1.1.2._CA-11: The results of the determination of soil microbial activity.

Parameter						Results obtained for soil:	
						Hoefchen am Hohenseh 4a	Dollendorf II
Aerobic phase	Soil biomass [mg microbial C/kg soil] in samples collected on DAT ¹⁾ :	0	Not treated sample			1089	3789
			Sample treated with blank application solution ⁵⁾			1075	3788
		15	Not treated sample			972	3612
			Sample treated with blank application solution ⁵⁾			998	3519
	Soil biomass expressed as %OC ²⁾ in samples collected on DAT:	0	Not treated sample			5.46	8.24
			Sample treated with blank application solution ⁵⁾			5.38	8.23
		15	Not treated sample			4.86	7.85
			Sample treated with blank application solution ⁵⁾			4.99	7.65
Anaerobic phase	Soil biomass [CFU/plate] ³⁾ in samples collected on DAT/DASF ⁴⁾	135/ 120	Not treated sample	Dilution	10 ⁻²	n. c. ⁶⁾	n. c. ⁶⁾
					10 ⁻³	67	62.67
					10 ⁻⁴	7.33	12.67
					10 ⁻⁵	1.67	0.33
			Sample treated with blank application solution ⁵⁾	Dilution	10 ⁻²	n. c. ⁶⁾	n. c. ⁶⁾
					10 ⁻³	36.67	59.33
					10 ⁻⁴	13	13.33
					10 ⁻⁵	0.67	1.33
	Soil biomass [CFU/g soil] ³⁾ in samples collected on DAT/DASF ⁴⁾	135/ 120	Not treated sample	Dilution	10 ⁻²	----	----
					10 ⁻³	6.70 E4	6.27 E3
					10 ⁻⁴	7.33 E4	1.27 E4
					10 ⁻⁵	1.67 E5	3.30 E3
			Sample treated with blank application solution ⁵⁾	Dilution	10 ⁻²	----	----
					10 ⁻³	3.67 E4	5.93 E3
					10 ⁻⁴	1.30 E5	1.33 E4
					10 ⁻⁵	6.70 E4	1.33 E4

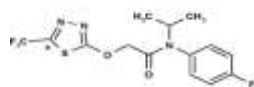
Footnotes to the table:

- 1) DAT = Days After Treatment;
- 2) Calculated by RMS using the declared OC content given in the table B.8.1.1.1.2._CA-10 above;
- 3) CFU = Colony Forming Units
- 4) DAT – Days After Treatment – descriptor for the whole experiment duration; DASF – Days After Soil Flooding – descriptor for the duration of anaerobic phase;
- 5) MeOH/water 1:1 solution applied in amount 369 µL/sample;
- 6) Not countable.

The test soils, representative for the agriculturally used area of the region of sampling, were taken from the fields of the history of cropping system and Plant Protection Products use known for the 5 years before sampling. It was determined that during that period the plant cover of that designated field was grassland on which no pesticides were used 5 years prior to soil sampling. Soil used in the experiment was taken with shovel from the top 20-cm layer, placed in plastic container (bag or bucket) and transferred to the experimental facility, where it was sieved through 2-mm sieve.

Water used in the experiment to flood the test soil at the beginning of anaerobic phase was ultrapure deionised water, generated by TKA Gen Pure UV/TOC water purification system. It was deoxygenated using N₂ for 4 days before use.

The test compound used in the experiment was the ¹⁴C-FOE 5043 radiolabelled in C5-Thiadiazole position, as shown below on figure B.8.1.1.1.2._CA-9.

**Figure B.8.1.1.1.2._CA-9:** The structural formula of the radiolabelled Flufenacet (FOE 5043) used in the experiment; the asterisk (*) indicates radiolabelling position (copied from the study report).

The specific radioactivity of the test compound used in the experiment was 1.54 MBq/mg. Its radiochemical purity, determined using both HPLC and TLC, was > 98%. The chemical purity of the test compound, determined using HPLC equipped with UV detector, was > 99%.

The test compound was used to prepare the **Stock solution** by dissolving the total delivered amount in methanol, to obtain the solution having a concentration of 2.09 mg Flufenacet/mL.

The **Stock solution** was used to prepare the **Application solution**, by diluting its aliquot in an adequate amount of CH₃OH/H₂O 1:1 (v/v) solvent, to obtain a solution having a concentration of 0.434 mg Flufenacet/mL and specific activity of 669 kBq/mL. The **Application solution** was prepared just before the treatment of the test soil in incubation vessels.

The study was performed in a static incubation test system, consisting of 300-mL Erlenmeyer flasks, to which test soil was introduced, and the traps for volatile compounds. In case of **aerobic incubation phase** the traps for volatile compounds were in form of glass columns filled with adequate sorbents. They were open on the top to grant the access of oxygen to incubation vessels. The aerobic-phase incubation vessels – biometer flask, is shown below, on figure B.8.1.1.1.2._CA-10.

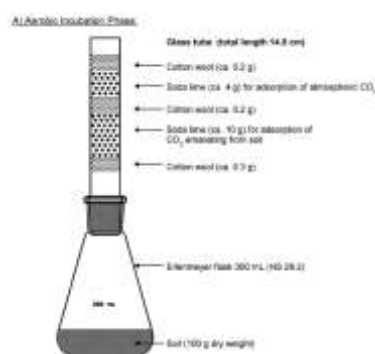


Figure B.8.1.1.1.2._CA-10: The biometer flask used in the aerobic phase of the experiment (scheme copied from the study report).

For purpose of **anaerobic incubation phase** the glass-column traps for volatiles were replaced with two-valve glass stoppers, introduced after flooding of the test soil in Erlenmeyer flasks, to which the plastic bags collecting volatiles were attached. The example incubation vessel used in that phase is presented below on figure B.8.1.1.1.2._CA-11.

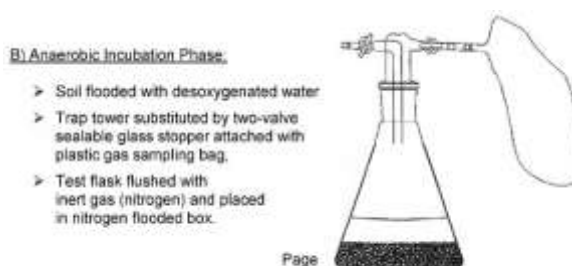


Figure B.8.1.1.1.2._CA-11: The incubation vessel used in the anaerobic phase of the experiment (scheme copied from the study report).

The incubation samples were prepared by weighing ~120 g of sieved soil (corresponding to 100 g d. w.) into each Erlenmeyer flask. Next the soil moisture in each flask was adjusted to ~55% MWHC by addition of the appropriate amount of deionised water. In case of Hoefchen am Hohenseh 4a soil it was 11.4 mL water/flask and for **Dollendorf II soil** – 21.6 mL water/flask.

Soil in the incubation vessels was treated in with characterised above **Application solution**, applied in amount 369 µL/flask, evenly to the soil surface, using Eppendorf pipette. That amount was assumed to correspond to the nominal application dose of 160 µg Flufenacet /100 g soil (d. w.). The exact application dose, measured during application by LSC and conformed by HPLC-radiodetection method, was 151.2 µg Flufenacet/100 g soil (d. w.) – 232 kBq/flask when expressed in radioactivity units. It was further called **actual application dose**. The

Applicant declared that the nominal application dose - 160 µg Flufenacet /100 g soil (d. w.), corresponded to the nominal application rate of 600 g Flufenacet/ha, assuming soil density of 1.5 g/cm³ and depth of the topsoil layer of 2.5 cm.

RMS repeated the calculations of the application rate using the **actual application dose**, to obtain the **actual application rate – A**. In calculations the depth of the soil layer was assumed to be 5 cm. Initially the soil density of 1.5 g/cm³ was used. As a next, refinement step the measured soil density values were used for each test soil to obtain the **actual application rates related to soil properties – A'**.

The resulting **actual application rate – A** = 1134 g/ha. When recalculated using the exact soil bulk densities of the test soils – 1.09 g/cm³ for Hoefchen am Hohenseh 4a soil and 1.03 g/cm³ for Dollendorf II soil, the application rates were as follows:

- for Hoefchen am Hohenseh 4a soil **A' = 824.04 g/ha**;
- for Dollendorf II soil **A' = 778.68 g/ha**.

The amount of so prepared incubation vessels was such, to grant duplicate samples per each sampling point. The sampling points were set to DAT (Days After Treatment) 0 and 15 for **aerobic incubation phase**, and DAT 15, 17, 21, 29 35, 48, 77, 107 and 135, corresponding to DASF (Days After Soil Flooding) 0, 2, 6, 14, 20, 33, 62, 90 and 120, for **anaerobic incubation phase**. The whole incubation period lasted for 135 days, of which 120 days covered incubation under anaerobic conditions.

After treatment all incubation vessels were closed with the tower traps for volatile compounds and placed in the dark, in the temperature-controlled incubation chamber, set to maintain the experimental conditions $T = 20 \pm 2^{\circ}\text{C}$ and $55 \pm 5\%$ MWHC. During that initial aerobic incubation period samples were taken for the analysis twice – on DAT 0 (beginning of aerobic incubation) and DAT 15 (end of aerobic incubation). Samples removed from incubation chamber were first gently ventilated, to transfer all volatiles formed in the head-space of Erlenmeyer flask to the traps for volatiles. They were then dissected into traps for volatiles and incubation flask containing test soil, and processed following the procedure presented on figure B.8.1.1.1.2._CA-12. It shall be noted that in case of DAT 0 samples, processed almost immediately after treatment with the test compound, the traps for volatile compounds were not set. That was due to the assumption made that no volatiles would be formed that early in the test system.

The soil in each vessel was extracted and analysed as entire sample. The extracted soil pellets were analysed for their content of NER fraction by LSC following combustion. Further characterization of NER fraction was not performed.

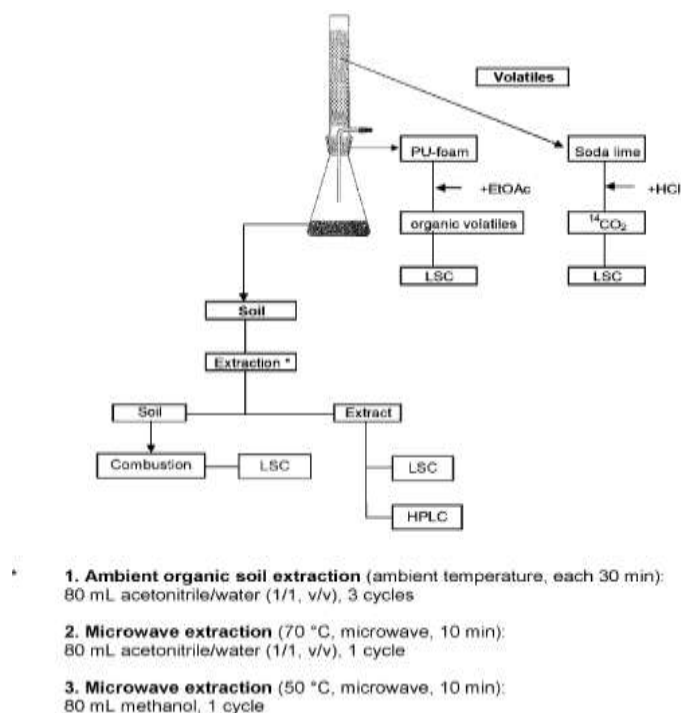


Figure B.8.1.1.1.2._CA-12: The schematic presentation of sample-processing procedure used for **aerobic-phase** samples (scheme copied from the study report).

The remaining incubation flasks, designated to be further incubated under anaerobic conditions, were dissected on DAT 15 in exactly the same way as described above. The removed traps were stored for later analysis. The soil in each flask was flooded with ~150 mL of de-oxygenated deionised water, to obtain the water layer of ~3 cm above the soil surface. Next vessels were gently shaken and sealed with double-valve glass stoppers, to get the incubation system presented above on figure B.8.1.1.1.2._CA-13. The flask were then flushed for 1 minute with argone, connected to air-tight plastic bag, flushed with N₂ to collect volatile degradates and the inlet valve was closed to grant anaerobicity of the incubation vessel throughout incubation period. The outlet valve – connected with plastic bag, was left open. Finally, so prepared incubation vessels were placed within incubation chamber, in a box flooded initially with Ar, then with N₂. The incubation temperature was the same as that for aerobic pre-incubation stage – $T = 20 \pm 2^\circ\text{C}$.

The incubation chamber used in **anaerobic incubation phase** is presented on figure B.8.1.1.1.2._CA-13.



Figure B.8.1.1.1.2._CA-13: The anaerobic incubation chamber used in the experiment (copied from the study report).

At the designated time points samples were removed from incubation chamber and connected to the volatiles-combustion oven unit, shown on figure B.8.1.1.1.2._CA-14, to remove all formed volatile compounds from the vessels' headspace and sampling bag.

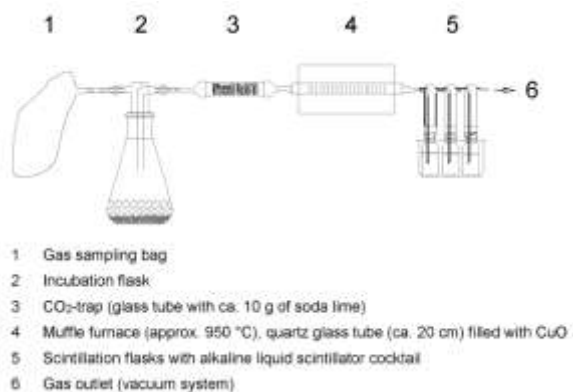


Figure B.8.1.1.1.2._CA-14: The scheme of the device used to evacuate and capture volatile compounds from anaerobic incubation vessels (copied from the study report).

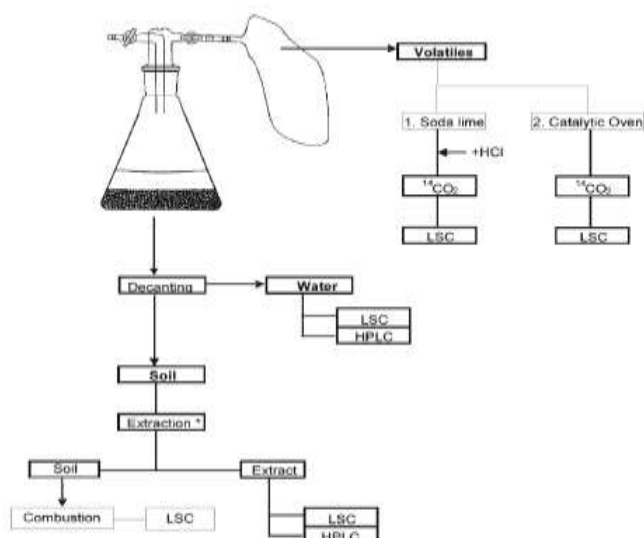
After that the flask were opened and anaerobic conditions monitored by measuring pH, oxygen content and redox potential of water layer, as well as redox potential of soil.

Then the whole samples were processed as shown below on figure B.8.1.1.1.2._CA-15. The water phase after decantation was centrifuged for ~10 min at ~4550xg to remove suspended soil particles. Cleared supernatants, after determination of their volume, were analysed for their content of radioactivity without being further concentrated, using HPLC and LSC.

The centrifugation pellets were added to remaining soil for further extraction.

The applied soil extraction procedure was the same as for aerobic soil. The whole soil portions from each vessels were subjected to extraction. The extracted soil pellets were analysed for their content of NER fraction by LSC following combustion. Further characterization of NER fraction was performed in DAT-135

(DASF-120) samples following the procedure presented on figure B.8.1.1.1.2._CA-16. For that purpose 25-g aliquots of both replicates were used.



1. Ambient organic soil extraction (ambient temperature, each 30 min):
80 mL acetonitrile/water (1/1, v/v), 3 cycles

2. Microwave extraction (70 °C, microwave, 10 min):
80 mL acetonitrile/water (1/1, v/v), 1 cycle

3. Microwave extraction (50 °C, microwave, 10 min):
80 mL methanol, 1 cycle

Figure B.8.1.1.1.2._CA-15: The schematic presentation of sample-processing procedure used for anaerobic-phase samples (scheme copied from the study report).



Figure B.8.1.1.1.2._CA-16: The schematic presentation of sample-processing procedure used for NER characterisation (scheme copied from the study report).

Also duplicate samples for determination of soil microbial activity were prepared. The samples were prepared in two variants – as not treated samples and samples treated with blank application solution. Three sets of incubation vessels were prepared, to cover three sampling points – two for aerobic phase (DAT-0 and DAT-15 samples) and one for anaerobic phase – DAT-135/DASF-120 sample. They were incubated in exactly the same way as other samples.

The determination of soil microbial activity during **aerobic incubation phase** was based on the method of substrate-induced initial respiratory response (SIR) and followed methodology described by Anderson & Domsch.

The method of the determination of soil microbial activity in anaerobic soil was based on a plate count assay for colony forming units.

All samples were analysed for the content of radioactivity using LSC method. The LSC (Liquid Scintillation Counting) analysis was performed using a LS6500 or LKB-Wallac 1219 Spectral counters.

The radioactivity in organic extracts and other liquid samples from HPLC analysis was determined in either:

- mini-vials, using the adequate (depending on expected RA content) sample aliquots and 2 mL of Quicksafe® A solution containing 5% of water; the counting time was 10 min and the background 12 – 16 cpm;
- maxi-vials, using the adequate (depending on expected RA content) sample aliquots and 7 mL of Quicksafe® A solution containing 5% of water; the counting time was 10 min and the background 22 – 23 cpm.

The same scintillation cocktail was used to determine the radioactivity in alkaline extracts, obtained during fractionation for characterisation of NER fraction in extracted DAT-135/DASF-120 soil pellets. The background for these measurements was 12 – 16 cpm.

The $^{14}\text{CO}_2$ captured in soda traps during aerobic phase of the experiment was liberated with 18% HCl_{aq} and released from the solution by flushing for 30 min with stream of N_2 , while samples were gently stirred.

The liberated $^{14}\text{CO}_2$, also that formed during anaerobic phase, was absorbed in Oxysolve 400 scintillation cocktail and radioactivity measured using LKB-Wallac 1219 Spectral counter. The counting time was 10 min and the background 17 – 20 cpm.

The radioactivity in solid samples – extracted soil pellets, was determined after combustion of three 1-g aliquots of dried and homogenised material. The resulting $^{14}\text{CO}_2$ was absorbed in 15 mL of Oxysolve C400 liquid. The counting time was 10 min and the background 17 – 20 cpm.

The instrumental limit of quantitation – LOQ_i , was set to double maximum instrument background count rate, defined as *max. background [cpm]*3/60* – equation used for conversion of cpm to Bq. The so determined instrumental LOQ_i values for different types of liquid samples were as follows:

- samples with scintillation cocktail of 2 mL Quicksafe A + 5% water: $\text{LOQ}_i = 0.8 \text{ Bq}$;
- samples with scintillation cocktail of 7 mL Quicksafe A + 5% water: $\text{LOQ}_i = 1.2 \text{ Bq}$;
- samples with scintillation cocktail of 15 mL Oxysolve C400, $\text{LOD}_i = 0.7 \text{ Bq}$ and $\text{LOQ}_i = 1.0 \text{ Bq}$.

Sample extracts were analysed using the following techniques:

- HPLC – primary identification and quantitation method for parent compound and its degradation products;
- TLC – primary and conformatory identification and quantitation method for the parent compound and its degradation products;
- LC-MS – identification method for parent compound and its degradation products;
- $^1\text{H-NMR}$ – supplementary identification method for parent compound in stock solution.

The RP-HPLC analysis was performed in a gradient mode. The system consisted of Agilent 1100 chromatograph equipped with Ramona Star radiodetector and DAD detector, set to $\lambda = 254 \text{ nm}$. The chromatographic separation was performed on a system consisting of Purospher Star $\text{C}_{18\text{e}}$ 4 mm * 4 mm * 5 μm guard column and Purospher Star $\text{C}_{18\text{e}}$ 250 mm * 4.6 mm * 5 μm chromatographic column. It worked in the following gradient regime:

- **Mobile phase A:** 5 mM aqueous ammonium formate +1% formic acid (985 mL Water + 10 mL HCOOH + 5 mL $\text{NH}_4\text{COOH}_{(\text{aq})}$ – 5 mM $\text{NH}_4\text{COOH}/265 \text{ mM HCOOH}$);
- **Mobile phase B:** 5 mM ammonium formate in acetonitrile +1% formic acid (985 mL CH_3CN + 10 mL HCOOH + 5 mL $\text{NH}_4\text{COOH}_{(\text{aq})}$ – 5 mM $\text{NH}_4\text{COOH}/265 \text{ mM HCOOH}$),
- **Gradient mode** used in elution is shown below in the table B.8.1.1.1.2._CA-12,
- Total run time was 65 minutes.

The flow rate was set to 1.0 mL/min. The chromatographic column was kept under the constant temperature $T = 40^\circ\text{C}$.

Table B.8.1.1.1.2._CA-12: The HPLC gradient mode used in the study.

Time [min]	Solvent ratio	
	Solvent A	Solvent B
0 - 5	100	0
5 - 55	Linear gradient	
55	5	95
5 - 60	5	95
60 - 62	Linear gradient	
62	100	0
62 - 65	100	0

The method had the following performance parameters:

- LOD = 10.6 Bq, corresponding to 0.33% AR;
- LOQ = 3* LOD – 31.8 Bq, corresponding to 1.0% AR.

The primary quantitation TLC analysis of polar fraction was performed in NP-TLC (normal phase TLC) mode. It was carried out on at ambient temperature, in saturated chamber, on silica gel Merck Si60, F₂₅₄, TLC plates. The solvent system used in the analysis was CH₃COOC₂H₅/CH₃CHOHCH₃/H₂O/CH₃COOH 65:24:11:1 (v/v/v/v) solution (CH₃CHOHCH₃ stands for 2-propanol). Separation distance for analysed material and reference compounds was 160 mm.

Two detectors were used:

- UV cabinet detector working at a wavelength $\lambda = 254$ nm;
- Bio-Imaging Analyser “BAS-2000” to detect and quantify radioactivity.

The conformatory TLC method was also performed in NP-TLC (normal phase TLC) mode. It was carried out on at ambient temperature, in saturated chamber and on silica gel Merck Si60, F₂₅₄, TLC plates. Two detectors were used:

- UV cabinet detector working at a wavelength $\lambda = 254$ nm;
- Bio-Imaging Analyser “BAS-2000” to detect and quantify radioactivity.

Two solvent system were used in the analysis:

- Eluent 1 (**Method A**) – CH₂Cl₂/CH₃COOC₂H₅ 8:2 (v/v) solution; separation distance was 160 mm;
- Eluent 2 (**Method B**) – CH₃COOC₂H₅/CH₃CHOHCH₃/H₂O/CH₃COOH 65:24:11:1 (v/v/v/v) solution (CH₃CHOHCH₃ stands for 2-propanol); separation distance was 80 mm.

The TLC method used for quantitative analysis of polar fraction had the following performance parameters:

- LOD = 0.30% AR;
- LOQ = 0.9% AR.

The LC-MS analysis was performed as either HPLC/MS or IEC/MS analysis.

HPLC/MS analysis was carried out using Agilent HP1000 HPLC system equipped with a Nucleodur Gravity C₁₈ chromatographic column (250 * 2 mm, 3 μ m), UV detector followed by the Ramona Star radiodetector and Q-Exactive mass spectrometer.

The parameters of chromatographic analysis were following:

- flow rate: 0.2 mL/min,
- elution mode: gradient,
- mobile phase:
 - **Solvent A:** H₂O + 0.1% HCOOH,
 - **Solvent B:** CH₃CN + 0.1% HCOOH.
- gradient programme is presented below in the table B.8.1.1.1.2._CA-13.

Table B.8.1.1.1.2._CA-13: Gradient programme used in HPLC/MS analysis.

<i>Time [min]</i>	<i>% solvent A (H₂O + 0.1% HCOOH)</i>	<i>% solvent B (CH₃CN + 0.1% HCOOH)</i>
0	95	5
1	95	5
25	5	95
35	5	95

The IEC/MS (Ion Exchange Chromatography) analysis was performed using Dionex ICS-500 system equipped with AS20 column (250 * 2 mm), Ramona Star radiodetector and MS spectrometer.

The parameters of chromatographic analysis were following:

- flow rate: 0.25 mL/min,
- elution mode: isocratic,
- mobile phase: 20mM KOH in water,
- elution time: 15 minutes.

Results and their discussion:

The monitoring of the experimental conditions demonstrated that the samples were incubated at the mean temperature $T = 19.7^{\circ}\text{C}$, ranging from 19.4°C to 19.9°C . The average incubation temperature and its range was within the limits of the assumed constant temperature $T = 20 \pm 2^{\circ}\text{C}$.

The soil moisture content during **aerobic incubation phase** was not monitored, as it was assumed that the incubation period was too short for substantial water losses to occur.

In case of **anaerobic incubation phase**, to justify not performing such control, the following assumptions were made:

- a) as soil was flooded no moisture maintenance was required throughout entire incubation period;
- b) incubation in a static system excluded any substantial losses of water from the test vessels.

The determination of the soil biomass in the test soils during the **aerobic incubation period** demonstrated no decrease of that parameter. It was also determined that during that period soil biomass was well above the recommended minimum level of 1% OC.

For **anaerobic incubation period** the test soil demonstrated to be fully viable.

The LSC analysis of the homogeneity of application of the kinetic samples conformed that it was homogenous, with $\text{RSD} = 1.8\%$

The application dose determined for DAT-0 samples was, on average, 232.8 kBq, equal to 151.2 μg Flufenacet/sample. That value was set as 100% AR.

The verification of the conditions during **anaerobic incubation phase** demonstrated that anaerobicity was maintained throughout that phase. The following changes in measured parameters were recorded (means of two replicates are given):

- for test system containing Hoefchen am Hohenseh 4a soil:
 - the concentration of O_2 in water layer decreased from 5.3 mg/L (60.5%) on DASF 0 to 0.3 mg/L (3.5%) on DASF 120;
 - the redox potential of water layer, expressed as E_{obs} , decreased from 203.5 mV on DASF 0 to -114.5 mV on DASF 120;
 - the redox potential of soil layer, expressed as E_{obs} , decreased from 241 mV to -170 mV on DASF 120;
 - pH of water phase increased from ~ 7.2 to ~ 7.8 during incubation period.
- for the test system containing Dollendorf II soil:
 - the concentration of O_2 in water layer decreased from 6.0 mg/L (67%) on DASF 0 to 0.1 mg/L (1.0%) on DASF 120;
 - the redox potential of water layer, expressed as E_{obs} , decreased from 168.5 mV on DASF 0 to -105.5 mV on DASF 120;
 - the redox potential of soil layer, expressed as E_{obs} , decreased from 183 mV to -133.5 mV on DASF 120;
 - pH of water phase decreased during incubation period from 8.5 to ~ 7.5 to then increase to 7.9.

The detailed results of these measurements are presented below, separately for each test soil system, in tables B.8.1.1.1.2._CA-14 (Hoefchen am Hohenseh 4a soil) and B.8.1.1.1.2._CA-15 (Dollendorf II soil).

Table B.8.1.1.1.2._CA-14: The results of the verification of the anaerobic conditions in test vessels containing Hoefchen am Hohenseh 4a soil.

Sample collected on:		Replicate	Results obtained for:							
DAT	DASF		Water phase					Soil		Buffer solution
			[O ₂]		Redox potential		pH	Redox potential		Redox potential
			mg/L	%	E _{obs} [mV]	E _H [mV]		E _{obs} [mV]	E _H [mV]	E _{obs} [mV]
15	0	1	5.3	60	167	373	7.3	245	451	224
		2	5.3	61	240	446	7.2	237	443	
17	2	1	2.5	28	174	380	7.1	223	429	224
		2	2.5	28	165	371	7.1	221	427	
21	6	1	1.6	18	180	387	7.3	92	299	223
		2	2.2	25	171	378	7.2	171	378	
29	14	1	2.4	28	170	376	7.3	-25	181	224
		2	2.6	29	153	359	7.3	-38	168	
35	20	1	2.4	27	180	386	7.6	-110	96	224
		2	2.2	25	157	363	7.6	-84	122	
48	33	1	2.3	26	-98	108	7.5	-160	46	224
		2	1.8	21	-120	86	7.5	-151	55	
77	62	1	0.8	9	-160	43	7.6	-186	17	227
		2	0.8	9	-153	50	7.8	-174	29	
105	90	1	0.2	2	-118	84	7.6	-151	51	228
		2	0.3	3	-110	92	7.6	-150	53	
135	120	1	0.3	4	-124	66	7.7	-171	19	240
		2	0.3	3	-105	85	8.0	-169	21	

Table B.8.1.1.1.2._CA-15: The results of the verification of the anaerobic conditions in test vessels containing Dollendorf II soil.

Sample collected on:		Replicate	Results obtained for:							
DAT	DASF		Water phase					Soil		Buffer solution
			[O ₂]		Redox potential		pH	Redox potential		Redox potential
			mg/L	%	E _{obs} [mV]	E _H [mV]		E _{obs} [mV]	E _H [mV]	E _{obs} [mV]
15	0	1	6.3	68	170	376	8.5	187	393	224
		2	5.7	66	167	373	8.5	179	385	
17	2	1	1.7	20	175	381	7.8	145	351	224
		2	2.0	24	175	381	7.8	125	331	
21	6	1	1.5	17	151	358	7.7	-54	153	223
		2	1.7	19	173	380	7.7	-55	153	
29	14	1	1.6	19	-111	95	7.5	-207	-1	224
		2	1.6	19	-110	96	7.5	-173	33	
35	20	1	1.8	20	-139	67	7.9	-172	34	224
		2	1.8	20	-117	89	7.9	-163	43	
48	33	1	1.7	19	-130	76	7.5	-168	38	224
		2	1.5	15	-151	55	7.8	-168	38	
77	62	1	0.9	9	-145	58	7.9	-160	43	227
		2	0.8	9	-157	46	8.0	-163	40	
105	90	1	0.4	4	-111	91	7.7	-141	61	228
		2	0.5	6	-99	103	7.7	-136	66	
135	120	1	0.1	1	-109	81	7.9	-135	55	240
		2	0.1	1	-102	88	7.9	-132	58	

The recovery of the applied radioactivity in the experimental soils was generally good, in line with the recommendations of the relevant Guidelines:

- for Hoefchen am Hohenseh 4a soil: on average 96.2% AR, with RSD = 1.4% and range of 93.3% AR – 98.3% AR (values given as the means of the two replicates);

- for Dollendorf II soil: on average 96.5% AR, with RSD = 2.0% and range of 92.9% AR – 98.9% AR (values given as the means of the two replicates).

The level of mineralization was low – up to 1.7% AR in test system with Hoefchen am Hohenseh 4a soil and up to 1.9% AR in test system containing Dollendorf II soil. It shall be noted that in case of samples incubated under aerobic/anaerobic conditions, all captured $^{14}\text{CO}_2$ was formed during aerobic pre-incubation phase. No other volatile compounds were found in the test systems.

The amount of NER fraction increased with time. For Hoefchen am Hohenseh 4a soil it reached the level of 16.9% AR during **aerobic incubation phase**, to then increase to 24.5% AR at the end of **anaerobic incubation phase** (DAT 135). In case of Dollendorf II soil it reached the level of 10.1% AR at the end of **aerobic incubation phase**, to then increase to 31.6% AR at the end of **anaerobic incubation phase** (DAT 135).

The results of further characterisation of NER fraction is presented below in the table B.8.1.1.1.2._CA-16.

Table B.8.1.1.1.2._CA-16: The results of characterisation of NER fraction.

AR determined as:		Results obtained for:							
		Hoefchen am Hohenseh 4a soil				Dollendorf II soil			
		Replicate 1		Replicate 2		Replicate 1		Replicate 2	
		[% AR]	[% NER]	[% AR]	[% NER]	[% AR]	[% NER]	[% AR]	[% NER]
Total NER (determined by LSC)		24.6	100	24.4	100	32.4	100	30.7	100
Fraction	Fulvic acids fraction	12.7	51.7	13.9	56.8	11.4	35.2	10.7	35.0
	Humic acids fraction	4.1	16.8	4.0	16.4	1.9	5.9	1.8	5.9
	Humin fractions	9.0	36.6	8.8	36.0	14.0	43.1	14.2	46.2
	Total recovered	25.8	105.1	24.6	109.2	27.3	84.2	26.7	87.0

It can be stated that in both soils the lowest amount of AR identified as NER fraction was associated with humic acids fraction. For Hoefchen am Hohenseh soil the amount of AR as NER associated with fulvic acids fraction was greater than that associated with humans, while in Dollendorf II soil that relationship was reversed. It was noted however that, while for Hoefchen am Hohenseh soil the HPLC-recoveries of AR identified as NER were good, even slightly above 100%, in case of Dollendorf soil they were well below 90% for both replicates.

During the aerobic incubation phase the radioactivity in the both systems remained mainly in extractable form – as Flufenacet and its degradation products. The concentration of Flufenacet declined sharply to reach the level of ~31 – 44% AR on DAT 15 (end of aerobic incubation phase). The following degradates were identified in soil during aerobic incubation period:

- FOE Thiadone – 4.3 – 5.9% AR on DAT 15,
- FOE Trifluoroethane sulfonic acid – 2.5 – 6.0% AR on DAT 15,
- Trifluoroacetic acid – 28.0 – 37.5% AR on DAT 15.

Additionally the small fraction of other metabolites – the so-called “Unidentified/Diffused Radioactivity”, was detected, not surpassing the level of 2.4% AR.

During anaerobic incubation phase the amount of extractable radioactivity (sum of that recovered in water phase and extracted from soil) was initially higher than that recovered at the same time point before soil flooding, what may indicate that the NER fraction at the end of aerobic incubation period contained some potentially extractable radioactivity. It decreased afterwards steadily to the level of 59.4 – 68.3% AR at the study's end (DAT 135/DASF 120).

Flufenacet steadily decreased during anaerobic phase from the level of ~35 – 43% AR at its beginning to ~3 – 6% AR at the end. No new degradation products were found and in case of those identified the amounts FOE Trifluoroethane sulfonic acid declined in both soils, while the concentration of Trifluoroacetic acid (TFA) increased. In case of FOE Thiadone no clear tendency was observed – in Hoefchen am Hohenseh 4a soil it steadily increased during that phase, while in Dollendorf II soil after initial increase its concentration declined.

The fraction of “other”, not identified degradates, if detected at all, was at a very low level and decreasing.

The detailed results of the experiment are presented below, separately for each test soils, in two sets of tables and graphs. In the table B.8.1.1.1.2._CA-17 and on figure B.8.1.1.1.2._CA-17 (the distribution of radioactivity in the test system on left-hand graph and the concentrations of the identified compounds in function of time on the right-hand one) are presented the results of the experiment with Hoefchen am Hohenseh 4a soil. Next set – table B.8.1.1.1.2._CA-18 and figure B.8.1.1.1.2._CA-18 the distribution of radioactivity in the test system on left-hand graph and the concentrations of the identified compounds in function of time on the right-hand one) presents the results of the experiment with Dollendorf II soil. Presenting the numerical results of the study RMS

decided to differentiate those obtained for aerobic and anaerobic phases by delicately shading grey the cells containing the former.

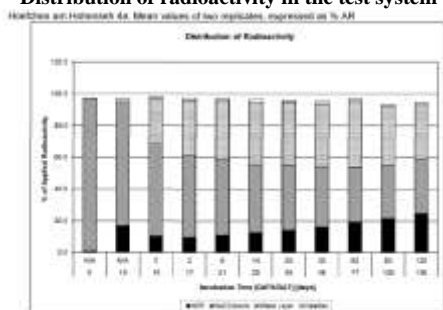
Table B.8.1.1.1.2._CA-17: The detailed results obtained for the test system with Hoefchen am Hohenseh 4a soil.

AR			Results [%AR] obtained for: ¹⁾										
			Aerobic incubation phase		Anaerobic incubation phase ²⁾								
					DAT 0	DAT 15	DAT 15 ³⁾ DASF 0	DAT 17 DASF 2	DAT 21 DASF 6	DAT 29 DASF 14	DAT 35 DASF 20	DAT 48 DASF 33	DAT 77 DASF 62
Extracted	Total extracted		96.4	78.1	86.6	86.4	84.4	82.3	80.3	77.6	76.0	70.1	68.3
	Water phase		N/A ⁹⁾	N/A ⁹⁾	28.4	34.8	36.7	39.3	39.5	39.3	41.0	36.9	34.2
	Soil phase	Ambient extract	90.8	73.0	54.4	48.0	44.1	39.3	37.6	34.6	31.4	29.5	30.8
		Microwave extract	4.2	3.3	2.9	2.5	2.5	2.6	2.3	2.6	2.4	2.4	2.3
		Methanol extract	1.4	1.8	0.9	1.1	1.2	1.0	1.0	1.1	1.2	1.2	0.9
Total soil extract		96.4	78.1	58.2	51.6	47.7	43.0	40.8	38.3	34.9	33.2	34.0	
In extract identified as: ⁴⁾	Flufenacet		96.4	30.8	42.8	38.8	33.3	25.5	22.4	18.2	13.0	9.7	6.4
	FOE Thiadone		n. d. ¹¹⁾	5.9	4.8	8.5	10.5	11.6	12.7	13.1	13.6	12.2	10.6
	FOE 5043-Trifluoroethanesulfonic acid		n. d. ¹¹⁾	2.5	5.1	5.0	4.0	1.4	2.8	4.2	2.1	2.2	2.3
	Trifluoroacetic acid		n. d. ¹¹⁾	37.5	31.4	32.8	36.5	43.5	42.3	42.1	47.3	46.0	47.9
	Others		n. d. ¹¹⁾	1.3	2.5	1.2	n. d. ¹¹⁾	n. d. ¹¹⁾	n. d. ¹¹⁾	n. d. ¹¹⁾	n. d. ¹¹⁾	n. d. ¹¹⁾	0.8
	Total identified ⁵⁾		96.4	78.1	86.6	86.4	84.4	82.0	80.3	77.6	76.0	70.1	68.0
Bound residues (NER fraction)			0.8	16.9	10.2	9.5	10.9	12.5	13.9	16.0	19.1	21.4	24.5
Volatile compounds	Aerobic phase	CO ₂ ⁶⁾	n. a. ¹⁰⁾	1.6	1.5	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6
		VOC	n. a. ¹⁰⁾	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
	Anaerobic phase	CO ₂ ⁷⁾	N/A ⁹⁾	N/A ⁹⁾	n. a. ¹⁰⁾	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.1	0.1
		VOC	N/A ⁹⁾	N/A ⁹⁾	n. a. ¹⁰⁾	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Total volatiles ⁸⁾			n. a. ¹⁰⁾	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.7	1.6
Total recovered			97.2	96.5	98.3	97.5	96.9	96.4	95.9	95.2	96.6	93.3	94.4

Footnotes to the table:

- 1) All reported values are the means of two replicates;
- 2) For anaerobic phase the data points are presented as both Days After Treatment (DAT) – continuous numbering of data points, and Days After Soil Flooding (DASF) to present the duration of anaerobic phase;
- 3) The values obtained for sample shortly after anaerobic conditions by soil flooding were generated;
- 4) The entire system values (for anaerobic phase sum of measured in water and soil);
- 5) The difference between “Total identified” and “Total extracted” may be due to rounding errors as well as clean-up and chromatographic losses;
- 6) Amounts found in soda lime traps, for anaerobic phase samples in traps set for 15-days aerobic preincubation;
- 7) Amounts found in KOH traps;
- 8) Sum of all volatiles;
- 9) Not Applicable - fraction not present in aerobic incubation samples;
- 10) Not available – it was assumed that at the time point no volatiles would form;
- 11) Not determined;

Distribution of radioactivity in the test system



Concentrations of identified compounds in function of time

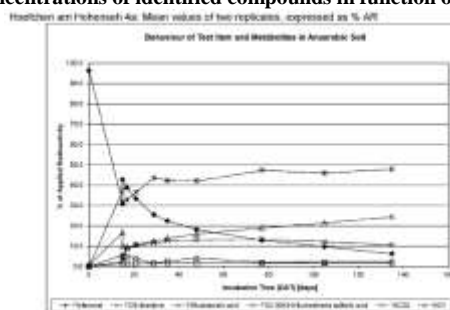


Figure B.8.1.1.1.2._CA-17: The graphical presentation of the results obtained for the test system with Hoefchen am Hohenseh 4a soil (schemes copied from the study report).

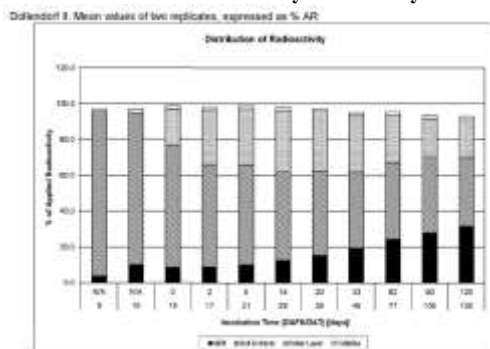
Table B.8.1.1.1.2._CA-18: The detailed results obtained for the test system with Dollendorf II soil.

AR			Results [%AR] obtained for: ¹⁾										
			Aerobic incubation phase		Anaerobic incubation phase ²⁾								
					DAT 0	DAT 15	DAT 15 ³⁾ DASF 0	DAT 17 DASF 2	DAT 21 DASF 6	DAT 29 DASF 14	DAT 35 DASF 20	DAT 48 DASF 33	DAT 77 DASF 62
Extracted	Total extracted		93.1	85.0	88.5	87.7	86.7	83.6	79.8	73.8	68.9	63.7	59.4
	Water phase		N/A ⁹⁾	N/A ⁹⁾	20.5	30.5	31.3	33.9	32.7	31.4	26.2	21.5	21.2
	Soil phase	Ambient extract	84.3	79.1	63.7	51.3	51.6	44.8	42.8	38.2	38.8	38.2	34.7
		Microwave extract	6.8	4.5	3.0	4.5	2.8	3.5	3.2	3.0	2.8	2.7	2.5
		Methanol extract	2.0	1.4	1.2	1.5	1.1	1.4	1.1	1.2	1.2	1.2	1.0
Total soil extract		93.1	85.0	69.7	57.2	55.4	49.7	47.1	42.4	42.7	42.2	38.1	
In extract identified as: ⁴⁾	Flufenacet		93.1	44.2	35.4	27.0	23.3	18.2	15.9	10.6	12.1	4.5	3.1
	FOE Thiadone		n. d. ¹¹⁾	4.3	7.1	11.3	12.4	11.5	11.9	8.7	7.7	5.3	2.7
	FOE 5043-Trifluoroethanesulfonic acid		n. d. ¹¹⁾	6.0	3.2	1.7	1.1	0.7	<LOD	0.8	0.7	<LOD	1.2
	Trifluoroacetic acid		n. d. ¹¹⁾	28.0	40.4	46.5	48.7	53.2	51.3	52.7	47.3	53.2	51.5
	Others		n. d. ¹¹⁾	2.4	2.4	1.1	1.0	n. d. ¹¹⁾	n. d. ¹¹⁾	<LOD	<LOD	n. d. ¹¹⁾	0.7
	Total identified ⁵⁾		93.1	85.0	88.5	87.7	86.5	83.6	79.0	73.0	67.8	63.0	59.2
Bound residues (NER fraction)			3.7	10.1	8.6	8.8	10.1	12.6	15.5	19.4	24.5	27.9	31.6
Volatile compounds	Aerobic phase	CO ₂ ⁶⁾	n. a. ¹⁰⁾	1.9	1.8	1.9	1.9	1.9	1.9	1.9	1.9	1.9	1.9
		VOC	n. a. ¹⁰⁾	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
	Anaerobic phase	CO ₂ ⁷⁾	N/A ⁸⁾	N/A ⁸⁾	n. a. ¹⁰⁾	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
		VOC	N/A ⁸⁾	N/A ⁸⁾	n. a. ¹⁰⁾	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
	Total volatiles ⁸⁾		n. a. ¹⁰⁾	2.0	1.8	1.9	1.9	1.9	1.9	1.9	1.9	2.0	1.9
Total recovered			96.9	97.0	98.9	98.4	98.8	98.0	97.2	95.1	95.4	93.6	92.9

Footnotes to the table:

- 1) All reported values are the means of two replicates;
- 2) For anaerobic phase the data points are presented as both Days After Treatment (DAT) – continuous numbering of data points, and Days After Soil Flooding (DASF) to present the duration of anaerobic phase;
- 3) The values obtained for sample shortly after anaerobic conditions by soil flooding were generated;
- 4) The entire system values (for anaerobic phase sum of measured in water and soil);
- 5) The difference between “Total identified” and “Total extracted” may be due to rounding errors as well as clean-up and chromatographic losses;
- 6) Amounts found in soda lime traps, for anaerobic phase samples in traps set for 15-days aerobic preincubation;
- 7) Amounts found in KOH traps;
- 8) Sum of all volatiles;
- 9) Not Applicable - fraction not present in aerobic incubation samples;
- 10) Not available – it was assumed that at the time point no volatiles would form;
- 11) Not determined;

Distribution of radioactivity in the test system



Concentrations of identified compounds in function of time

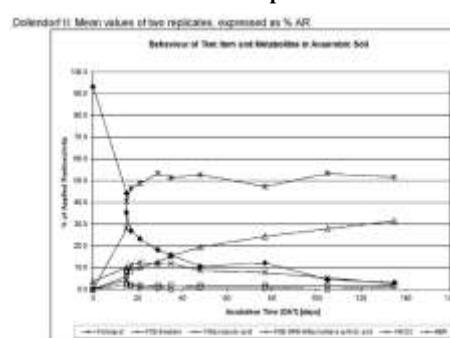


Figure B.8.1.1.1.2._CA-18: The graphical presentation of the results obtained for the test system with Dollendorf II soil (schemes copied from the study report).

The results presented above show that, in line with the criteria set by SANCO/211/2000 Guidance Document on the Assessment of the Relevance of Metabolites, FOE Thiadone and Trifluoroacetic acid should be considered as major degradation products for the degradation of Flufenacet within Thiadiazole moiety in soil under anaerobic conditions. On the basis of the results obtained in this experiment the following transformation scheme for the [Thiadiazole-5-¹⁴C] Flufenacet was proposed by the Applicant (Figure B.8.1.1.2._CA-18). The scheme comprises processes occurring during both aerobic and anaerobic phases.

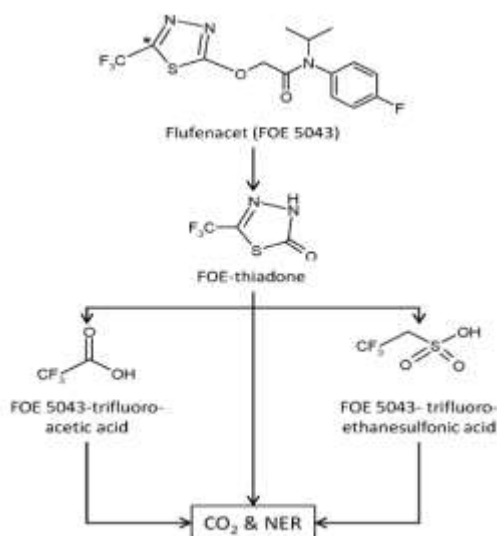


Figure B.8.1.1.2._CA-18: The proposed transformation scheme of [Thiadiazole-5-¹⁴C] Flufenacet in aerobic/anaerobic soil (scheme copied from the study report).

The kinetic analysis of the results of this study will be presented under the relevant point, further down this report – please refer to the point B.8.1.1.2.1.2.

Summary: degradation of flufenacet in soil under anaerobic conditions

The route of degradation of the acetanilide herbicide Flufenacet in anaerobic soil was examined in three soils – one from the US and two European. The test compound – Flufenacet, was radiolabelled in one of the following two positions:

- uniformly in phenyl ring – compound tested on one US soil,
- in position C5 of Thiadiazole moiety – examined in two EU soils.

The experiments performed to determine the transformation pattern of Flufenacet in soil under anaerobic conditions consisted of two phases – aerobic preincubation phase and anaerobic incubation phase. RMS decided to present the key results of the experiments taking into account both phases. In case of aerobic preincubation phase the results are given for the terminal time point of that phase.

The key results for the examination of transformation of Flufenacet in anaerobic soils in the area of formation of terminal degradation products – mineralisation expressed as CO₂ and NER fraction, are presented below in the table B.8.1.1.1.2._CA-19. To differentiate the results obtained for aerobic phase from those for anaerobic phase the former were shaded light grey. It shall be noted that under anaerobic conditions mineralisation, if occurred at all, was minimal. No other volatile compounds were identified during either aerobic or anaerobic phases. The level of NER formed under anaerobic conditions (net formation) was comparable to that observed in aerobic soils.

Table B.8.1.1.1.2._CA-19: The levels of the terminal degradation products – CO₂ and NER fraction formed in soil during examination of the transformation pattern of Flufenacet in soil under anaerobic conditions.

Study/ radiolabelling position	Soil		Results obtained for aerobic phase		Results obtained for anaerobic phase ¹⁾					
	Name	Type (USDA)	CO ₂ [%AR] – end of phase	NER [%AR] – end of phase	Mineralisation level – CO ₂ formed [% AR]			NER level [% AR]		
					Beginning of phase	Max.	Net anaero- bic ²⁾	Beginning of phase	Max.	Net anaero- bic ³⁾
Pangilinan & Smith [1994]/ ¹⁴ C-phenyl	Howe	Sandy loam	1.4 (DAT 30)	8.4 (DAT 30)	1.4 (DAT 30 DAF 0)	1.8 (DAT 210 DAF 180)	0.4	8.4 (DAT 30 DAF 0)	32.6 (DAT 210 DAF 180)	24.2 (DAT 210 DAF 180)
Heinemann [2012]/ ¹⁴ C-5- Thiadiazole	HH ⁴⁾	Silt loam	1.6 (DAT 15)	16.9 (DAT 15)	1.6 (DAT 15 DAF 0)	1.7 (DAT 105 DAF 90)	0.1	10.2 (DAT 15 DAF 0)	24.5 (DAT 135 DAF 120)	14.3 (DAT 135 DAF 120)
	DD ⁵⁾	Loam	1.9 (DAT 15)	10.1 (DAT 15)	1.8 (DAT 15 DAF 0)	1.9 (DAT 105 DAF 90)	<0.1 ⁶⁾	8.6 (DAT 15 DAF 0)	31.6 (DAT 135 DAF 120)	23.0 (DAT 135 DAF 120)

Footnotes to the table:

- 1) In case of Howe soil the results for the beginning of anaerobic phase are the same as those for the end of aerobic phase. In case of soils HH and DD they are different, because there were available the results obtained immediately after generating the anaerobic conditions;
- 2) "Net anaerobic" is a difference between the total amount of CO₂ formed and that determined in aerobic traps for volatiles;
- 3) "Net anaerobic" is a difference between maximum determined level of NER and that measured at the beginning of anaerobic phase;
- 4) HH stands for *Hoefchen am Hohenseh 4a* soil;
- 5) DD stands for *Dollendorf II* soil;
- 6) At the time point where maximum CO₂ level of 2.0% AR was recorded, the amount recovered for aerobic volatile traps was 1.9% AR and from anaerobic volatile traps <0.1 AR. The slightly higher total amount may be due to either rounding or losses during extraction. In that soil the level of mineralization, expressed as recovered CO₂ in anaerobic phase was <0.1% AR;

The examination of the extracted fraction enabled the identification of one new degradate, not identified in aerobic soils – FOE Thioglycolate. All other identified degradation products were those already found in aerobic soils. On that basis it can be stated that the transformation pattern of Flufenacet in soil under anaerobic conditions would not differ significantly from that determined in aerobic soils. The key results of the profiling of degradation products in anaerobic soils are presented below in table B.8.1.1.1.2._CA-20. To differentiate the results obtained for aerobic phase from those for anaerobic phase the former were shaded light grey.

Table B.8.1.1.2_CA-20: The results of the profiling of Flufenacet and its degradation products.

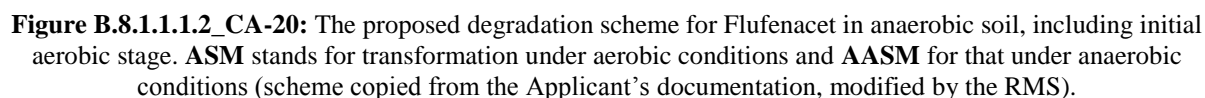
Study/ radiolabelling position	Soil		Results obtained for aerobic phase		Results obtained for anaerobic phase ¹⁾				
	Name	Type (USDA)	Identified compound	Amount [% AR] at the end of phase	Identified compound	Amount [% AR] measured at:			Anaerobic metabolite (yes/no)
						Beginning of phase	Max.	Net anaerobic ²⁾	
Pangilinan & Smith [1994]/ ¹⁴ C-phenyl	Howe	Sandy loam	Flufenacet	69.0 (DAT 30)	Flufenacet	69.0 (DAT 30/ DAF 0)	39.0 ⁶⁾ (DAT 210/ DAF 180)	N/A ⁸⁾	N/A ⁸⁾
			FOE Oxalate	11.2 (DAT 30)	FOE Oxalate	11.2 (DAT 30/ DAF 0)	14.5 (DAT 60/ DAF 30)	3.3 (DAT 60/ DAF 30)	Yes
			FOE Sulfonic acid	6.6 (DAT 30)	FOE Sulfonic acid	6.6 (DAT 30/ DAF 0)	6.6 (DAT 30/ DAF 0)	0.0	No
			FOE Alcohol	0.0 (DAT 30)	FOE Alcohol	0.0 (DAT 30/ DAF 0)	1.4 (DAT 153/ DAF 123)	1.4 (DAT 153/ DAF 123)	Yes
			FOE TGS ³⁾	2.6 (DAT 30)	FOE TGS ³⁾	2.6 (DAT 30/ DAF 0)	2.6 (DAT 30/ DAF 0)	0.0	No
					FOE Thioglycolate	0.0 (DAT 30/ DAF 0)	1.7 (DAT 60/ DAF 30)	1.7 (DAT 60/ DAF 30)	Yes
Heinemann [2012]/ ¹⁴ C-5- Thiadiazole	HH ⁴⁾	Silt loam	Flufenacet	30.8 (DAT 15)	Flufenacet	42.8 (DAT 15/ DASF 0)	6.4 ⁶⁾ (DAT 135/ DASF 120)	N/A ⁸⁾	N/A ⁸⁾
			FOE Thiadone	5.9 (DAT 15)	FOE Thiadone	4.8 (DAT 15/ DASF 0)	13.6 (DAT 77/ DASF 62)	8.8 (DAT 77/ DASF 62)	Yes
			FOE 5043- Trifluoroethane- sulfonic acid	2.5 (DAT 15)	FOE Tri- fluoroethane sulfonic acid	5.1 (DAT 15/ DASF 0)	4.2 ⁷⁾ (DAT 48/ DASF 33)	4.2 ⁷⁾ (DAT 48/ DASF 33)	Yes
			Trifluoroacetic acid	37.5 (DAT 15)	Trifluoroacetic acid	31.4 (DAT 15/ DASF 0)	47.9 (DAT 135/ DASF 120)	16.5 (DAT 135/ DASF 120)	Yes
	DD ⁵⁾	Loam	Flufenacet	44.2 (DAT 15)	Flufenacet	35.4 (DAT 15/ DASF 0)	3.1 ⁶⁾ (DAT 135/ DASF 120)	N/A ⁸⁾	N/A ⁸⁾
			FOE Thiadone	4.3 (DAT 15)	FOE Thiadone	7.1 (DAT 15/ DASF 0)	12.4 (DAT 21/ DASF 6)	5.3 (DAT 21/ DASF 6)	Yes
			FOE 5043- Trifluoroethane- sulfonic acid	6.0 (DAT 15)	FOE Tri- fluoroethane sulfonic acid	3.2 (DAT 15/ DASF 0)	3.2 (DAT 15/ DASF 0)	0.0	No
			Trifluoroacetic acid	28.0 (DAT 15)	Trifluoroacetic acid	40.4 (DAT 15/ DASF 0)	53.2 (DAT 105/ DASF 90)	12.8 (DAT 105/ DASF 90)	Yes

Footnotes to the table:

- 1) In case of Howe soil the results for the beginning of anaerobic phase are the same as those for the end of aerobic phase. In case of soils HH and DD they are different, because were available the results obtained immediately after generating the anaerobic conditions;
- 2) "Net anaerobic" is a difference between the maximum amount determined in anaerobic phase and that at its beginning;
- 3) FOE TGS – FOE Thioglycolate sulfonate;
- 4) HH stands for *Hoefchen am Hohenseh 4a* soil;
- 5) DD stands for *Dollendorf II* soil;
- 6) Flufenacet is the active substance, therefore not forming in soil. For that reason its concentration at the end of incubation period is given to show the level of decline;
- 7) In that soil the concentrations of FOE Trifluoroethane sulfonic acid initially decreased, to increase afterwards reaching maximum on the indicated time point. It was assumed that this maximum can be attributed totally to the amount of that compound formed under anaerobic conditions;
- 8) N/A – not applicable (parent compound);

The results of the determination of transformation pathway of Flufenacet in anaerobic soil demonstrated that it would not significantly differ, qualitatively and quantitatively, from that observed in aerobic soil.

The degradation products that may require further consideration for the risk assessment are the same as identified during examination of the degradation pattern of Flufenacet in aerobic soil: FOE Oxalate, FOE Thiadone and Trifluoroacetic acid. The proposed whole transformation pattern determined during examination of degradation of Flufenacet in anaerobic soil, is presented below on figure B.8.1.1.2_CA-20.



Route of degradation (anaerobic) in soil (Regulation (EU) N° 283/2013, Annex Part A, point 7.1.1.2)

Metabolites that may require further consideration for risk assessment - name and/or code, % of applied (range and maximum)

<p><i>0.4 %</i> after <i>180 d</i>, [¹⁴C-<i>Phenyl</i>]-label (n = <i>1</i>)</p> <p><i><0.1 - 0.1%</i> after <i>90 d</i>, [¹⁴C-<i>5-Thiadiazole</i>]-label (n = <i>2</i>)</p> <p><i>24.2 %</i> after <i>180 d</i>, [¹⁴C-<i>Phenyl</i>]-label (n = <i>1</i>)</p> <p><i>14.3 – 23.0 %</i> after <i>120 d</i>, [¹⁴C-<i>5-Thiadiazole</i>]-label (n = <i>2</i>)</p>
<p><i>FOE Oxalate – 14.5 %</i> at <i>30 d</i> (n = <i>1</i>); [¹⁴C-<i>Phenyl</i>] label;</p> <p><i>FOE Thiadone – 8.8 %</i> at <i>62 d</i> (n = <i>2</i>);</p> <p>[¹⁴C-<i>5-Thiadiazole</i>] label;</p> <p><i>Trifluoroacetic acid (TFA) – 16.5 %</i> at <i>120 d</i> (n = <i>2</i>); [¹⁴C-<i>5-Thiadiazole</i>] label;</p>
<p>Sterile conditions: <i>not examined</i></p>

B.8.1.1.1.3. – Soil photolysis

For the purpose of the former evaluation of Flufenacet for its authorisation in the EU the Applicant submitted one study examining photodegradation of that compound on the soil surface. That study Flufenacet used as the test compound was uniformly radiolabelled in the phenyl ring. The study was found acceptable and briefly summarised in the assessment Report for Flufenacet prepared by the then-RMS – France. For the purpose of the current assessment the study was re-evaluated for its compliance with the current Guidelines and is summarised below as *Study 1*.

That study however did not address the issue of would-be phototransformation within the Thiadiazole moiety. To fill that GAP the Applicant submitted a study on soil photolysis of FOE-Thiadone. According to the Applicant, the study was performed on the request of US EPA, but in the EU it is evaluated for the first time, therefore it was considered a newly submitted study. It was evaluated and is summarised below as *Study 2*.

Study 1:

Report: Kasper A. M., Shadrack B. A., (1995): “Photolysis of [Phenyl-U-¹⁴C] FOE 5043 on Sandy Loam.”; Bayer Corporation (formerly Miles Inc.), Agriculture Division, P. O. Box 4913, Kansas City, Missouri 64120-0013, USA; study No. F3082101/F3082102 (Bayer); unpublished Miles Report No. MR 106247; 22 June 1995; study reference number: M-002145-01-1;

Guidelines: The study was performed to comply with the following Guidelines:

- US. EPA Guidelines for Pesticide Registration, Subdivision N, Section 161-3, Soil Photolysis Study.

GLP: Yes

RMS comments: The study had been evaluated for the previous authorisation of Flufenacet in the EU. Its summary can be found under the point B.7.1.1.2.2.1., in section B.7 of the Annex B to the Monograph prepared by the RMS – France, for Flufenacet. For the purpose of the current assessment the study was evaluated for its compliance with the following guidelines:

- US. EPA Guidelines for Pesticide Registration, Subdivision N, Section 161-3, Soil Photolysis Study (indicated as reference Guideline in the study report);
- US EPA Guideline OPPTS 835.2410 – Photodegradation on Soil;
- SETAC Procedures for Assessing the Environmental Fate and Ecotoxicity of Pesticides, Part 1 – Fate and Behaviour in the Environment, chapter 2: Soil Photolysis, SETAC 1995;
- OECD Guidelines for the Testing of Chemicals, Proposal for a New Guideline – Phototransformation of Chemicals on Soil Surface, Draft Document January 2002 (additional reference document);

RMS stated that the study was compliant with the provisions of the Guidelines listed above, therefore it was found acceptable and is summarised below.

Summary:

The aim of the study was to examine photodegradation of Flufenacet in soil surface through:

- a) determining the half-life of that compound when exposed to artificial sunlight;
- b) identifying the transformation pattern and in particular the degradation products formed in amounts greater than 10% AR.

The test soil used in the experiment was Howe Sandy loam soil, used also to examine the route of degradation of Flufenacet in aerobic and anaerobic soil. The characteristic of the test soil, as provided in the study report, is given below, in table B.8.1.1.1.3._CA-1. RMS noted that the test soil was Sandy loam, according to USDA classification. SETAC Guidelines and Draft OECD Guideline recommend to use Silty loam or Clay loam soil rather than any Sandy soil. On the other hand, according to these Guidelines, the test soil used in the experiment should be one of those used in the examination of transformation of the test compound in aerobic soils.

The US Guidelines list sandy loam soil as one of the recommended test soils, also indicating that the test soil should be the same as used to examine the transformation of the test compound in soil under aerobic conditions. As a result, it can be stated that the test soil, although being sandy soil, was selected correctly, in line with the provisions of the current Guidelines.

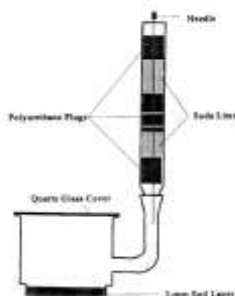
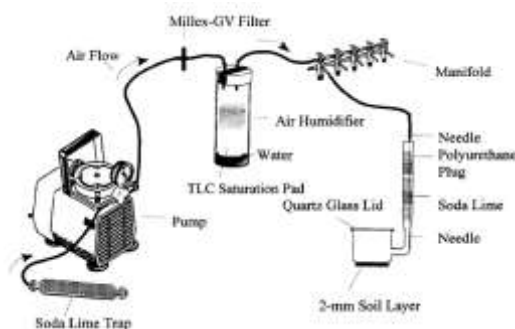
Table B.8.1.1.1.3._CA-1: The characteristic of soil used in the study.

Parameter	Soil:
Soil origin	Howe, Indiana, USA
Soil type (as reported in the study)	Shipshe Sandy loam
Soil type (USDA, calculated by RMS)	US Sandy loam
Particle size distribution	Sand [%]
	67.6
	Silt [%]
	20.0
	Clay [%]
	12.4
pH	6.4
Organic matter content (OM) [%]	1.16
Organic carbon content (C _{org}) [%] ¹⁾	0.67
Cation Exchange Capacity – CEC [mEq/100g]	5.44
Bulk density (disturbed) [g/cm ³]	1.62
Moisture holding capacity at ½ bar [%]	13.0
Soil microbial activity expressed as [CFU/g soil] ²⁾ at the beginning of the study (DAT 0)	2.3 E6

Footnotes to the table:

- 1) Value recalculated by the RMS from that reporting OM content given in the study report using the following equation: OM = 1.724 * OC;
 2) CFU/ g soil = Colony Forming Units/gram of test soil (determined using plate count agar method).

The test soil was sampled from 0-6 inch (0 – 15.24 cm) top layer, from the pesticide-free field (Bayer Research Farm in Howe, Indiana, USA). It was shipped to the test laboratory, placed outdoors and planted with alfalfa to maintain its microbiological viability until it was used. Immediately before the experiment began the test soil was taken to the laboratory where it was air-dried and sieved through a 2-mm sieve. Next its 3.1-g (d. w.) portions were placed in photolysis vessels presented below on figure B.8.1.1.1.3._CA-1. The amount of test soil per vessel was such, to obtain 2-mm thick soil layer. Each test vessels contained removable quartz glass cover and was equipped with a volatile trapping column, attached to the side-arm of the vessel, through which a needle was passed. The needle was joined to the air-humidifying apparatus, presented on figure B.8.1.1.1.3._CA-2. That way the adequate moisture content of the test soil was ensured, and hence its microbiological viability throughout incubation period.

**Figure B.8.1.1.1.3._CA-1:** Test vessel used in the experiment (copied from the study's report).**Figure B.8.1.1.1.3._CA-2:** The air-humidifying apparatus used to keep the test soil moist during the experiment (copied from the study's report).

The test compound was [Phenyl- $U\text{-}^{14}\text{C}$] Flufenacet, delivered in form of benzene stock solution, shown below on figure B.8.1.1.1.3._CA-3. It had a specific radioactivity of 66.5 mCi/mmol corresponding to 4.062 E5 dpm/ μg . The concentration of the stock solution was 11.82 mg Flufenacet/mL. Test compound was applied to the test soil in form of the **Application solution** prepared in 5 mL CH_3CN , containing 0.001278195 mmol of Flufenacet (0.085 mCi when expressed in specific radioactivity units). The nominal concentration of **Application solution** was 2.55639 E-4 mmol Flufenacet/mL (corresponding to 37,735,660.16 dpm/mL). The real concentration of **Application solution**, determined by LSC, was 37,970,325 dpm/mL, what corresponded to 2.57228 E-4 mmol Flufenacet/mL. Its radiochemical purity was 98.0% when determined by HPLC and 99.8% when determined by TLC.

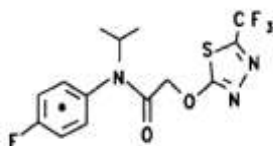


Figure B.8.1.1.1.3._CA-3: The structural formula of the test compound; radiolabelling position indicated with an asterisk (copied from the study report).

0.2 mL (7,594,065 dpm) of the **Application solution** was used to treat 3.1 g (d. w.) of soil in each photolysis vessel. The applicant declared that amount gave the application dose of 6.2 ppm Flufenacet, corresponding to application rate of ~0.9 lb/acre (~1008.55 g/ha – recalculated by RMS) assuming 1-cm soil layer. That value was verified by RMS and was demonstrated to be slightly lower – 6.03 ppm, what corresponded to 904.5 g/ha (~0.81 lb/acre), assuming the soil depth of 1 cm and soil bulk density of 1.5 g/cm³.

For standard EU assumptions with regard to calculation of application rate – soil layer depth of 5 cm and soil density (default) of 1.5 g/cm³, the application rate corresponding to application dose of 6.03 mg /kg would be **A = 4522.5 g/ha**.

The **Application solution** was applied to the soil surface using 0.25-mL Hamilton syringe. Solvent – acetonitrile was allowed to evaporate for 5 minutes. Then, to adjust soil moisture to the target value of **75% of ½ bar**, the appropriate amount of water (0.225 mL per test vessel) was added (it was assumed that ½ bar moisture is equivalent to field moisture capacity). Next vessels were covered with quartz glass covers, trapping columns attached and all joints sealed with Parafilm. The so prepared vessels were weighed and dark control samples wrapped with aluminium foil to exclude light.

In total twelve photolysis incubation vessels were prepared – 8 as irradiated samples and 4 as the dark controls.

Test vessels were placed in Suntest CPS unit, equipped with Heraeus xenon-arc lamp as light source. It is presented below on figure B.8.1.1.1.3._CA-4. The lamp was equipped with a UV-filter to cut-off all radiation below $\lambda = 290$ nm.

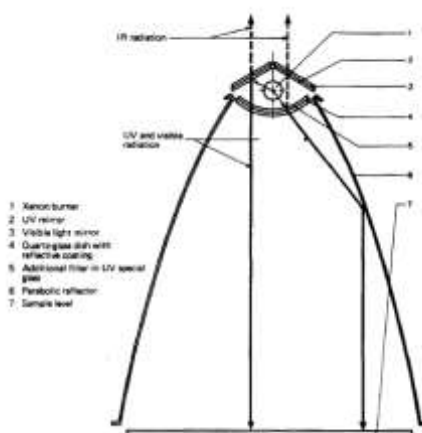


Figure B.8.1.1.1.3._CA-4: The Suntest CPS unit used in the experiment (copied from the study report).

The vessels were kept in the incubation chambers for up to 246 h, or 10.25 Suntest days (24-hours periods), under constant exposure to the light emitted by xenon-arc lamp. That exposure period was determined to match a 30-days exposure to sunlight at worst case conditions in Phoenix, Arizona. That estimate was based on the following assumptions:

- total irradiance <800 nm measured in a weather station in Phoenix, AZ (site: New River), on 23rd June 1988 was **681.7 W/m²** (68%),
- total radiant exposure measured at the same site on the same day was **29.5 MJ/m²**.

The calculated from these values daily “global irradiation” at noon on the 23rd June 1988 in Phoenix, AZ, was **20 MJ/m²**.

Using that value it was determined that simulating such irradiation conditions with Suntest unit operating at 680 W/m² would result in **8.2-h** exposure corresponding to one solar day under the worst case conditions assumed above. Using that value the time of irradiation corresponding to the required in Guidelines 30-days exposure to natural sunlight was determined.

The experiment was performed under the constant temperature of 25⁰C. Additionally, all test vessels – irradiated and dark controls (wrapped with aluminium foil to cut the light off), were placed in the water bath set to the constant temperature $T = 25 \pm 1^{\circ}\text{C}$.

The conditions in the irradiation chamber – temperature and light intensity were constantly monitored and recorded.

The samples were incubated for up to 10.25 days, period corresponding to 30 days of natural sunlight, calculated using the assumptions presented above. At designated sampling points two irradiated and one dark-control samples were taken for analysis. The sampling protocol (sampling dates and number of samples collected at each time point) is provided below in the table B.8.1.1.1.3._CA-2.

Table B.8.1.1.1.3._CA-2: The sampling protocol used in the study.

Sampling interval	Sampling time for:			Samples collected – type and number
	Suntest unit (real sampling dates)		Natural sunlight (calculated) [days]	
	[hours]	[days]		
1	0	0	0	Irradiated samples – 2 vessels; dark control – 1 vessel;
2	66	2.75	8	Irradiated samples – 2 vessels; dark control – 1 vessel;
3	123	5.13	15	Irradiated samples – 2 vessels; dark control – 1 vessel;
4	186	7.75	22.7	Irradiated samples – 2 vessels; dark control – 1 vessel;
5	246	10.25	30	Irradiated samples – 2 vessels; dark control – 1 vessel;

After sample removal, at specified sampling intervals, from the incubation/irradiation chamber, tower traps for volatile compounds removed and processed for the content of radioactivity. The test vessels were weighed and soil samples extracted entirely to characterise quantitatively and qualitatively the radioactivity in soil. The extraction procedure is presented schematically below on figure B.8.1.1.1.3._CA-5.

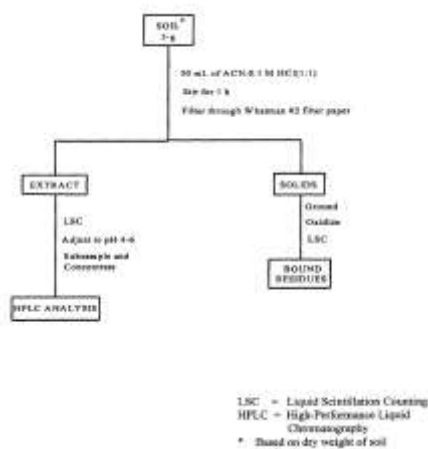


Figure B.8.1.1.1.3._CA-5: Soil extraction procedure used in the experiment (copied from the study report).

The collected extracts were concentrated and analysed by HPLC – method used for quantitation of extracted radioactivity and identification of extract's constituents, and TLC – conformatory method.

The extracted soil pellets were ground, oxidised and analysed by LSC for the content of radioactivity.

The collected traps for volatile compounds were analysed in a following way:

- Polyurethane plugs were removed, rinsed with 3 mL of CH_3CN and both rinse and the plug were analysed for the content of radioactivity using LSC;
- $^{14}\text{CO}_2$ captured in soda lime was liberated using the apparatus presented on figure B.8.1.1.3._CA-6. This was done by placing the whole 4-g portion of soda lime from each trapping column in 250-mL Erlenmeyer flask containing 10 mL of H_2O , to which 15 mL of concentrated HCl was added. The system was vented with N_2 and released $^{14}\text{CO}_2$ captured in a set of three scintillation vials, each containing 15 mL of scintillation cocktail – Carbo-Sorb E and Permafluor E⁺ 2:5 (v/v). The content of vials was analysed quantitatively by LSC.

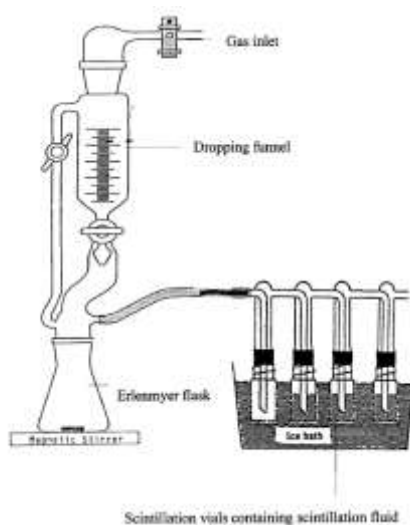


Figure B.8.1.1.3._CA-6: The apparatus used to liberate $^{14}\text{CO}_2$ from soda lime traps (copied from the study report).

All samples were analysed for the content of radioactivity using LSC method. The LSC (Liquid Scintillation Counting) analysis was performed using a Packard Tri-Carb Model 4640 counter, equipped with automatic external standardisation.

Liquid samples were analysed in triplicate, with 15 of Ultima Gold solution added to 0.1-mL aliquots of the analysed sample. The minimum sensitivity of LSC analysis for those samples was $7.8 \text{ E-}4$ ppm. It corresponded to 60 cpm when expressed as Lowest Acceptable Gross Count Rate (LAGC) and 30 cpm for Lowest Acceptable Net Count Rate (LANC), assuming Average Background (BCGK) of 30 cpm ($\text{LAGC} = 2 \times \text{BCGK}$ and $\text{LANC} = \text{LAGC} - \text{BCGK}$). The greatest probable error $\text{GPE} = 9.54\%$.

Solid samples - ~100 mg aliquots, were oxidised using Packard Model 306 sample oxidizer. Generated $^{14}\text{CO}_2$ was trapped on 6 mL Carbo-sorb E and 15 mL Perma Fluor E⁺. The minimum sensitivity of LSC analysis for those samples was $7.8 \text{ E-}4$ ppm. It corresponded to 60 cpm when expressed as Lowest Acceptable Gross Count Rate (LAGC) and 30 cpm for Lowest Acceptable Net Count Rate (LANC), assuming Average Background (BCGK) of 30 cpm ($\text{LAGC} = 2 \times \text{BCGK}$ and $\text{LANC} = \text{LAGC} - \text{BCGK}$). The greatest probable error $\text{GPE} = 9.54\%$.

Sample extracts were analysed using the following techniques:

- HPLC – major identification and quantitation method for parent compound and its degradation products;
- TLC – conformatory method for the parent compound and its degradation products;
- LC-MS – conformatory identification method for parent compound and its degradation products.

The HPLC analysis was performed using a Shimadzu SCL-6A HPLC chromatograph coupled to Ramona 5-LS radioactivity monitor and Shimadzu SPD-6A UV detector set to $\lambda = 280 \text{ nm}$. The system was equipped with

PRP-1, 5 μ m, 150 x 4.1 mm chromatographic column (Hamilton Co., Reno) and PRP-1 cartridge as a guard column. The chromatographic separation was performed in a gradient mode, using the mobile phase consisting of:

- water + 0.4% CH₃COOH as **Solvent A**, and
- CH₃CN + 0.4% CH₃COOH as **Solvent B**.

Gradient elution lasted 90 minutes. Its parameters are shown below in the table B.8.1.1.1.3._CA-3. The flow rate was set to 2 mL/min.

Table B.8.1.1.1.3._CA-3: The HPLC gradient mode used in the study.

Time [min]	Solvent ratio	
	<i>Solvent A – Water + 0.4% CH₃COOH</i>	<i>Solvent B – Acetonitrile + 0.4% CH₃COOH</i>
0	100	0
0-15	Linear gradient	
15	70	30
15 - 65	Linear gradient	
65	40	60
65 - 70	Linear gradient	
70	0	100
70 - 80	0	100
80 - 90	Linear gradient	
90	100	0

The LOD for chromatographic method, in reference to the performance of the used radioactivity detector, was determined to be 4000 dpm, what corresponded to 1.0% AR. The value was determined experimentally on the basis of the comparison of radioactivity injected and integrated area under the chromatographic peak. The linearity of the analysis, expressed as r^2 , was: $r^2 = 1.00$. Sample recoveries from the column were on average 97.4%.

The identification of the chromatographic peaks was performed by means of the comparison of their retention times R_t with those of the standards. The retention times of the known reference standards are presented below in the table B.8.1.1.1.3._CA-4.

Table B.8.1.1.1.3._CA-4: HPLC identification of Flufenacet and its degradation products in the study.

Compound	HPLC identification – retention time (R_t) [min]:
<i>Flufenacet (FOE 5043)</i>	70.0
<i>FOE Alcohol</i>	33.7
<i>FOE Oxalate</i>	16 – 20 ¹⁾
<i>FOE Sulfonic acid</i>	18 – 23 ²⁾
<i>FOE Methylsulfoxide</i>	25.3
<i>FOE Methylsulfone</i>	38.4
<i>FOE 5043 N-isomer</i>	74.4

Footnotes to the table:

- 1) Due to the variability of R_t for that compound – it ranged from 16 min. to 20 min. overlapping the range of R_t for FOE Sulfonic acid, the co-chromatography was used to verify whether the compound was indeed present in the analysed sample;
- 2) Due to the variability of R_t for that compound – it ranged from 18 min. to 23 min. overlapping the range of R_t for FOE Oxalate, the co-chromatography was used to verify whether the compound was indeed present in the analysed sample.

The TLC analysis of the extracts was performed as RP-TLC (reversed phase TLC). It was carried out on Whatman KC₁₈F TLC plates, having a dimensions 20x20 cm and 200- μ m thick, with a fluorescent indicator. The solvent system used to develop the TLC plates was CH₃CN:CH₃OH:0.5N NaCl_{aq} 2:2:1 (v/v) solution. The identification of each individual constituent of the analysed extract was performed by means of the comparison of R_f values with those of the known standards. In case of Flufenacet the average $R_f = 0.52$.

The quantitative analysis was performed using RITA 68000 Radio-TLC analyser. The LOD of the method was experimentally determined to be 300 dpm, what enabled to detect the radioactivity residues at the level of at least 1 % AR. The linearity of the analysis, expressed as r^2 was: $r^2 = 0.9998$.

The LC-MS analysis was performed using Varian 5040 HPLC equipped with a Hamilton PRP-1 150 x 4.1 mm chromatographic column and Berthold LB 505-HPLC Radioactivity Monitor, coupled with Finnigan MAT 90 MS detector.

The parameters of gradient were following:

- **Mobile phase A:** Water,
- **Mobile phase B:** CH₃OH,
- **Gradient mode:** linear from 0% B at 0 min to 100% B at 30 min.

The flow rate was set to 0.8 mL/min.

The reported parameters of MS detector were following:

- Spectrometer operated in either positive or negative mode,
- aerosol temperature: 210⁰C,
- 0.2 M ammonium acetate added post column at rate of 0.2 mL/min.

The UV-Vis absorption spectra of Flufenacet were determined at different pH – pH = 5, pH = 7 and pH = 9, using Shimadzu UV 260 spectrometer with a slit of 0.8 nm. The absorption spectrum was scanned within the wavelength range of $\lambda = 190 - 400$ nm.

Results and their discussion:

The absorption spectrum of Flufenacet, recorded at various pH for the wavelength range of $\lambda = 190 - 400$ nm, is presented below on figure B.8.1.1.1.3._CA-7. It shows that the maximum absorption for the test compound occurred at $\lambda \approx 220$ nm and the effective absorption range may be estimated to occur within the range of $\lambda = 200 - 250$ nm. Within the environmentally relevant range of $\lambda = 290 - 400$ nm the absorption of radiation was residual, what may indicate that the direct photolysis of Flufenacet on the soil surface would be negligible.

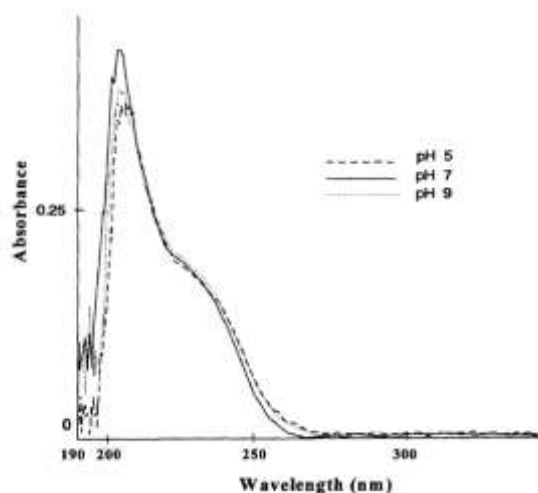


Figure B.8.1.1.1.3._CA-7: The UV-Vis absorption spectrum of Flufenacet recorded for $\lambda = 190 - 400$ nm (copied from the study report).

The examination of the microbial viability of the test soil showed that it was viable at the beginning of the study – it contained 2.3 E6 CFU/g. That parameter was not further examined.

The irradiated samples in the Suntest unit and dark control samples in the water bath were kept in the constant temperature $T = 25 \pm 1^{\circ}\text{C}$. The dark control samples in the Suntest unit were incubated at slightly lower temperature $T = 22 \pm 1^{\circ}\text{C}$. That slight -3°C , difference in incubation temperature of the two dark control samples sets was considered to have no impact on the obtained results.

The changes in the soil moisture of the samples were determined at sampling. That was done in order to check whether continuous purging of the photolysis vessels with humidified air to keep soil moisture at deserved level and by that maintain soil microbially active, was an adequate measure. The results are shown below in the table B.8.1.1.1.3._CA-5. They are presented as % change in soil moisture in comparison to the level determined on Day 0 of the incubation/irradiation. On their basis it can be stated that soil moisture was kept on the target, or even slightly higher, level, throughout the incubation phase in both irradiated and the dark control samples.

Table B.8.1.1.3_CA-5: The results of the determination of changes in soil moisture content during the experiment.

Sampling interval ¹⁾	Sampling time point		% change in soil moisture recorded in:	
	Suntest days	Natural sunlight days	Irradiated samples	Dark control
2	2.75	8.0	+12.5	+5.6
3	5.13	15.0	+12.2	+3.2
4	7.75	22.7	+8.6	+3.8
5	10.25	30.0	+9.4	+2.4

Footnotes to the table:

1) the results for sampling interval 1 – Day 0, are not given, as they serve as a reference point – 0% change;

The characteristics of the light source – xenon lamp, is presented below in graphical form on figures B.8.1.1.1.3_CA-8 – spectral irradiance graph, and B.8.1.1.1.3_CA-9 – comparison of spectral distribution of xenon lamp used in the experiment and that of the natural sunlight.

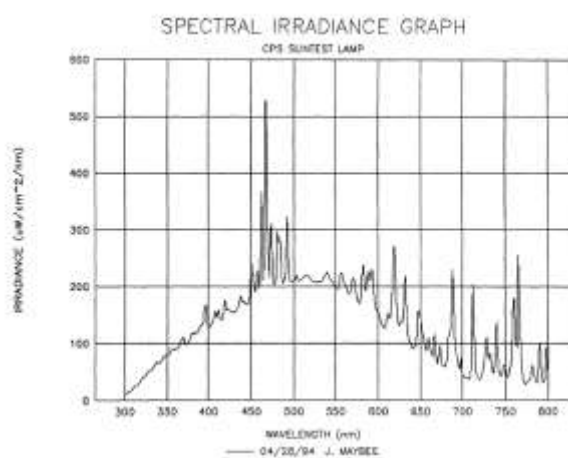


Figure B.8.1.1.3_CA-8: Spectral characteristic of the light source – xenon lamp, used in the study (copied from the study report).

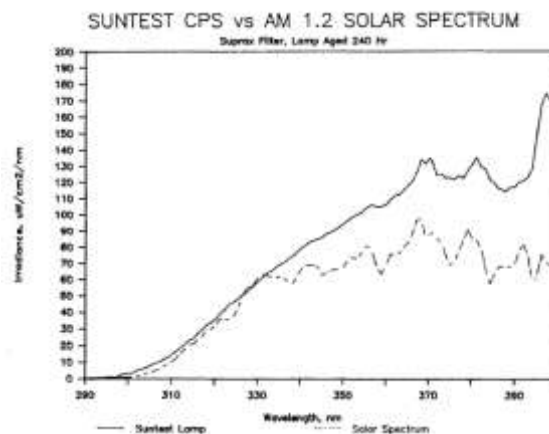


Figure B.8.1.1.3_CA-9: The comparison of the spectra of xenon lamp used in the study and of the natural sunlight (copied from the study report).

The quantitative analysis of extracts, extracted soil pellets and traps for volatile compounds, showed that the recovery of applied radioactivity throughout the study was within the recommended range:

- for irradiated samples it ranged from 98.6% AR to 102.7% AR;
- for dark control samples it was in range of 98.0 – 101.1% AR.

The recovered radioactivity was predominantly in form of extractable fraction, which slightly decreased during the experiment from 101.2% AR to 95.4% AR in irradiated samples and from 100.4% AR to 95.2 - 96.5% AR in the dark control. That decrease was correlated with increase of the amount of NER fraction formed during the experiment – up to 3.2% AR in irradiated samples and 4.4% AR in the dark control.

The level of mineralisation was not significant – 0.2% AR in irradiated samples and 0.1% AR in the dark control.

The decrease of the concentration of Flufenacet in the irradiated samples and in the dark control was comparable – from 98.4% AR at the beginning of the study to 91.2% AR at its end in irradiated samples and from 98.4% AR at the beginning of the study to 87.2% AR at its end in the dark control. The slightly faster decline in concentration of Flufenacet in the dark control samples may indicate that the degradation should be attributed rather to microbial degradation than light-induced transformation process, the conclusion drawn by the Applicant and presented in the study report.

The following degradation products were identified in both irradiated samples and dark control:

- FOE Oxalate,
- FOE Sulfonic acid,
- FOE Methylsulfoxide,
- FOE Alcohol,
- Flufenacet N-isomer.

In addition two “Unknown” fractions were found, not further identified because their concentrations at any sampling point in the study were <0.5% AR.

The compounds listed above were detected in both types of samples and in comparable amounts, what may indicate that the same transformation mechanisms were involved in degradation of Flufenacet in both irradiated and dark control samples. All that may indicate that photolysis on the soil surface is not a relevant mechanism of transformation of Flufenacet in soil. That conclusion was conformed by the results of the kinetic analysis presented in the study's report.

The detailed results of the experiment are presented below, in the table B.8.1.1.1.3_CA-6.

Table B.8.1.1.1.3_CA-6: The detailed results of the experiment.

AR		Results [%AR] obtained for:								
		Dark control samples – Suntest days					Irradiated samples – Suntest days (upper row) and Natural sunlight days ¹⁾ (bottom row)			
							0	2.75	5.13	7.75
Extracted		100.4	99.0	95.2	96.0	96.5	101.2	96.2	97.2	95.4
In extract identified as:	Flufenacet	98.4	95.0	89.5	88.6	87.2	98.2	92.6	94.0	91.2
	FOE Oxalate	n. d. ³⁾	1.1	1.8	3.3	4.6	0.2	0.4	0.2	0.6
	FOE Sulfonic acid	n. d. ³⁾	0.5	1.1	1.6	2.2	0.2	0.4	n. r. ⁶⁾	0.3
	FOE Methylsulfoxide	n. d. ³⁾	0.3	0.3	0.5	0.6	n. r. ⁶⁾	0.3	0.5	0.7
	FOE Alcohol	n. d. ³⁾	0.2	0.2	0.3	0.4	0.5	0.6	0.8	1.0
	FOE N-Isomer	1.7	1.7	1.8	1.3	1.5	1.6	1.6	1.4	1.6
	Unknown 1	n. d. ³⁾	0.1	0.3	0.3	n. r. ⁶⁾	0.2	0.1	0.1	n. r. ⁶⁾
	Unknown 2	0.3	0.1	0.2	0.1	n. r. ⁶⁾	0.3	0.2	0.2	n. r. ⁶⁾
Total identified		100.4	99.0	95.2	96.0	96.5	101.2	96.2	97.2	95.4
Bound residues (NER fraction)		n. d. ³⁾	2.1	2.7	4.2	4.4	1.5	2.3	2.7	3.2
Volatile compounds	CO ₂	n. a. ⁴⁾	n. an. ⁵⁾	0.1	0.1	0.1	<0.1	0.1	0.2	0.2
	VOC	n. a. ⁴⁾	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
	Total volatiles ²⁾	n. a. ⁴⁾	<0.1	0.1	0.1	0.1	<0.1	0.1	0.2	0.2
Total recovered		100.4	101.1	98.0	100.3	101.0	102.7	98.6	100.1	98.8

Footnotes to the table:

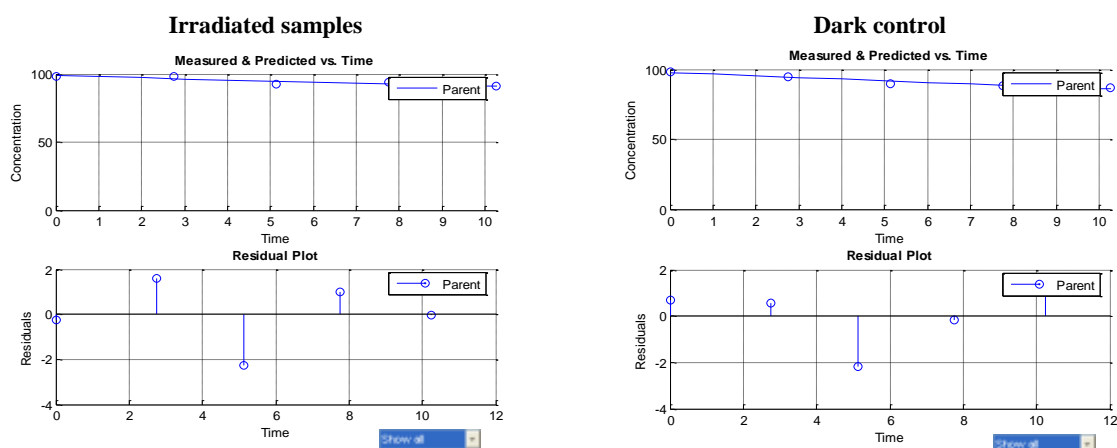
- 1) The Day 0 values for irradiated samples not reported here, as these are identical to those given for the dark control samples; all results for irradiated samples are the means of two replicates;
- 2) Sum of all volatiles as given in the study report;
- 3) n. d – not determined;
- 4) n. a. – not available, it was assumed that at the time point no volatiles would form;
- 5) n. an – not analysed, hence no value provided;
- 6) n. r – not reported; the analysis of the available results showed that the compound was not found in measurable amounts at that time point;

The data obtained for Flufenacet were further kinetically examined. The analysis was performed using first order kinetics and linear-regression model. As it does not comply with the current standards, set by FOCUS Kinetics Guidance (FOCUS, 2006) it was repeated by the RMS. It was performed using KinGUI 1.1 kinetic tool developed by Bayer. The input data used in the repeated kinetic analysis are presented below in the table B.8.1.1.1.3_CA-7. The analysis was performed using solely the SFO model.

Table B.8.1.1.1.3._CA-7: The data for Flufenacet used in the kinetic examination performed by RMS.

Irradiated sample			Dark control sample	
Time point [days]		Concentration of Flufenacet [% AR]	Time point [days]	Concentration of Flufenacet [% AR]
Suntest days (real time point)	Natural Sunlight Days (converted time point)		Suntest days (real time point)	
0.00	0.0	98.4	0.00	98.4
2.75	8.0	98.2	2.75	95.0
5.13	15.0	92.6	5.13	89.5
7.75	22.7	94.0	7.75	88.6
10.25	30.0	91.2	10.25	87.2

The results of the repeated kinetic analysis of the data obtained for Flufenacet are presented below in graphical form on figure B.8.1.1.1.3._CA-10 and in the numerical form in table B.8.1.1.1.3._CA-8.

**Figure B.8.1.1.1.3._CA-10:** The graphical results of the examination of the soil photolysis of Flufenacet.**Table B.8.1.1.1.3._CA-8:** The numerical results of the examination of the soil photolysis of Flufenacet.

Type of samples	Kinetic model	Model parameters	Statistical evaluation of the parameter					Statistical evaluation of the fit	
			Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2
					Lower	Upper			
Irradiated	SFO	M_0	98.670	1.355	94.359	102.982	-----	1.116	0.796
		k	0.0076	0.0022	5.3 E-4	0.0148	0.0209		
Dark control	SFO	M_0	97.723	1.2143	93.859	101.587	-----	1.027	0.923
		k	0.0124	0.0021	0.0059	0.0189	0.0046		

The degradation rate constant k was higher in the dark control than in irradiated sample, what indicated that in the dark control the degradation of Flufenacet was faster than in the sample exposed to the light. This was confirmed by the DT_{50} values calculated by the model, which were as follows:

- for irradiated sample $DT_{50} = 90.72$ days;
- for the dark control sample $DT_{50} = 55.90$ days

The more detailed results of the kinetic analysis of the data obtained for Flufenacet is presented further down the report, under the point B.8.1.1.2.1.3.

Conclusions:

On the basis of the obtained result it may be stated that Flufenacet is not prone to photolysis on the soil surface. The relevance of that process for the overall degradation of Flufenacet in soil is hence negligible.

Study 2:

Report: Lentz N. R., Bloomberg A. M., (2001): “Soil Photolysis of Thiadone on Loamy Sand (A Metabolite of FOE 5043).”; Ricerca LLC, Department of Environmental and Metabolic Fate, 7528 Auburn Road, Painesville, Ohio 44077, USA (performing laboratory) for Bayer Corporation, Agriculture Division, P. O. Box 4913, Kansas City, MO 64120, USA; Ricerca document No. 7410-0055-EF-001, study No. F3082103 (Bayer); Bayer Report No. 108721; 21 June 2001; study reference number: M-106297-01-1;

Guidelines: The study was performed to comply with the following Guidelines:

- US. EPA Guidelines for Pesticide Registration, Subdivision N, Section 161-3, Soil Photolysis Study.

GLP: Yes;

RMS comments: This is a newly submitted study, the aim of which was to further examine the photolytic degradation of Flufenacet in soil through the determination of the would-be photodegradation of one of its major degradation products – FOE Thiadone. It was evaluated for its compliance with the following guidelines:

- US. EPA Guidelines for Pesticide Registration, Subdivision N, Section 161-3, Soil Photolysis Study (indicated as reference Guideline in the study report);
- US EPA Guideline OPPTS 835.2410 – Photodegradation on Soil;
- SETAC Procedures for Assessing the Environmental Fate and Ecotoxicity of Pesticides, Part 1 – Fate and Behaviour in the Environment, chapter 2: Soil Photolysis, SETAC 1995;
- OECD Guidelines for the Testing of Chemicals, Proposal for a New Guideline – Phototransformation of Chemicals on Soil Surface, Draft Document January 2002 (additional reference document);

RMS stated that the study was compliant with the provisions of the Guidelines listed above, therefore it was found acceptable and is summarised below.

Summary:

The aim of the study was to examine photodegradation of FOE Thiadone – the metabolite of Flufenacet, on the soil surface through:

- a) determining the half-life of that compound when exposed to artificial sunlight;
- b) identifying the transformation pattern, and in particular the degradation products formed in amounts greater than 10% AR.

The test soil used in the experiment was loamy san soil from Janesville, Iowa, USA. That soil was declared to be also used to examine the rate of degradation FOE Thiadone in soil under aerobic conditions. Its characteristic, as provided in the study report, is given below, in table B.8.1.1.1.3._CA-9. RMS noted that the test soil was Loamy sand, according to USDA classification. SETAC Guidelines and Draft OECD Guideline recommend to use Silty loam or clay loam soil rather than any sandy soil. These Guidelines also recommend however, that the test soil should be the same as used in examination of the degradation of the test compound in soil under aerobic conditions. RMS stated that that requirement was fulfilled.

Additionally, the selected soil is admissible according to the provisions of US EPA Guideline OPPTS 835.2410 – Photodegradation on Soil, when cross-referenced to the US EPA Guideline OPPTS 835.4100 – Aerobic Degradation in Soil.

As a result, it can be stated that the test soil, although being sandy soil, was selected correctly, in line with the provisions of the current Guidelines.

The test soil was sampled from the area in Iowa, on which maize was grown and which was selected for monitoring of the residues of Flufenacet in GW compartment. In the study report it was declared to come from the field not being treated with any pesticide during the period 1995 - 1998. After being shipped to the test laboratory, the test soil was air-dried and sieved through 2-m sieve to remove all skeletal elements.

Table B.8.1.1.1.3._CA-9: The characteristic of soil used in the study.

Parameter	Soil:
Soil origin	Janesville, Iowa, USA
Soil type (as reported in the study)	Loamy sand
Soil type (USDA, calculated by RMS)	US Loamy sand
Particle size distribution	Sand [%]
	79.2
	Silt [%]
	12.0
	Clay [%]
	8.8
pH	7.2
Organic matter content (OM) [%]	1.91
Organic carbon content (C _{org}) [%] ¹⁾	1.11
Cation Exchange Capacity – CEC [mEq/100g]	5.64
Bulk density [g/cm ³]	1.34
Moisture holding capacity at ½ bar [%]	9.92
Soil microbial activity expressed as [CFU/g soil] ²⁾ determined:	at the beginning of the study (DAT 0)
	9.7 E6 – soil bacteria/ 0.12 E6 – soil fungi
	at the end of the study (DAT 14)
	13 E6 – soil bacteria/ 0.13 E6 – soil fungi

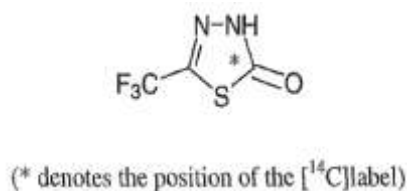
Footnotes to the table:

- 1) Value recalculated by the RMS from that reporting OM content given in the study report using the following equation: OM = 1.724 * OC;
 2) CFU/ g soil = Colony Forming Units/gram of test soil (determined using plate count agar method).

The experiment was performed in 59-mL (2 oz.) flint glass sample jars with either quartz glass lids (irradiated samples) or opaque screw caps (dark control samples). The number of these vessels was 36. To each of them were weighed 5-g. (d.w.) portions of the test soil, having a moisture content adjusted to 75% of ½ bar. These samples were treated with the test compound applied as **Application solution** characterised further down the report. The target application dose (theoretical) was 3.2 ppm – a half of the application dose of Flufenacet used in a previously summarised **Study 1**. 1 day later additional samples were prepared, assigned as A-H, micro1 and micro 2. They were treated in the same way as other samples in 59-mL flint glass jars.

Additionally, 4 separate samples were prepared for quantitation of volatile compounds formed during experiment (including CO₂). For that purpose were used larger flint glass jars, having a volume of 500 mL, also equipped with either quartz glass lids or opaque screw caps. To each of them was weighed 15-g. (d. w.) portion of the test soil, brought to a moisture content of 75% of ½ bar. These samples were treated with three times higher amount of the test compound, to obtain application dose of 9.6 ppm. The incubation vessels were equipped with modified lids/screw caps – in each were drilled two 1/8 inch (3.175 mm) holes, through which the incubation vessel was attached to the device collecting volatile compounds.

The test compound was [2-¹⁴C]-Thiadone, having a specific activity of 50 mCi/mmol, corresponding to 652680 dpm/μg. It was provided in form of a solution in acetone (**Stock solution**), having a volume of 9 mL and containing 6 mCi (0.12 mmol) of the test compound. **Stock solution** was shipped and stored frozen until being used. The structural formula of the test compound, with radiolabelling position indicated by an asterisk, is presented below on figure B.8.1.1.1.3._CA-11.

**Figure B.8.1.1.1.3._CA-11:** The structural formula of [2-¹⁴C]-Thiadone used in the experiment (copied from the study report).

Stock solution was used to prepare the a **Application solution**, used to treat soil in test vessels. To do that 650 μL of the **Stock solution**, containing 1.690 mg of FOE Thiadone, was transferred to 25-mL volumetric flask, evaporated to dryness under the stream of N₂, and the residue redissolved in 2.5 mL of CH₃CN. The solution was brought to volume with HPLC grade water and analysed by LSC to determine its exact concentration. Additionally the HPLC analysis (with LSC detection) was performed to determine the radiopurity of the so prepared **Application solution**. Its measured concentration was 16.9 μg/250 μL (11,030,600 dpm/250 μL) and radiochemical purity 95.3%.

The 250- μ L aliquots of so prepared **Application solution** were used to treat soil in each of the 36 sample jars. It was dispensed to the soil surface using 250- μ L Hamilton gas-tight syringe. The amount of the **Application solution** added to each jar was such to obtain the fortification level of 3.2 ppm FOE Thiadone. That value was calculated using the following assumptions: 100% conversion of Flufenacet to Thiadone, application dose for Flufenacet (from **Study 1**) of 6.9 ppm, molecular weight of Flufenacet $M = 363$ g/mol and that of FOE Thiadone $M = 170$ g/mol.

All samples designated to be irradiated were sealed immediately after treatment with quartz lids weighed and placed in the water bath set to $T = 20 \pm 1^\circ\text{C}$ in irradiation chamber. The dark control samples immediately after being treated with the test compound were sealed with opaque screw caps, weighed and stored in the dark at $T = 20 \pm 1^\circ\text{C}$ until being analysed.

The Day-0 samples were extracted immediately after treatment with the test compound.

Four larger samples, designated for determination of the volatile compounds, were treated each with 750 μ L of the **Application solution**. Two of them were then immediately sealed with drilled quartz glass lids, attached to the flow-through devices collecting volatile compounds and placed in the water bath set to $T = 20 \pm 1^\circ\text{C}$ in irradiation chamber. Two remaining samples, serving as dark controls, were also sealed immediately after treatment with opaque screw caps, attached to the devices collecting volatile compounds and placed in the dark under the constant temperature $T = 20 \pm 1^\circ\text{C}$.

The device for collecting volatile compound consisted of:

- a small pump pumping moisturized air thorough each sample placed at the beginning of the inlet branch (common for all samples);
- Carbotrap™ 400 cartridge, collecting VOC fraction, followed by three traps filled each with ~ 100 mL of 1N NaOH_{aq} to collect formed CO_2 , at the end of the outlet branch (separate for each vessel).

All samples designated to be irradiated were placed on a fibreglass tray filled with water up to the level of 2.54 cm. Water continuously circulated, at rate 15 L/min through a constant-temperature bath set to $T = 20 \pm 1^\circ\text{C}$. The area on which they were placed was ~ 50.8 cm in diameter, irradiated by a Xenon lamp (artificial light source). Samples were rotated at each sampling point in order to equalize the amount of radiation received by each of them. The samples were irradiated for up to 14 days in 12-hours light/12-hours darkness regime.

The light source used in the experiment was a 5000-W Xenon lamp, emitting light in range of $\lambda > 290$ nm – a range of natural sunlight reaching the soil surface. Lower wavelengths were eliminated using appropriate filters. It was monitored for the intensity of light emitted within the range of $\lambda = 250 - 750$ nm, subsequently compared to the intensity of the natural sunlight recorded for Painesville, OH, in June.

The design of the irradiation device used in the experiment is shown below on figure B.8.1.1.1.3._CA-12.

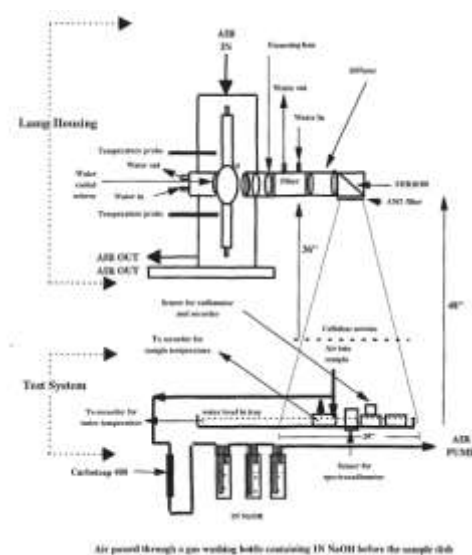


Figure B.8.1.1.1.3._CA-12: The schematic presentation of the photolysis system used in the experiment (copied from the study report).

At the designated time points – Day 0.5, Day 1, Day 2, Day 3, Day 5, Day 7, Day 10 and Day 14, duplicate irradiated and dark-control samples were taken for further analysis. On the same time points the alkaline solutions from CO_2 -traps were taken for analysis after being replaced with fresh portions of 1N NaOH_{aq} . The

Carbotrap cartridges for collecting VOCs were changed and analysed on the following sampling points: Day 3, Day 7, Day 10 and Day 14.

Soil from each sample collected at the designated time-points listed above was processed and analysed quantitatively and qualitatively for residues of [^{14}C] Thiadone using the analytical procedure presented below on figure B.8.1.1.1.3._CA-13. The 5-g portions of test soils were taken for the analysis.

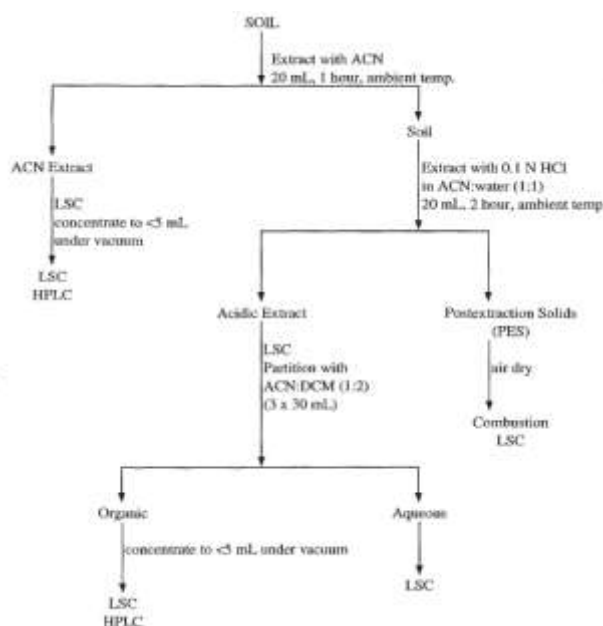


Figure B.8.1.1.1.3._CA-13: The sample-processing procedure used in the experiment (copied from the study report).

The extracted soil pellets were allowed to air dry at ambient temperature, ground and their three 500-mg aliquots analysed after combustion for radioactivity content.

The collected VOC-traps was analysed, after combustion of their content, for captured radioactivity using LSC method.

The radioactivity trapped in each alkaline trap for $^{14}\text{CO}_2$ was determined by LSC. That was done in 2-mL aliquots to which 10 mL of liquid scintillation cocktail was added. The conformation of that trapped radioactivity was $^{14}\text{CO}_2$, was done in a following way:

- the content of alkaline traps for $^{14}\text{CO}_2$ collected at each sampling point was pooled;
- next to its 2-mL aliquots was added 5 mL of 5% BaCl_2 /5% NH_4Cl aqueous solution;
- sample was then thoroughly mixed and formed solid precipitated by centrifugation;
- finally supernatants analysed by LSC.

All samples were analysed for the content of radioactivity using LSC method. The LSC (Liquid Scintillation Counting) analysis was performed using either Tractor Mark V Model 5303 LS counter or Beckman LS 6500 counter.

Liquid samples were analysed in duplicate with 5 mL or 10 mL of Ultima Gold liquid scintillation cocktail. The counting of each analysed sample lasted for 2 minutes. The detection limit was calculated to be 87 dpm with 95% confidence level. The average background level was set to 38 dpm.

Solid samples (500-mg aliquots) were analysed in triplicate by their combustion in biological oxidiser. The evolved $^{14}\text{CO}_2$ was trapped in 20 mL of Carbon 14 Cocktail and counted by LSC. The results were corrected for oxidiser efficiency, determined to be in range of 95-102%.

Sample extracts were analysed using the following techniques:

- HPLC – major identification and quantitation method for parent compound and its degradation products;
- LC-MS – conformatory identification method for parent compound and its degradation products.

The HPLC analysis was performed using a Waters™ HPLC system equipped with autosampler, Tunable Absorbance Detector and fraction collector, coupled to one of the following LSC detectors:

- Radiomatic A-500 Radio-chromatography Detector;
- IN/US β -RAM Radio-HPLC Detector.

The system was equipped with Phenomenex Luna™, 5 μ m C18, 150 x 4.6 mm chromatographic column and Zorbax® Rx-C18 10 x 4.6 mm guard column. The chromatographic separation was performed in a gradient mode, using the mobile phase consisting of:

- water + 0.4% CH₃COOH as **Solvent A**, and
- CH₃CN + 0.4% CH₃COOH as **Solvent B**.

Gradient elution lasted 70 minutes. Its parameters are shown below in the table B.8.1.1.1.3._CA-9. The flow rate was set to 1.0 mL/min.

Table B.8.1.1.1.3._CA-9: The HPLC gradient mode used in the study.

Time [min]	Solvent ratio	
	<i>Solvent A – Water + 0.4% CH₃COOH</i>	<i>Solvent B – Acetonitrile + 0.4% CH₃COOH</i>
0	100	0
0 – 40	Linear gradient	
40	30	70
40 – 60	Hold	
60	30	70
60 – 61	Gradient	
61	100	0
61 – 70	100	0

The minimum detection limit for HPLC method was 300 dpm and its linearity, expressed as r^2 , was: $r^2 = 0.99$. The average recovery of the chromatographed samples was 97.1%.

Using these values, the LOD for CH₃CN extracts, when 50- μ L sample was injected onto chromatographic column, was 0.6% AR. For CH₃CN/0.1N HCl extracts (the same analysed volume) the LOD was 2.8% AR.

The identification of the chromatographic peaks was performed by means of the comparison of their retention times R_t with those of the standards.

The LC-MS analysis was performed using Finnigan SSQ710 LC/MS device equipped with a Phenomenex Columbus 5 μ m C8 100 x 2 mm LC column. The chromatographic analysis was carried out in a gradient mode. Its parameters were following:

- **Mobile phase A:** 0.05% HCOOH in Water,
- **Mobile phase B:** CH₃OH,
- **Gradient mode:** A/B 1:1 hold 2 min to A/B 3:7 at 8 min, or A/B 100:0 hold 1 min to A/B 1:1 at 5 min.

The flow rate was set to 0.2 mL/min.

The reported parameters of MS detector were following:

- Ionization mode: (-)ESI;
- Mass range: 115 – 300 amu;
- Scan rate: 1.5 sec/scan;
- Source temperature: 220°C;
- ESI spray voltage: 4.0 kV.

The UV-Vis absorption spectrum of Thiadone was determined using GBC 918 UV-Vis spectrometer with a slit of 2 nm. The absorption spectrum was scanned within the wavelength range of $\lambda = 200 - 800$ nm at a scanning rate 720 nm/min.

Results and their discussion:

The absorption spectrum of FOE Thiadone recorded for the wavelength range of $\lambda = 200 - 800$ nm is presented below on figure B.8.1.1.1.3._CA-14. It shows that the effective absorption occurred within the wavelength range of $\lambda = 200 - 270$ nm. Within the environmentally relevant range of $\lambda = 290 - 800$ nm it was residual, although some absorption was observed at $\lambda = 290$ nm. That, according to the Applicant, possibly explained the observed slight enhancement of degradation of Thiadone in irradiated samples.

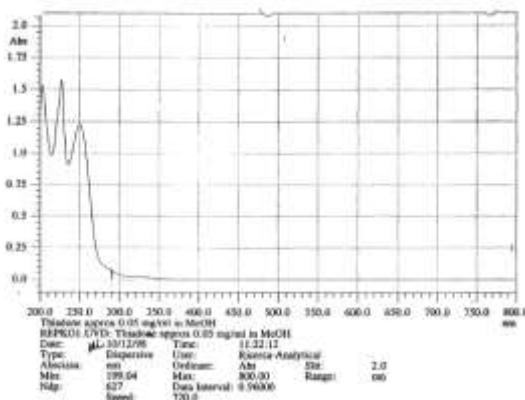


Figure B.8.1.1.3._CA-14: The UV-Vis absorption spectrum of FOE Thiadone recorded for $\lambda = 200 - 800$ nm (copied from the study report).

The examination of the microbial viability of the test soil showed that it was viable at the beginning of the study – it contained 9.7 E6 CFU/g of bacteria and 0.12 E6 CFU/g of fungi. It was demonstrated to be biologically viable throughout the study – measured at the end of irradiation/incubation content of bacteria was 13 E6 CFU/g and that of fungi – 0.13 E6 CFU/g of fungi.

The monitoring of incubation temperature showed that both irradiated and dark control samples were kept in the constant temperature $T = 20 \pm 1^\circ\text{C}$.

The changes in the soil moisture of the samples were determined at sampling. That was done in order to check whether continuous purging of the photolysis vessels with humidified air, to keep soil moisture at deserved level and by that maintain it microbially active, was an adequate measure. The results are shown below in the table B.8.1.1.3._CA-10, as % change in soil moisture in comparison to the level determined on Day 0 of the incubation/irradiation. On their basis it can be stated that soil moisture was kept on the target level throughout the incubation phase in both irradiated and the dark control samples.

Table B.8.1.1.3._CA-10: The results of the determination of changes in soil moisture content during the experiment.

Sampling interval ¹⁾	Sampling time point	% change in soil moisture recorded in:			
		Irradiated samples		Dark control	
		Replicate 1	Replicate 2	Replicate 1	Replicate 2
2	Day 0.5	+4.33	+7.38	-0.13	not recorded
3	Day 1	not recorded	not recorded	not recorded	not recorded
4	Day 2	-0.40	+2.95	-0.43	-0.34
5	Day 3	+2.78	+3.56	-0.19	-0.69
6	Day 5	-0.15	+3.80	+4.56	-0.35
7	Day 7	not recorded	+3.16	+0.09	+0.69
8	Day 10	+2.54	+2.27	-0.34	-0.37
9	Day 14	not recorded	not recorded	not recorded	not recorded

Footnotes to the table:

1) The results for sampling interval 1 – Day 0, are not given, as they serve as a reference point – 0% change;

The characteristics of the light source – xenon lamp, is presented in a graphical form on figure B.8.1.1.3._CA-15 (comparison of spectral distribution of xenon lamp used in the experiment and natural sunlight).

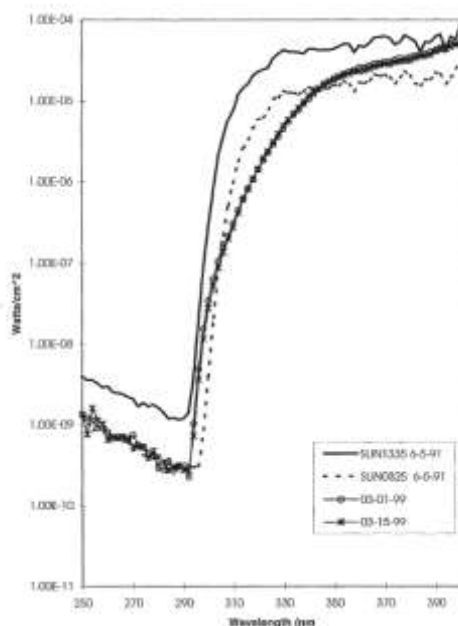


Figure B.8.1.1.1.3_CA-15: The comparison of the spectra of xenon lamp used in the study and of natural sunlight (copied from the study report).

The quantitative analysis of extracts, extracted soil pellets and traps for volatile compounds showed that the recovery of applied radioactivity throughout the study was within the recommended range:

- for irradiated samples it ranged from 93.8 – 102.1% AR, with mean recovery 97.7% AR;
- for dark control samples it was in range of 93.1 – 102.1% AR with mean recovery 97.9% AR.

The level of radioactivity extracted from soil decreased with time:

- in irradiated samples from 101.6% AR on Day 0 to 14.5 %AR on Day 14;
- in dark control samples from 101.6% AR on Day 0 to 17.3 %AR on Day 14.

It was correlated with the formation of volatile compounds, mainly CO₂, detected on Day 14 in amounts:

- 62.5% AR (total volatiles) in irradiated samples;
- 60.1% AR (total volatiles) in dark control samples.

It was also correlated with the formation of NER fraction, comparable in irradiated and dark control samples.

It reached the maximum level on DAT 10:

- 21.2% AR in irradiated samples,
- 17.1% AR in the dark control samples.

After that time point a slight decrease was observed.

The decrease of the concentration of FOE Thiadone in the irradiated samples and in the dark control was comparable, and looked as follows:

- for irradiated samples from 96.7% AR at the beginning of the study to 7.2% AR at its end (Day 14);
- for the dark control samples 96.7% AR at the beginning of the study to 13.3% AR at its end (Day 14).

The slightly faster decline in concentration of FOE Thiadone in the irradiated samples may be due to residual light absorption at $\lambda = 290$ nm, but in general it may be stated that the degradation should be attributed rather to microbial degradation than light-induced transformation process. Such conclusion was drawn by the Applicant and presented in the study report.

Apart from FOE Thiadone following compounds were identified in both irradiated samples and dark control:

- propionic acid conjugate of FOE Thiadone,
- Other fraction,
- fortification impurity (1),
- fortification impurity (2).

Propionic acid conjugate of FOE Thiadone was detected in higher amounts in dark control samples while the levels of the other fractions detected were comparable. That may indicate that the same transformation mechanisms were involved in degradation of FOE Thiadone in both irradiated and dark control samples. Therefore, photolysis on the soil surface does not seem to be a relevant mechanism of transformation of FOE

Thiadone in soil. That conclusion was conformed by the results of the kinetic analysis presented in the study's report.

The detailed results of the experiment are presented below, in two tables: B.8.1.1.1.3_CA-11 for irradiated samples and B.8.1.1.1.3_CA-12 for the dark control.

Table B.8.1.1.1.3_CA-11: The detailed results of the experiment obtained for irradiated samples.

AR		Results [%AR] obtained for the sampling time point ¹⁾ :								
		Day 0	Day 0.5	Day 1	Day 2	Day 3	Day 5	Day 7	Day 10	Day 14
Extracted	CH ₃ CN extract	98.4	73.4	75.2	47.1	43.5	32.4	17.8	11.6	6.3
	CH ₃ CN/HCl extract	3.2	7.6	4.1	9.1	11.7	9.1	13.2	11.3	8.2
	Total extracted	101.6	81.0	79.3	56.2	55.2	41.5	31.0	22.9	14.5
In extract identified as:	FOE Thiadone	96.7	79.2	77.3	52.3	48.2	35.2	21.6	12.5	7.2
	Propionic acid conjugate of FOE Thiadone	n. f. ³⁾	0.6	0.9	2.3	4.7	3.8	5.4	6.1	2.9
	Fortification impurity (1) (<i>R_t</i> = 22.5-23.5 min)	0.5	0.2	n. f. ³⁾	0.5	n. f. ³⁾	n. f. ³⁾	0.9	n. f. ³⁾	n. f. ³⁾
	Fortification impurity (2) (<i>R_t</i> = 50.0-51.5 min)	1.2	0.9	1.1	1.1	1.1	0.9	0.8	0.8	1.1
	Others	3.2	0.1	n. f. ³⁾	n. f. ³⁾	1.2	1.6	2.3	3.5	3.3
	Total identified	101.6	81.0	79.3	56.2	55.2	41.5	31.0	22.9	14.5
	Bound residues	0.5	6.8	6.3	14.4	16.4	14.5	20.9	21.2	19.4
Volatile compounds	CO ₂	n. d. ⁴⁾	6.0	11.2	23.4	27.9	38.8	43.8	53.5	57.8
	VOC	n. d. ⁴⁾	n. a. ⁵⁾	n. a. ⁵⁾	n. a. ⁵⁾	1.0	1.0	2.8	3.9	4.7
	Total volatiles²⁾	n. d.⁴⁾	6.0	11.2	23.4	28.9	39.8	46.5	57.4	62.5
Total recovered		102.1	93.8	96.8	94.0	100.5	95.8	98.5	101.5	96.4

Footnotes to the table:

- 1) All values are the averages of two replicates;
- 2) Sum of all volatiles as given in the study report;
- 3) n. f. – not found; the compound not detected at that time point;
- 4) n. d. – not determined as at that time point no volatile compounds were expected to be formed;
- 5) n. a. – not analysed;

Table B.8.1.1.1.3_CA-12: The detailed results of the experiment obtained for the dark control.

AR		Results [%AR] obtained for the sampling time point:								
		Day 0	Day 0.5	Day 1	Day 2	Day 3	Day 5	Day 7	Day 10	Day 14
Extracted	CH ₃ CN extract	98.4	81.1	75.6	63.4	55.1	43.3	30.2	19.1	11.7
	CH ₃ CN/HCl extract	3.2	5.2	4.7	5.9	10.4	8.4	13.3	10.4	5.6
	Total extracted	101.6	86.3	80.3	69.2	65.5	51.7	43.5	29.5	17.3
In extract identified as:	FOE Thiadone	96.7	83.6	78.1	65.7	59.8	41.1	28.9	18.3	13.3
	Propionic acid conjugate of FOE Thiadone	n. f. ³⁾	0.2	0.4	1.3	3.6	7.7	12.0	8.6	2.1
	Fortification impurity (1) (<i>R_t</i> = 22.5-23.5 min)	0.5	1.0	0.9	0.7	0.7	1.0	0.5	0.4	n. f. ³⁾
	Fortification impurity (2) (<i>R_t</i> = 50.0-51.5 min)	1.2	1.3	0.9	1.2	1.0	0.9	0.9	0.7	0.8
	Others	3.2	0.2	n. f. ³⁾	0.4	0.4	1.0	1.2	1.5	1.1
	Total identified	101.6	86.3	80.3	69.3	65.5	51.7	43.5	29.5	17.3
	Bound residues	0.5	2.9	4.6	6.8	8.9	13.9	14.4	17.1	15.7
Volatile compounds	CO ₂	n. d. ⁴⁾	5.9	11.2	18.1	24.2	33.9	41.3	51.2	57.6
	VOC	n. d. ⁴⁾	n. a. ⁵⁾	n. a. ⁵⁾	n. a. ⁵⁾	0.8	0.8	1.7	2.0	2.5
	Total volatiles²⁾	n. d.⁴⁾	5.9	11.2	18.1	25.0	34.7	43.0	53.2	60.1
Total recovered		102.1	95.1	96.1	94.2	99.4	100.3	100.9	99.8	93.1

Footnotes to the table:

- 1) All values are the averages of two replicates;
- 2) Sum of all volatiles as given in the study report;
- 3) n. f. – not found; the compound not detected at that time point;
- 4) n. d. – not determined as at that time point no volatile compounds were expected to be formed;
- 5) n. a. – not analysed;

The data obtained for FOE Thiadone were further kinetically examined. The analysis was performed using first order kinetics and linear-regression model. As it does not comply with the current standards, set by FOCUS Kinetics Guidance (FOCUS, 2006) it is not presented here.

Instead RMS performed its own kinetic analysis of the data using KinGUI 1.1 kinetic tool developed by Bayer. The input data used in that analysis, identical with those used by the Applicant in the original study report, are presented below in the table B.8.1.1.1.3._CA-13. The average values were used in the fitting.

Table B.8.1.1.1.3._CA-13: The data for FOE Thiadone used in the kinetic examination performed by RMS.

Time point	Concentration of FOE Thiadone in:					
	Irradiated samples			Dark control samples		
	Replicate 1	Replicate 2	Average	Replicate 1	Replicate 2	Average
Day 0	96.52	96.92	96.7	96.52	96.92	96.7
Day 0.5	74.22	84.03	79.2	85.08	82.10	83.6
Day 1	76.95	77.53	77.3	79.12	76.98	78.1
Day 2	52.80	51.65	52.3	67.66	63.64	65.7
Day 3	42.77	53.50	48.2	65.13	54.34	59.8
Day 5	35.51	34.67	35.2	47.31	34.82	41.1
Day 7	21.65	21.48	21.6	22.61	34.91	28.9
Day 10	11.13	13.85	12.5	21.80	14.71	18.3
Day 14	6.30	7.94	7.2	12.41	13.94	13.3

The results of the repeated kinetic analysis of the data obtained for FOE Thiadone are presented below in graphical form on figure B.8.1.1.1.3._CA-16 and in the numerical form in table B.8.1.1.1.3._CA-14. Only results obtained using SFO model are presented. The detailed results of the kinetic analysis of the results of the study are provided under the point B.8.1.1.2.1.3.

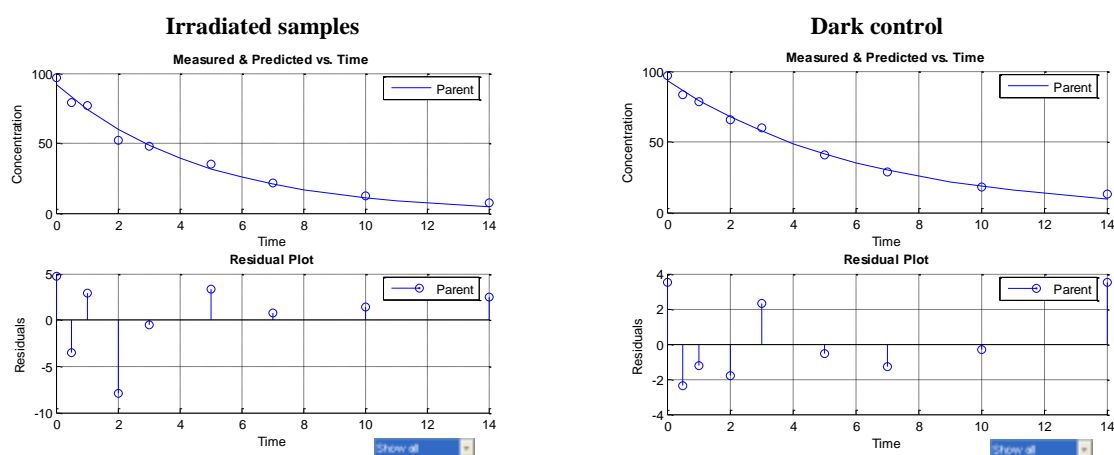


Figure B.8.1.1.1.3._CA-16: The graphical results of the examination of the soil photolysis of FOE Thiadone.

Table B.8.1.1.1.3._CA-14: The numerical results of the examination of the soil photolysis of FOE Thiadone.

Type of samples	Kinetic model	Model parameters	Statistical evaluation of the parameter					Statistical evaluation of the fit	
			Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2
					Lower	Upper			
Irradiated	SFO	M_0	91.999	2.887	85.174	98.826	----	6.250	0.985
		k	0.2120	0.0162	0.1736	0.2503	1.8 E-6		
Dark control	SFO	M_0	93.209	1.580	89.474	96.943	----	3.229	0.994
		k	0.1612	0.0070	0.1447	0.1776	3.6 E-8		

The degradation rate constant k was slightly higher in the irradiated samples than in the dark control, what indicates that in former samples the degradation was faster. That was conformed by the DT_{50} values calculated by the model, which were as follows:

- for irradiated sample $DT_{50} = 3.27$ days;
- for the dark control sample $DT_{50} = 4.30$ days

That phenomenon may be partly attributed to the fact that the residual absorption was observed for FOE Thiadone at $\lambda = 290$ nm. At the same time it was noted that dark controls were drier than irradiated samples, what may have influenced the activity of soil microorganisms and hence slow down the degradation of the test compound. It shall be also noted that the difference in DT_{50} values was not that significant to indicate substantial contribution of phototransformation processes to the degradation of FOE Thiadone in soil. Finally, the comparison of the metabolite profiles in irradiated and dark control samples does not seem to indicate that light-induced processes played a significant, if any, role in degradation of FOE Thiadone on the soil surface.

Conclusions:

On the basis of the obtained result it may be stated that FOE Thiadone may be prone to some photolysis on the soil surface, but the process is not expected to significantly contribute to the degradation of that compound in soil. It shall also be pointed out that the probability that FOE Thiadone occurs in significant amounts on the soil surface is minimal and hence the relevance of soil photolysis for the overall degradation of FOE Thiadone in soil should be considered negligible.

Summary: Photodegradation of Flufenacet on soil surface

The soil photolysis of Flufenacet was examined in one soil – US Sandy loam, using the test compound radiolabelled in one position – uniformly at phenyl ring. The experiment was performed using soil that was demonstrated to be biologically viable throughout the whole irradiation/incubation period. Samples were irradiated with artificial light (Xenon lamp) continuously for 10.25 days, corresponding to 30 days of natural summer sunlight (conditions relevant for Phoenix, Arizona, USA). The key results of the examination are presented below in the table B.8.1.1.1.3_CA-15.

Table B.8.1.1.1.3_CA-15: The key results obtained for Flufenacet in soil photolysis study

Parameter		Results obtained for:	
		Irradiated sample	Dark control
Terminal transformation products	Mineralisation (CO ₂) at the end of the study	0.2% AR; DAT ²⁾ 10.25; 30 th DNS ³⁾	0.1% AR; DAT ²⁾ 10.25; 30 th DNS ³⁾
	Max. NER level	3.2% AR; DAT ²⁾ 10.25; 30 th DNS ³⁾	4.4% AR; DAT ²⁾ 10.25; 30 th DNS ³⁾
Identified compounds	Flufenacet – amount at study's end	91.2 AR; DAT ²⁾ 10.25; 30 th DNS ³⁾	87.2 AR; DAT ²⁾ 10.25; 30 th DNS ³⁾
	FOE Oxalate – max. amount	0.6% AR; DAT ²⁾ 10.25; 30 th DNS ³⁾	4.6% AR; DAT ²⁾ 10.25; 30 th DNS ³⁾
	FOE Sulfonic acid – max. amount	0.4% AR; DAT ²⁾ 5.13; 15 th DNS ³⁾	2.2% AR; DAT ²⁾ 10.25; 30 th DNS ³⁾
	FOE Methylsulfoxide – max. amount	0.7% AR; DAT ²⁾ 10.25; 30 th DNS ³⁾	0.6% AR; DAT ²⁾ 10.25; 30 th DNS ³⁾
	FOE Alcohol – max. amount	1.0% AR; DAT ²⁾ 10.25; 30 th DNS ³⁾	0.4% AR; DAT ²⁾ 10.25; 30 th DNS ³⁾
	FOE N-isomer ¹⁾ – max. amount	1.8% AR; DAT ²⁾ 5.13; 15 th DNS ³⁾	0.3% AR; DAT ²⁾ 2.75; 8 th DNS ³⁾
Kinetics of the process	rate constant k [days ⁻¹]	0.0076	0.0124
	DT_{50} [days]	90.72	55.90

Footnotes to the table:

- 1) N-isomer of Flufenacet (for the structural formula, please refer to the table in Appendix 1 - List of Evaluated Compounds;
- 2) DAT stands for Days After Treatment, the real sampling point in the experiment;
- 3) DNS – Days of Natural Sunlight, the sampling point related to the Natural Summer Day sunlight conditions in Tucson Arizona, USA

On the basis of these results it was stated that Flufenacet is not prone to photolytical degradation on the soil surface, therefore soil photolysis will not be a relevant degradation mechanism of Flufenacet in soil.

Additionally the potential of phototransformation of FOE Thiadone – the major degradation product of Flufenacet, on soil surface was examined. This was done on one biologically viable soil – US Loamy sand, using the test compound radiolabelled in C2 position. The experiment lasted for 14 days and samples were irradiated with artificial light – emitted by Xenon lamp, bearing the characteristic (wavelength range and light intensity) comparable to that determined for natural summer sunlight at Painesville, OH, USA in June (averaged intensity). The irradiation was carried out in regime 12h irradiation/12 h darkness.

It was demonstrated that the degradation of FOE Thiadone was rapid in both irradiated and dark control samples, with high level of mineralisation – ~57% AR at the study's end (DAT 14) and up to 21% AR in form of NER. The concentrations of FOE Thiadone at the study's end were 7.2% AR in irradiated samples and 13.3% AR in the dark control. The determined kinetic parameters for the degradation of FOE Thiadone were:

- in irradiated samples $k = 0.2120 \text{ day}^{-1}$ and $DT_{50} = 3.27 \text{ days}$;
- in the dark control $k = 0.1612 \text{ day}^{-1}$ and $DT_{50} = 4.30 \text{ days}$.

Faster degradation of FOE Thiadone observed in irradiated samples was postulated in the study report to be due to the fact that the compound displayed residual absorption of UV-light at $\lambda = 290 \text{ nm}$. RMS however noticed that the difference was not substantial and it may be due to other factors, such as slightly lower microbial activity in dark control samples resulting from lower soil moisture content.

It was also stated that only one transformation product, common also to that radiolabelling position in examining degradation of Flufenacet in aerobic and anaerobic soils, was detected – propionic acid conjugate of Thiadone, formed in greater amounts in dark control samples.

All that may indicate that also in case of the Thiadiazole moiety of Flufenacet phototransformation on soil surface may not be a relevant degradation process of for that compound. The statement is valid also for the degradation products observed for Thiadiazole moiety, and FOE Thiadone in particular. That may also be due to the fact that it may not be present on the soil surface in amounts sufficient to make soil photolysis relevant transformation mechanism.

The proposed final set of endpoints is presented below, in format recommended for the EU-agreed endpoints (SANCO/12483/2014-rev.2; 12 December 2014).

Route of degradation (photolysis) on soil (Regulation (EU) N° 283/2013, Annex Part A, point 7.1.1.3)

Metabolites that may require further consideration for risk assessment - name and/or code, % of applied (range and maximum)

Mineralisation at study end

Non-extractable residues at study end

Not relevant – Flufenacet was demonstrated to be not prone to photolytical degradation on the soil surface.

0.2 % after 10.25 days, [¹⁴C-Phenyl]-label (n= 1) – irradiated sample;

0.1 % after 10.25 days, [¹⁴C-Phenyl]-label (n= 1) – dark control

3.2 % after 10.25 days, [¹⁴C-Phenyl]-label (n= 1) – irradiated sample

4.4 % after 10.25 days, [¹⁴C-Phenyl]-label (n= 1) – dark control

B. 8.1.1.1.4. – Route of degradation in soil – summary and conclusions

The route of degradation of the acetanilide herbicide Flufenacet in aerobic soil was extensively examined in eight agricultural soils – seven originating from the EU and one from US. The test compound – Flufenacet, was radiolabelled in one of the following three following positions:

- uniformly in phenyl ring – compound tested on four soils,
- position C2 in thiadiazole moiety – test performed on one soil,
- position C5 in thiadiazole moiety – examined in four soils.

These data were presented in five unpublished studies submitted specifically for the purpose of this assessment. Additionally the data relevant for determining transformation pattern of Flufenacet in aerobic soil, relevant for regulatory purposes, were found in one scientific paper, examining the degradation of Flufenacet radiolabelled uniformly in phenyl ring in two US soils. That study was based on a non-GLP regulatory study, conceived as a bridging study for laboratory and field experiments on the degradation of Flufenacet in soil. That study was verified by RMS and found acceptable. Therefore the results of the literature study based on it were included into evaluation.

The key results of the examination of transformation of Flufenacet are presented in the tabularised form below (tables B.8.1.1.1.4._CA-1 – B.8.1.1.1.4._CA-4), separately for the compound radiolabelled in phenyl ring and in thiadiazole moiety.

Table B.8.1.1.1.4._CA-1: The levels of mineralisation and NER fraction formed, and identified degradation products in experiments with [Phenyl-U-¹⁴C] Flufenacet.

Study	Soil		Level of mineralisation [% AR]:		Level of NER [% AR]:			Identified degradation products
	Name	Type (USDA)	After ~100 days	at the study's end	Max.	After ~100 days	at the study's end	
Kelley <i>et al.</i> ; 1995	BBA 2.2	Loamy sand	12.6 DAT 100	14.2 DAT 120	42.3 DAT 120	37.3 DAT 100	42.3 DAT 120	FOE Sulfonic acid; FOE Oxalate; FOE TGS; FOE Methylsulfoxide; FOE Methylsulfone
	Laacherhof	Silt loam	20.8 DAT 100	23.8 DAT 120	37.1 DAT 120	29.9 DAT 100	37.1 DAT 120	FOE Sulfonic acid; FOE Oxalate; FOE TGS; FOE Methylsulfoxide; FOE Methylsulfone
	Hofchen im Tal	Silt loam	10.2 DAT 100	12.0 DAT 120	58.0 DAT 120	56.2 DAT 100	58.0 DAT 120	FOE Sulfonic acid; FOE Oxalate; FOE TGS; FOE Methylsulfoxide; FOE Methylsulfone
Pangilinan & Smith; 1994	Howe	Sandy loam	2.7 DAT 91	5.9 DAT 365	17.7 DAT 271	16.3 DAT 91	16.5 DAT 365	FOE Sulfonic acid; FOE Oxalate; FOE Alcohol; FOE TGS; FOE Methylsulfoxide; FOE Chloroacetanilide;
Bloomberg <i>et al.</i> ; 2002	Fresno	Sandy loam	14.1 ¹⁾ DAT 88	14.1 ¹⁾ DAT 88	41.6 ²⁾ DAT 88	41.6 ²⁾ DAT 88	41.6 ²⁾ DAT 88	FOE Sulfonic acid; FOE Oxalate; FOE Alcohol;
	Chualar	Sandy loam	5.8 ¹⁾ DAT 88	5.8 ¹⁾ DAT 88	46.4 ²⁾ DAT 19	31.6 ²⁾ DAT 88	31.6 ²⁾ DAT 88	FOE Sulfonic acid; FOE Oxalate; FOE Alcohol;

Footnotes to the table:

1) Value estimated as a difference between the reported “total AR recovered” and the theoretical 100% AR;

2) The value is the sum of NER fraction in topsoil (0-3 cm) and subsoil (3-13 cm) for the given tie point; as in the subsoil the detected radioactivity was not further examined, but considered to represent NER fraction, in fact that value may be an overestimate;

Table B.8.1.1.1.4._CA-2: Concentrations and classification of soil degradation products identified in experiments with [Phenyl-¹⁴C] Flufenacet

Degradation product	Maximum [% AR] in soil, detected on:						Classification according to SANCO/221/2000	Justification ¹⁾
	BBA 2.2	Laacherhof	Hofchen im Tal	Howe	Fresno	Chualar		
FOE Sulfonic acid	25.4 DAT 100	26.3 DAT 100	13.5 DAT 100	7.7 DAT 180	2.4 DAT 88	1.3 DAT 88	major/relevant for GW assessment	> 10% AR
FOE Oxalate	6.6 DAT 28	15.6 DAT 28	10.0 DAT 28	26.5 DAT 365	13.0 DAT 46	7.6 DAT 88	major/relevant for GW assessment	>10% AR
FOE Alcohol	n. d.	n. d.	n. d.	2.1 DAT 44, DAT 65	8.1 DAT 88	21.2 DAT 88	major/relevant for GW assessment	>10% AR
FOE TGS	3.3 DAT 56	5.5 DAT 28	1.9 DAT 28	3.7 DAT 180	n. d. ²⁾	n. d. ²⁾	minor/not relevant for GW assessment	Not meeting any of the criteria
FOE Methyl-sulfoxide	1.1 DAT 28, DAT 56	3.5 DAT 56	1.5 DAT 56	0.6 DAT 28	n. d. ²⁾	n. d. ²⁾	minor/not relevant for GW assessment	Not meeting any of the criteria
FOE Methyl-sulfone	6.6 DAT 100	4.3 DAT 120	5.6 DAT 120	n. d.	n. d. ²⁾	n. d. ²⁾	major/relevant for GW assessment	>5% AR at study end, increasing
FOE Chloroacet-anilide	n. d. ²⁾	n. d. ²⁾	n. d. ²⁾	5.1 DAT 44	n. d. ²⁾	n. d. ²⁾	minor/not relevant for GW assessment	Not meeting any of the criteria

Footnotes to the table:

- 1) Justification based on the criteria set by the Guideline SANCO/221/2000, listed under the point 4 on page 6:
“As a minimum, degradation products must be characterized and identified by the notifiers to the extent that it is technically feasible and their relevance must be assessed, if one of the following conditions applies:
a) *Metabolites, which account for more than 10% of the amount of active substance added in soil at any time during the studies; or*
b) *which account for more than 5% of the amount of active substance added in soil in at least two sequential measurements during the studies; or*
c) *for which at the end of soil degradation studies the maximum of formation is not yet reached.*
- 2) Compound not detected in that soil.

Table B.8.1.1.1.4._CA-3: The levels of mineralisation and NER fraction formed, and identified degradation products in experiments with [Thiadiazole-¹⁴C] Flufenacet.

Study/ radiolabelling position	Soil		Level of mineralisation [% AR]:		Level of NER [% AR]:			Identified degradation products
	Name	Type (USDA)	after ~100 days	at the study's end	Max.	after ~100 days	at the study's end	
Pangilinan & Smith; 1994a [Thiadiazole-2- ¹⁴ C]	Howe	Sandy loam	31.9 DAT 90	50.9 DAT 368	6.9 DAT 270	6.2 DAT 90	6.5 DAT 368	FOE Thiadone
Hein; 2012 [Thiadiazole-5- ¹⁴ C]	Hoefchen am Hohenseh 4a	Silt loam	5.7 DAT 120	5.7 DAT 120	13.5 DAT 60	12.5 DAT 120	12.5 DAT 120	FOE Thiadone; FOE 5043-Trifluoroethane-sulfonic acid; Trifluoroacetic acid (TFA)
Hein; 2012a [Thiadiazole-5- ¹⁴ C]	Laacherhof AXXa	Loamy sand	5.6 DAT 121	5.6 DAT 121	18.6 DAT 63	17.2 DAT 121	17.2 DAT 121	FOE Thiadone; FOE 5043-Trifluoroethane-sulfonic acid; Trifluoroacetic acid (TFA)
	Dollendorf II	Clay loam	6.5 DAT 121	6.5 DAT 121	11.5 DAT 63	10.6 DAT 121	10.6 DAT 121	FOE Thiadone; FOE 5043-Trifluoroethane-sulfonic acid; Trifluoroacetic acid (TFA)
	Laacherhof Wurmwiiese	Loam	4.6 DAT 121	4.6 DAT 121	18.6 DAT 35, DAT 63	17.2 DAT 121	17.2 DAT 121	FOE Thiadone; FOE Trifluoroethane-sulfonic acid; Trifluoroacetic acid (TFA)

Table B.8.1.1.1.4._CA-4: Concentrations and classification of soil degradation products identified in experiments with [Thiadiazole-¹⁴C] Flufenacet

Degradation product	Maximum [% AR] in soil, detected on:					Classification according to SANCO/221/2000	Justification ¹⁾
	Howe	Hoefchen am Hohenseh 4a	Laacherhof AXxa	Dollendorf II	Laacherhof Wurmweise		
FOE Thiadone	3.9 DAT 7	5.8 DAT 10	2.8 DAT 7	5.6 DAT 10	4.6 DAT	major/relevant for GW assessment	> 5% AR at two consecutive time points
FOE Trifluoroethanesulfonic acid	n. d. ²⁾	6.0 DAT 14	4.4 DAT 10	3.4 DAT 10	1.9 DAT 10	major/relevant for GW assessment	> 5% AR at two consecutive time points
TFA (Trifluoroacetic acid)	n. d. ²⁾	77.7 DAT 87	74.1 DAT 121	81.5 DAT 91	74.8 DAT 91	major/relevant for GW assessment	> 10% AR

Footnotes to the table:

1) Justification based on the criteria set by the Guideline SANCO/221/2000, listed under the point 4 on page 6:

“As a minimum, degradation products must be characterized and identified by the notifiers to the extent that it is technically feasible and their relevance must be assessed, if one of the following conditions applies:

- a) Metabolites, which account for more than 10% of the amount of active substance added in soil at any time during the studies; or*
- b) which account for more than 5% of the amount of active substance added in soil in at least two sequential measurements during the studies; or*
- c) for which at the end of soil degradation studies the maximum of formation is not yet reached.*

2) Compound not detected in that soil.

The transformation pattern of Flufenacet in soil was examined only on biologically viable soil. That was due to the fact that, on the basis of available results it was assumed that all transformation processes were predominantly or solely biologically-mediated. It was postulated that the initial step of the degradation was the cleavage of the test item on bridging oxygen of the thiadiazole heterocycle. The further sequence for the thiadiazole moiety is presented below:

- tautomerisation of keto-enol functional group, resulting in formation of FOE Thiadone,
- hydrolytical opening of thiadone ring and further oxidation resulting in formation of either FOE 5043-Trifluoroethanesulfonic acid or Trifluoroacetic acid (TFA), or else simple products of mineralisation and NER fraction – ultimate transformation products;
- further transformation of FOE 5043-Trifluoroethanesulfonic acid or Trifluoroacetic acid (TFA) to the simple products of mineralisation and NER fraction – ultimate transformation products.

In case of the moiety containing fluorophenyl ring next postulated step was the formation of the transient FOE Cysteine- or FOE Glutathione conjugates, undergoing subsequent quick transformation to FOE Methylsulfoxide, FOE Alcohol and FOE Chloroacetanilide. As possible side-processes were postulated direct formation of FOE Chloroacetanilide and FOE Alcohol. It shall be noted that FOE Chloroacetanilide may be not only a genuine degradation product, but also, and possibly to greater extent, analytical artefact. However, as the issue was not satisfactorily clarified, the RMS's proposal is to consider FOE Chloroacetanilide a genuine degradation product.

Additionally, as in course of evaluation FOE Alcohol was identified to be a potentially major degradation product, the additional assessment was performed to determine whether, in absence of data for that compound, the exposure assessment for FOE Alcohol may be considered to be covered by that for its immediate degradate – FOE Oxalate.

The Applicant in course of the discussion on the nature of FOE Alcohol made a following statement (the text is copied directly from the Applicant's e-mail; the “outdoor soil metabolism study” refers to the cited study by Shadrack and Kasper [1995]):

We cannot reconstruct what the reason for the accumulation or artificial formation of FOE alcohol (aka FOE hydroxy) was in that outdoor soil metabolism study, but we have several other laboratory studies, as well as EU and US field studies, which demonstrate, that FOE alcohol is a minor, transient metabolite, not accumulating at all, but rather being further oxidized quickly to FOE oxalate.

RMS having analysed the results provided by the study by Shadrack and Kasper [1995], reproduced in the publication by Bloomberg et al. [2002], noted that the compound was formed in greater amounts in Chualar soil, having lower OC content and slightly lower microbial activity of the two soils used in the experiment. Taking into account the fact that FOE Alcohol was also detected only in the study by Pangilinan and Smith [1994], performed on another soil having low OC content and microbial activity, but not in the study by Kelley et al [1995], all that may indicate that FOE Alcohol is indeed a transient, fast degrading compound, that would appear in higher amounts and for longer only in weak soils.

To further demonstrate that it was possible to cover the exposure assessment for FOE Alcohol with that for its immediate degradate – FOE Oxalate, RMS performed the comparative analysis by means of QSAR calculations, carried out with EPI Suite ver. 4.10 (September 2010) tool. The results of that assessment indicate that the properties of both compounds relevant for their environmental fate and behaviour are comparable. Therefore the exposure assessment performed for FOE Oxalate may be considered as covering that for FOE Alcohol.

The route of degradation of the acetanilide herbicide Flufenacet in anaerobic soil was examined in three soils – one from the US and two European. The test compound – Flufenacet, was radiolabelled in one of the following two positions:

- uniformly in phenyl ring – compound tested on one US soil,
- in position C5 of Thiadiazole moiety – examined in two EU soils.

The experiments performed to determine the transformation pattern of Flufenacet in soil under anaerobic conditions consisted of two phases – aerobic preincubation phase and anaerobic incubation phase. RMS decided to present the key results of the experiments taking into account both phases. In case of aerobic preincubation phase the results are given for the terminal time point of that phase.

The key results for the examination of transformation of Flufenacet in anaerobic soils in the area of formation of terminal degradation products – mineralisation expressed as CO₂ and NER fraction, are presented below in the table B.8.1.1.1.4._CA-5. To differentiate the results obtained for aerobic phase from those for anaerobic phase the former were shaded light grey. It shall be noted that under anaerobic conditions mineralisation, if occurred at all, was minimal. No other volatile compounds were identified during either aerobic or anaerobic phases. The level of NER formed under anaerobic conditions (net formation) was comparable to that observed in aerobic soils.

Table B.8.1.1.1.4._CA-5: The levels of the terminal degradation products – CO₂ and NER fraction formed in soil during examination of the transformation pattern of Flufenacet in soil under anaerobic conditions.

Study/ radiolabelling position	Soil		Results obtained for aerobic phase		Results obtained for anaerobic phase ¹⁾					
	Name	Type (USDA)	CO ₂ [%AR] – end of phase	NER [%AR] – end of phase	Mineralisation level – CO ₂ formed [% AR]			NER level [% AR]		
					Beginning of phase	Max.	Net anaero- bic ²⁾	Beginning of phase	Max.	Net anaero- bic ³⁾
Pangilinan & Smith [1994]/ ¹⁴ C-phenyl	Howe	Sandy loam	1.4 (DAT 30)	8.4 (DAT 30)	1.4 (DAT 30 DAF 0)	1.8 (DAT 210 DAF 180)	0.4	8.4 (DAT 30 DAF 0)	32.6 (DAT 210 DAF 180)	24.2 (DAT 210 DAF 180)
Heinemann [2012]/ ¹⁴ C-5- Thiadiazole	HH ⁴⁾	Silt loam	1.6 (DAT 15)	16.9 (DAT 15)	1.6 (DAT 15 DAF 0)	1.7 (DAT 105 DAF 90)	0.1	10.2 (DAT 15 DAF 0)	24.5 (DAT 135 DAF 120)	14.3 (DAT 135 DAF 120)
	DD ⁵⁾	Loam	1.9 (DAT 15)	10.1 (DAT 15)	1.8 (DAT 15 DAF 0)	1.9 (DAT 105 DAF 90)	<0.1 ⁶⁾	8.6 (DAT 15 DAF 0)	31.6 (DAT 135 DAF 120)	23.0 (DAT 135 DAF 120)

Footnotes to the table:

- 1) In case of Howe soil the results for the beginning of anaerobic phase are the same as those for the end of aerobic phase; in case of soils HH and DD they are different, because were available the results obtained immediately after generating the anaerobic conditions;
- 2) Net anaerobic is a difference between the total amount of CO₂ formed and that determined in aerobic traps for volatiles;
- 3) Net anaerobic is a difference between maximum determined level of NER and that measured at the beginning of anaerobic phase;
- 4) HH stands for *Hoefchen am Hohenseh 4a* soil;
- 5) DD stands for *Dollendorf II* soil;
- 6) At the time point where maximum CO₂ level of 2.0% AR was recorded, the amount recovered for aerobic volatile traps was 1.9% AR and from anaerobic volatile traps <0.1 AR; the slightly higher total amount may be due to either rounding or losses during extraction; in that soil the level of mineralization, expressed as recovered CO₂ in anaerobic phase was <0.1% AR;

The examination of the extracted fraction enabled the identification of one new degradate, not identified in aerobic soils – FOE Thioglycolate. All other identified degradation products were those already found in aerobic soils. On that basis it can be stated that the transformation pattern of Flufenacet in soil under anaerobic conditions would not differ significantly from that determined in aerobic soils. The key results of the profiling of degradation products in anaerobic soils are presented below in table B.8.1.1.1.4._CA-6. To differentiate the results obtained for aerobic phase from those for anaerobic phase the former were shaded light grey.

Table B.8.1.1.1.4_CA-6: The results of the profiling of Flufenacet and its degradation products.

Study/ radiolabelling position	Soil		Results obtained for aerobic phase		Results obtained for anaerobic phase ¹⁾				
	Name	Type (USDA)	Identified compound	Amount [% AR] at the end of phase	Identified compound	Amount [% AR] measured at:			Anaerobic metabolite (yes/no)
Pangilinan & Smith [1994]/ ¹⁴ C-phenyl	Howe	Sandy loam	Flufenacet	69.0 (DAT 30)	Flufenacet	69.0 (DAT 30/ DAF 0)	39.0 ⁶⁾ (DAT 210/ DAF 180)	N/A ⁸⁾	N/A ⁸⁾
			FOE Oxalate	11.2 (DAT 30)	FOE Oxalate	11.2 (DAT 30/ DAF 0)	14.5 (DAT 60/ DAF 30)	3.3 (DAT 60/ DAF 30)	Yes
			FOE Sulfonic acid	6.6 (DAT 30)	FOE Sulfonic acid	6.6 (DAT 30/ DAF 0)	6.6 (DAT 30/ DAF 0)	0.0	No
			FOE Alcohol	0.0 (DAT 30)	FOE Alcohol	0.0 (DAT 30/ DAF 0)	1.4 (DAT 153/ DAF 123)	1.4 (DAT 153/ DAF 123)	Yes
			FOE TGS ³⁾	2.6 (DAT 30)	FOE TGS ³⁾	2.6 (DAT 30/ DAF0)	2.6 (DAT 30/ DAF0)	0.0	No
					FOE Thioglycolate	0.0 (DAT 30/ DAF 0)	1.7 (DAT 60/ DAF 30)	1.7 (DAT 60/ DAF 30)	Yes
Heinemann [2012]/ ¹⁴ C-5- Thiadiazole	HH ⁴⁾	Silt loam	Flufenacet	30.8 (DAT 15)	Flufenacet	42.8 (DAT 15/ DASF 0)	6.4 ⁶⁾ (DAT 135/ DASF 120)	N/A ⁸⁾	N/A ⁸⁾
			FOE Thiadone	5.9 (DAT 15)	FOE Thiadone	4.8 (DAT 15/ DASF 0)	13.6 (DAT 77/ DASF 62)	8.8 (DAT 77/ DASF 62)	Yes
			FOE 5043- Trifluoroethane- sulfonic acid	2.5 (DAT 15)	FOE 5043- Trifluoroethane- sulfonic acid	5.1 (DAT 15/ DASF 0)	4.2 ⁷⁾ (DAT 48/ DASF 33)	4.2 ⁷⁾ (DAT 48/ DASF 33)	Yes
			Trifluoroacetic acid	37.5 (DAT 15)	Trifluoroacetic acid	31.4 (DAT 15/ DASF 0)	47.9 (DAT 135/ DASF 120)	16.5 (DAT 135/ DASF 120)	Yes
	DD ⁵⁾	Loam	Flufenacet	44.2 (DAT 15)	Flufenacet	35.4 (DAT 15/ DASF 0)	3.1 ⁶⁾ (DAT 135/ DASF 120)	N/A ⁸⁾	N/A ⁸⁾
			FOE Thiadone	4.3 (DAT 15)	FOE Thiadone	7.1 (DAT 15/ DASF 0)	12.4 (DAT 21/ DASF 6)	5.3 (DAT 21/ DASF 6)	Yes
			FOE 5043- Trifluoroethane- sulfonic acid	6.0 (DAT 15)	FOE 5043- Trifluoroethane- sulfonic acid	3.2 (DAT 15/ DASF 0)	3.2 (DAT 15/ DASF 0)	0.0	No
			Trifluoroacetic acid	28.0 (DAT 15)	Trifluoroacetic acid	40.4 (DAT 15/ DASF 0)	53.2 (DAT 105/ DASF 90)	12.8 (DAT 105/ DASF 90)	Yes

Footnotes to the table:

- 1) In case of Howe soil the results for the beginning of anaerobic phase are the same as those for the end of aerobic phase; in case of soils HH and DD they are different, because were available the results obtained immediately after generating the anaerobic conditions;
- 2) Net anaerobic is a difference between the maximum amount determined in anaerobic phase and that at its beginning;
- 3) FOE TGS – FOE Thioglycolate sulfoxide;
- 4) HH stands for *Hoefchen am Hohenseh 4a* soil;
- 5) DD stands for *Dollendorf II* soil;
- 6) Flufenacet is the active substance, therefore not forming in soil; as a result its concentration at the end of incubation period is given to show the level of decline;
- 7) In that soil the concentrations of FOE Trifluoroethane sulfonic acid initially decreased, to increase afterwards reaching maximum on the indicated time point; it was assumed that this maximum can be attributed totally to the amount of that compound formed under anaerobic conditions;
- 8) N/A – not applicable (parent compound);

The results of the determination of transformation pathway of Flufenacet in anaerobic soil demonstrated that it would not significantly differ, qualitatively and quantitatively, from that observed in aerobic soil.

The degradation products that may require further consideration for the risk assessment are the same as identified during examination of the degradation pattern of Flufenacet in aerobic soil: FOE Oxalate, FOE Thiadone and Trifluoroacetic acid.

The soil photolysis of Flufenacet was examined in one soil – US Sandy loam, using the test compound radiolabelled in one position – uniformly at phenyl ring. The experiment was performed using soil that was demonstrated to be biologically viable throughout the whole irradiation/incubation period. Samples were irradiated with artificial light (Xenon lamp) continuously for 10.25 days, corresponding to 30 days of natural summer sunlight (conditions relevant for Phoenix, Arizona, USA). The key results of the examination are presented below in the table B.8.1.1.1.4._CA-7.

Table B.8.1.1.1.4._CA-7: The key results obtained for Flufenacet in soil photolysis study

Parameter		Results obtained for:	
		Irradiated sample	Dark control
<i>Terminal transformation products</i>	Mineralisation (CO ₂) at the end of the study	0.2% AR; DAT ²⁾ 10.25; 30 th DNS ³⁾	0.1% AR; DAT ²⁾ 10.25; 30 th DNS ³⁾
	Max. NER level	3.2% AR; DAT ²⁾ 10.25; 30 th DNS ³⁾	4.4% AR; DAT ²⁾ 10.25; 30 th DNS ³⁾
<i>Identified compounds</i>	Flufenacet – amount at study's end	91.2 AR; DAT ²⁾ 10.25; 30 th DNS ³⁾	87.2 AR; DAT ²⁾ 10.25; 30 th DNS ³⁾
	FOE Oxalate – max. amount	0.6% AR; DAT ²⁾ 10.25; 30 th DNS ³⁾	4.6% AR; DAT ²⁾ 10.25; 30 th DNS ³⁾
	FOE Sulfonic acid – max. amount	0.4% AR; DAT ²⁾ 5.13; 15 th DNS ³⁾	2.2% AR; DAT ²⁾ 10.25; 30 th DNS ³⁾
	FOE Methylsulfoxide – max. amount	0.7% AR; DAT ²⁾ 10.25; 30 th DNS ³⁾	0.6% AR; DAT ²⁾ 10.25; 30 th DNS ³⁾
	FOE Alcohol – max. amount	1.0% AR; DAT ²⁾ 10.25; 30 th DNS ³⁾	0.4% AR; DAT ²⁾ 10.25; 30 th DNS ³⁾
	FOE N-isomer ¹⁾ – max. amount	1.8% AR; DAT ²⁾ 5.13; 15 th DNS ³⁾	0.3% AR; DAT ²⁾ 2.75; 8 th DNS ³⁾
<i>Kinetics of the process</i>	rate constant k [days ⁻¹]	0.0076	0.0124
	DT ₅₀ [days]	90.72	55.90

Footnotes to the table:

- 1) N-isomer of Flufenacet (for the structural formula, please refer to the table in Appendix 1 - List of Evaluated Compounds);
- 2) DAT stands for Days After Treatment, the real sampling point in the experiment;
- 3) DNS – Days of Natural Sunlight, the sampling point related to the natural summer day sunlight conditions in Tucson Arizona, USA

On the basis of these results it was stated that Flufenacet is not prone to photolytical degradation on the soil surface, therefore soil photolysis will not be a relevant degradation mechanism of Flufenacet in soil. Additionally the potential of photodegradation of FOE Thiadone on soil surface was examined. Although it was demonstrated that the process might contribute to transformation of FOE Thiadone in soil, its relevance is estimated to be minimal, also because FOE Thiadone is not expected to occur on the soil surface in significant, if any, amounts.

On the basis of the results of the studies examining route of degradation of Flufenacet in soil under various conditions a following overall transformation scheme was proposed (figure B.8.1.1.1.4._CA-1):

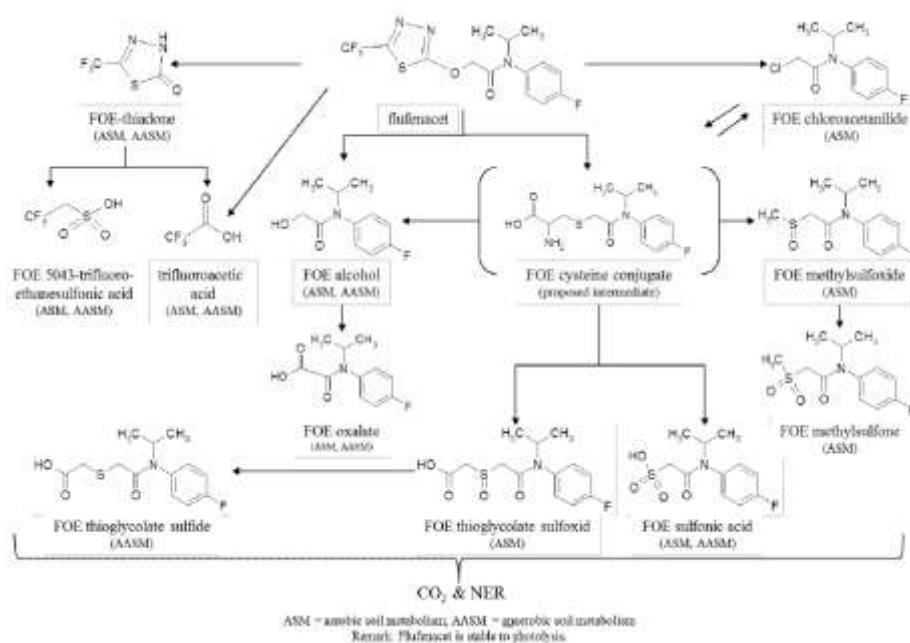


Figure B.8.1.1.1.4_CA-1: A postulated transformation scheme for Flufenacet in soil, as proposed by the Applicant, verified and approved by the RMS (scheme copied from the Applicant's documentation).

Finally the results considered to be definitive endpoints derived from the examination of the route of degradation of Flufenacet in soil are presented below (in format recommended for the EU-agreed endpoints – SANCO/12483/2014-rev.2; 12 December 2014).

Route of degradation (aerobic) in soil (Regulation (EU) N° 283/2013, Annex Part A, point 7.1.1.1)

Mineralisation after 100 days	2.7 % after 91 d, [¹⁴ C- <i>U-Phenyl</i>]-label (n= 1) 10.2 – 20.8 % after 100 d, [¹⁴ C- <i>U-Phenyl</i>]-label (n= 3) 31.9 % after 90 d, [¹⁴ C-2- <i>Thiadiazole</i>]-label (n= 1) 4.5 – 6.5 % after 120-121 d, [¹⁴ C-5- <i>Thiadiazole</i>]-label (n= 4)
Non-extractable residues after 100 days	16.3 % after 91 d, [¹⁴ C- <i>U-Phenyl</i>]-label (n= 1) 29.9 – 56.2 % after 100 d, [¹⁴ C- <i>U-Phenyl</i>]-label (n= 3) 6.2 % after 90 d, [¹⁴ C-2- <i>Thiadiazole</i>]-label (n= 1) 10.6 – 17.2 % after 120-121 d, [¹⁴ C-5- <i>Thiadiazole</i>]-label (n= 4)
Metabolites requiring further consideration - name and/or code, % of applied (range and maximum)	FOE Sulfonic acid – max. 26.3 % at 100 d (n= 6); [¹⁴ C- <i>U-Phenyl</i>] label; FOE Alcohol – max. 21.2 % at 88 d (n= 3); [¹⁴ C- <i>U-Phenyl</i>] label; FOE Oxalate – max. 26.5 % at 365 d (n= 6); [¹⁴ C- <i>U-Phenyl</i>] label; FOE Methylsulfone – max. 6.6 % at 100 d (n= 3); [¹⁴ C- <i>U-Phenyl</i>] label; FOE Thiadone – max. 5.8 % at 10 d (n= 5); [¹⁴ C-2- <i>Thiadiazole</i>] & [¹⁴ C-5- <i>Thiadiazole</i>] labels FOE 5043-Trifluoroethanesulfonic acid – max. 6.0 % at 14 d (n= 4); [¹⁴ C-5- <i>Thiadiazole</i>] label Trifluoroacetic acid (TFA) – max. 81.5 % at 91 d (n= 4); [¹⁴ C-5- <i>Thiadiazole</i>] label Sterile conditions: <i>not examined</i>

Route of degradation (anaerobic) in soil (Regulation (EU) N° 283/2013, Annex Part A, point 7.1.1.2)

Mineralisation after 100 days	0.5 % after 180 d, [¹⁴ C- <i>Phenyl</i>]-label (n= 1) <0.1 - 0.1 % after 90 d, [¹⁴ C-5- <i>Thiadiazole</i>]-label (n= 2)
Non-extractable residues after 100 days	24.2 % after 180 d, [¹⁴ C- <i>Phenyl</i>]-label (n= 1) 14.3 – 23.0 % after 120 d, [¹⁴ C-5- <i>Thiadiazole</i>]-label (n= 2)
Metabolites that may require further consideration for risk assessment - name and/or code, % of applied (range and maximum)	FOE Oxalate – 14.5 % at 30 d (n= 1); [¹⁴ C- <i>Phenyl</i>] label; FOE Thiadone – 8.8 % at 62 d (n= 2); [¹⁴ C-5- <i>Thiadiazole</i>] label; Trifluoroacetic acid (TFA) – 16.5 % at 120 d (n= 2); [¹⁴ C-5- <i>Thiadiazole</i>] label; Sterile conditions: <i>not examined</i>

Route of degradation (photolysis) on soil (Regulation (EU) N° 283/2013, Annex Part A, point 7.1.1.3)

Metabolites that may require further consideration for risk assessment - name and/or code, % of applied (range and maximum)	<i>Not relevant – Flufenacet was demonstrated to be not prone to photolytical degradation on the soil surface.</i>
Mineralisation at study end	0.2 % after 10.25 days, [¹⁴ C- <i>Phenyl</i>]-label (n= 1) – irradiated sample; 0.1 % after 10.25 days, [¹⁴ C- <i>Phenyl</i>]-label (n= 1) – dark control
Non-extractable residues at study end	3.2 % after 10.25 days, [¹⁴ C- <i>Phenyl</i>]-label (n= 1) – irradiated sample 4.4 % after 10.25 days, [¹⁴ C- <i>Phenyl</i>]-label (n= 1) – dark control

B.8.1.1.2. – Rate of degradation

The degradation kinetics of Flufenacet and its degradation and transformation products in soil was thoroughly examined in several studies, both in the laboratory and under field conditions. The results of that examination, in form of the summaries of the submitted studies, are presented below, under the relevant data points.

B.8.1.1.2.1. – Laboratory studies

The degradation of Flufenacet in soil under aerobic conditions was extensively examined in five studies, three evaluated for the previous authorisation of Flufenacet in the EU (“old studies”) and two newly submitted studies, summarised in this Renewal Assessment Report under the point B.8.1.1.1.1. as respectively **Study 1**, **Study 2** and **Study 4** (“old studies”), and **Study 5** and **Study 6** (“new studies”). The two new studies contained the results of the kinetic evaluation of the data obtained for Florasulam performed according to the current standards (FOCUS Kinetics). Also, for the purpose of the present evaluation, the Applicant submitted a study that examined the rate of degradation of Flufenacet in one soil. The results of all these studies were further evaluated in five study reports, aimed specifically on the kinetic evaluation of the data in line with the current standards. Therefore, the Applicant submitted in total six studies examining the rate of degradation of Flufenacet, alone or together with its degradation products, in aerobic soils.

To cover the issue of the rate of degradation of the major soil degradation and transformation products of Flufenacet in aerobic soil the Applicant submitted another fourteen studies, of which three were the existing studies, assessed already during the previous evaluation of Flufenacet for its authorisation in the EU. The remaining eleven were new/newly submitted studies.

Of these, five were examining the rate of degradation of FOE Sulfonic acid, three were aimed on the determination of the kinetic endpoints for FOE Methylsulfone, two were performed for FOE Thiadone and remaining two for Trifluoroacetic acid. The remaining two were the old studies, submitted for the previous evaluation of Flufenacet in the EU, presenting the kinetic assessment of the data obtained for degradation products.

In total the Applicant submitted 22 studies specifically aimed on the determination of rate of degradation of Flufenacet and its degradation products in aerobic soil under laboratory conditions. All they are evaluated and summarised below, under the point B.8.1.1.2.1.1. of the Renewal Assessment Report.

The results of the kinetic analysis were further evaluated in three separate study reports aimed on the identification of the kinetic endpoints suitable for modelling exposure assessment. In case of the endpoints identified as suitable for GW and SW modelling they were also normalised and the assumptions and results of the normalisation procedure presented in the adequate reports. Although these three reports are closely associated with issues related to the representative formulation, RMS decided to summarise them, in their parts related to the critical evaluation of the kinetic endpoints determined in aerobic soil, in this part of the Renewal Assessment Report under the point B.8.1.1.2.1.1.

Additionally two peer-reviewed publications presenting the results of the determination of the kinetic endpoints for the degradation of Flufenacet in aerobic soil in the laboratory were identified by RMS as relevant for this assessment. RMS considers the studies supplementary and not to be used to derive the regulatory endpoints. Never the less, as they provide the values of reference conforming the findings of the evaluated study reports, their summaries are provided at the end of the subchapter.

The results of the two studies examining the transformation of Flufenacet in anaerobic soil were kinetically evaluated by the Applicant and presented in the study report issued specifically for that purpose. The study is summarised as **Study 1** under the point B.8.1.1.2.1.2. of this report. Additionally the Applicant presented the key results of the kinetic analysis of the data in the study by Heinemann [2012] already summarised as **Study 2** under the point B.8.1.1.1.2. of this report. They will be briefly evaluated under the point B.8.1.1.2.1.2.

In case of soil photolysis the Applicant has not submitted any new study examining the rate of photolytic transformation of Flufenacet or any of its degradation and transformation products on the soil surface. The RMS performed the kinetic analysis of the results obtained in the two studies summarised under the point B.8.1.1.1.3. of this report. The results are presented under the point B.8.1.1.2.1.3. of this report.

The last point in this section – B.8.1.1.2.1.4., is a summary of all findings in the area of the determination of the degradation kinetics in soil in the laboratory. It will provide the key results of that examination.

B.8.1.1.2.1.1. – Aerobic degradation

The rate of degradation of Flufenacet in soil under aerobic conditions was determined in twenty two studies submitted by the Applicant. The examination of the degradation kinetics of Flufenacet in aerobic soil was based on the results of five studies aimed also on the determination of the degradation pathway of Flufenacet in soil, which are summarised under the point B.8.1.1.1.1. as **Study 1** [Kelley et al; 1995], **Study 2** [Pangilinan & Smith; 1994], **Study 4** [Pangilinan & Smith; 1994a], **Study 5** [Hein; 2012] and **Study 6** [Hein; 2012a]. Additionally, the Applicant submitted one study aimed on the determination of the rate of degradation of Flufenacet in aerobic soil. That study is summarised below as **Study 1**. Kinetic evaluation of the data from that study, as well as from other studies listed above, in which [Phenyl-U-¹⁴C] Flufenacet was used, was performed according to provisions of FOCUS Kinetics Guideline [FOCUS; 2006] and presented in separate study report, summarised in this section as **Study 2**. Additionally the same data set was examined in order to derive trigger endpoints for FOE Oxalate and Flufenacet. The results are presented as **Study 3**. Also the results obtained in the studies performed with [Thiadiazole-2-¹⁴C] Flufenacet, and [Thiadiazole-5-¹⁴C] Flufenacet were kinetically evaluated in line with recommendations given by FOCUS. In case of the experiment with [Thiadiazole-5-¹⁴C] Flufenacet, the kinetic examination of the data for Flufenacet to determine the best-fit kinetics according to FOCUS was already performed and presented in the study reports **Study 5** [Hein; 2012] and **Study 6** [Hein; 2012a]. RMS decided to present that evaluation under this point as relevant for presentation of the results of kinetic evaluation of the data. Therefore those two studies, in the area of the kinetic assessment they provide, will be summarised here as **Study 4** and **Study 5**, respectively. Additionally, the data of those two studies were further kinetically examined in two separate studies summarised under this point:

- **Study 6**, aimed on the determination of trigger endpoints for FOE 5043-trifluoroethanesulfonic acid;
- **Study 7**, in which the kinetic endpoints for modelling were determined.

Finally the results of the kinetic examination of the data for [Thiadiazole-2-¹⁴C] Flufenacet, obtained in already evoked **Study 4** [Pangilinan & Smith; 1994a], will be presented as **Study 8**.

The Applicant also submitted fourteen study reports aimed specifically on the determination of the kinetic endpoints for the major soil degradation products of Flufenacet identified during examination of the route of degradation of that compound in soil. Of them three were submitted and evaluated for the previous authorisation of Flufenacet in the EU (“old” studies) while the remaining eleven are new/newly submitted studies. Two of the “old” studies were found to be not compliant with the provisions of FOCUS Kinetic Guideline. For that reason only their summaries given in the previous Assessment Report will be presented and these studies will not be taken into account in the assessment. The remaining twelve studies will be summarised according to the current standards as **Studies 9 – 20**.

It was noted that none of the listed above reports contained the results of the normalisation of the obtained endpoints. The Applicant decided to perform the normalisation of the modelling endpoints in two separate reports, issued in support of the main study reports presenting the results of the model exposure assessment for Groundwater and Surface Water compartments. The reports presented also the justification for the selection of all input parameters for modelling exposure assessment. The Applicant issued three such reports, one for each type of modelling exposure assessment, including soil. RMS decided to summarise them, in the area relevant for this assessment point, as **Studies 23 – 25**.

Finally, the literature search enabled the identification of two scientific papers relevant in the area of the determination of the rate of degradation of Flufenacet in aerobic soil. These studies are considered supplementary and indicated as not to be used to derive the regulatory endpoints. However, RMS decided to summarise them, as providing supplementary data, at the end of this section as **Study 26** and **Study 27**.

The following eight studies, summarised below as **Studies 1 – 8**, examine the rate of degradation of Flufenacet, alone or with its degradation products, in aerobic soil in the laboratory. Two of them – **Study 4** and **Study 5** which are route-and rate-of degradation studies, were summarised also under the point B.8.1.1.1.1. of this Renewal Assessment Report as **Study 5** and **Study 6** respectively.

Study 1:

Report: Hellpointner E., (1999): “Aerobic Degradation of Flufenacet in Lysimeter Soil Laacherhof AXXa.”; Bayer AG, Institute for Metabolism Research and Residue Analysis, D-513468 Leverkusen, Federal Republic of Germany; study No. M1250988-3, unpublished study Report No. MR-388/99; 23 July 1999; study reference number: M-009592-01-1;

Guidelines: The study was performed to comply with the following Guidelines:

- BBA Guideline for the Official Testing of Plant Protectants, Part IV, 4-1, 1986;
- EC Commission Directive 95/36/EC amending Council Directive 91/414/EEC Annexes I + II, Fate and behaviour in the Environment. 14th July 1995;
- SETAC Procedures for Assessing the Environmental Fate and Ecotoxicity of Pesticides, March 1995;

GLP: Yes;

RMS comments: This is a newly submitted study, provided specifically for purpose of evaluation of Flufenacet for the renewal of its authorisation in the EU. The study was evaluated for its compliance with the following two Guidelines:

- OECD Guideline 307 – Aerobic and Anaerobic transformation in Soil; in the area of the compliance of the analytical protocol with current standards;
- FOCUS (2006) “Guidance Document on Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration.” Report of the FOCUS Work Group on Degradation Kinetics, EC Document Reference SANCO/10058/2005 version 2.0, 434 pp., and “Generic guidance for Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration”, versions 1.0 (issued on 23 November 2011) and 1.1 (issued on 18 December 2014); for the compliance of the kinetic analysis of the obtained data with current EU recommendations in the area of kinetic analysis of the data.

It was stated that the study complied with the provisions with OECD 307 Guideline and no deviations from the tow listed above Guidelines were declared/stated. RMS noticed that although the study was performed using the radiolabelled compound, the identification of the degradation products was not performed. Therefore the study cannot be considered as providing the relevant data in the area of elucidating the route of degradation of Flufenacet and may be considered solely as a rate-of-degradation study. It was also determined that the kinetic analysis was not performed in line with the provisions of FOCUS Kinetics Guidance Document. The issue is discussed in detail in the summary of the study provided below.

As a result, the study is acceptable as providing the data for determination of the degradation kinetics of Flufenacet in the test soil used in the experiment. Its summary is given below.

Summary:

The aim of the study was to determine the rate of degradation of Flufenacet and kinetic endpoints for that compound in one soil incubated under aerobic conditions – lysimeter soil Laacherhof AXXa. That soil was used in several lysimeter studies with Flufenacet.

The soil was sampled from the test field – a pasture on which no pesticides were used since 1988, shortly before the study began – on 16th April 1999. It was taken from the top 16-cm layer. The amount of soil taken for the experiment was ~7 kg. Its moisture during sampling was ~16% (MWHC).

The soil was transferred to the test laboratory and there processed about a week before the experiment started, by removing the skeletal parts (stones, plant parts), the gentler air-drying the remaining soil and sieving it through 2-mm sieve. After that the soil was characterised for its properties, and the results of that analysis are presented below in the table B.8.1.1.2.1.1._CA-1.

Table B.8.1.1.2.1.1._CA-1: The characteristic of soil used in the study.

Parameter		Soil:	
Soil origin		<i>Laacherhof AXXa</i>	
Soil type (USDA)		<i>Monheim/ Rheinland/ North Rhine-Westphalia/ Germany</i>	
Particle size distribution		Sandy loam	
	Sand (50 µm – 2 mm) [%]	71.77	
	Silt (2 – 50 µm) [%]	16.47	
	Clay (< 2 µm) [%]	11.76	
pH value in distilled water		7.0	
pH value in 0.01M CaCl ₂		6.1	
Organic carbon content (C _{org}) [%] ¹⁾		1.41	
Organic matter content (OM) [%] ²⁾		2.42	
Cation Exchange Capacity – CEC [mEq/100g]		9.61	
Bulk density [g/cm ³]		2.5	
Water holding capacity	Maximum [g H ₂ O/100 g soil d. w.]	34.4	
	50% MWHC [g H ₂ O/100 g soil d. w.]	17.2	
Soil biomass expressed in mg microbial C/kg soil ³⁾ :	At the beginning of the study – DAT 0	667 (rep. 1)	702 (rep. 2)
	The end of the study – DAT 56	392 (rep. 1)	356 (rep. 2)
Soil biomass expressed as %OC ⁴⁾ :	At the beginning of the study – DAT 0	5.85 (rep. 1)	6.15 (rep. 2)
	The end of the study – DAT 56	3.44 (rep. 1)	3.12 (rep. 2)

Footnotes to the table:

- 1) Measured value;
- 2) Value calculated by the Applicant using the following equation: OM = 1.724*OC;
- 3) Determined using the method by Anderson&Domsch;
- 4) Recalculated by the RMS, using the reported OC = 2.5%;

At the beginning of the experiment the 100-g (d. w.) aliquots of the air-dried test soil were weighed into 300-mL Erlenmeyer flasks, brought to 50% MWHC by addition of the appropriate amount of deionised water (7.14 per flask), weighed and closed with quartz wool stoppers. They were then pre-incubated under the experiment conditions (in the dark at T = 20⁰C) for about 7 days before being treated with the test compound. The stoppers were removed at application. The application rate was set to 480 g Flufenacet /ha – the pre-emergence application rate in maize (corn). It was the same rate as used in two lysimeter studies with Flufenacet.

The test compound used in the experiment was [Phenyl-U-¹⁴C] Flufenacet, having a specific activity of 2.0 MBq/mg and radiochemical purity (determined by radio-HPLC) > 95%. Its structural formula is presented below on the figure B.8.1.1.2.1.1_CA-1.

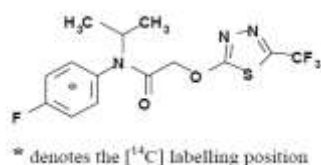


Figure B.8.1.1.2.1.1._CA-1: The structural formula of the radiolabelled Flufenacet used in the experiment (copied from the study report).

It was stored deep-frozen until being used. When used, the whole sample was first dissolved in 5 mL of CH₃CN to obtain the stock solution having a concentration (determined by LSC) of 19 kBq/10µL, corresponding to 0.95 mg Flufenacet/mL, and radiochemical purity > 95%. The stock solution was stored in the dark and under cool conditions until being used to prepare the application solution.

The application solution was prepared by diluting 1.7 mL of the stock solution with the appropriate amount of distilled water to obtain the solution having a target volume of 12.00 mL. That volume was calculated on the basis of the assumption that for treatment of the individual test vessel should be used 70 µL of the stock solution diluted with distilled water to the volume of 500 µL. It was stated that the volume of Application solution was sufficient to treat 24 samples with 500-µL portions.

The concentration of the Application solution was determined to be 14.340 kBq/50 µL, corresponding to 0.1434 mg Flufenacet/mL. Its radiochemical purity, determined using radio-TLC was 96% and the content of organic solvent (acetonitrile) – 14% (v/v).

To obtain the target application rate of 480 g Flufenacet/ha, corresponding to application dose of 0.064 mg Flufenacet/100 g soil d. w. (0.064 mg/kg soil d. w.), or 135 kBq/test vessel (application dose calculated using the standard assumptions – soil bulk density $d = 1.5 \text{ g/cm}^3$ and soil layer $l = 5 \text{ cm}$), 0.475 mL of the application solution was introduced to the test soil in each incubation vessel using microlitre syringe. The organic solvent was allowed to evaporate for 10 minutes, then the soil moisture was brought to designated 50%-level by re-weighing the test vessels and adding the appropriate amount of distilled water. So prepared samples were further called kinetic samples.

The homogeneity and stability of the application solution, as well as the exact amount of the test compound applied to each test vessel, were determined at application by means of LSC and radio-TLC.

Alongside kinetic samples were set the samples for the determination of the soil biomass at the end of the study (on DAT 56). They were prepared in the same way as kinetic samples, with exception that they were treated with blank application solution (not containing the test compound).

All treated incubation vessels were sealed with the traps for volatile compounds, to get the biometer flasks shown below on figure B.8.1.1.2.1.1._CA-2, and placed in the dark in the temperature-controlled room, to be incubated for up to 56 days at constant temperature $T = 20^\circ\text{C}$.

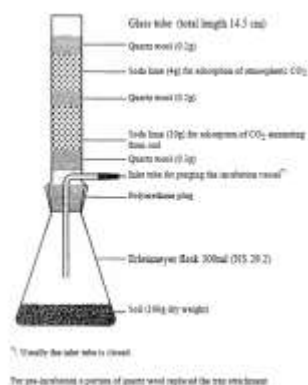


Figure B.8.1.1.2.1.1._CA-2: The biometer flask used in the experiment (copied from the study report).

Samples were taken for processing and analysis at designated time points – on DAT (Days After Treatment) 0, 0.1, 1, 3, 7, 14, 28, 42 and 56. At these time points duplicate samples were taken for analysis. The exception was DAT-0 time point, at which triplicate analysis was performed. Also in case of DAT-0 samples the traps for volatile compounds were not set, as it was assumed that no formation of volatile compounds was not expected then.

The soil moisture content was controlled in 30-days intervals by weighing the biometer flask less the traps and, if necessary, adjusting it by adding the appropriate amount of distilled water.

At designated time points the duplicate samples were removed from the incubation chamber for further processing. First the vessels were purged with humid air for 10 minutes to transfer all volatile compounds to the traps for volatile compounds. Then the traps were removed for further processing and the soil in Erlenmeyer flask immediately extracted. The extraction was performed with 80-mL portions of CH_3CN , in three 50-min. cycles consisting of 30-min. shaking at ambient temperature and 20-min., centrifugation at 9000 G and decantation with filtration of cleared supernatants. The collected supernatants were combined into one organic extract. At the beginning of the first extraction cycle the whole soil portion was quantitatively transferred from the Erlenmeyer flask to centrifuging baker – the extraction vessel, with the 1st 80-mL portion of the extracting agent. The organic extracts were analysed by LSC and HPLC on the day of extraction or the day after.

Each filter paper was pressed into four pellets and analysed, after combustion, for radioactivity content by LSC.

The extracted soil pellets were analysed for radioactivity content, after combustion, by LSC.

The recovered traps for volatile compounds were stored deep frozen until being analysed. Firstly they were dissected into polyurethane plugs (PU) and soda lime fillings. The PU plugs were extracted for 20 min. with 25 mL of CH_3CN on ultrasonic bath. Three 0.5-mL aliquots of so obtained extracts were then analysed for the radioactivity content using LSC. The radioactivity ($^{14}\text{CO}_2$) absorbed by soda lime was liberated with 18% HCl and transferred in the stream of N_2 to three vessels containing LS cocktail (20-mL mixture of Carbosorb E and PremafluorE⁺), using the apparatus presented below on figure B.8.1.1.2.1.1._CA-3.

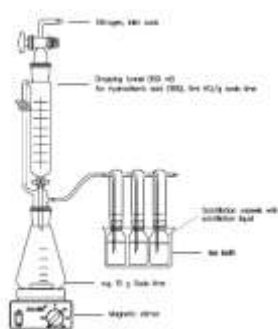


Figure B.8.1.1.2.1.1_CA-3: The apparatus used to liberate $^{14}\text{CO}_2$ from soda lime traps (copied from the study's report).

All samples were analysed for the content of radioactivity using LSC method.

The LSC (Liquid Scintillation Counting) analysis of liquid samples was performed using LS 6500 spectral counter. The radioactivity in all organic extracts was determined in mini-vials, using the sample aliquots of up to 0.5 mL and 2 mL of Quicksafe[®] A solution. The counting time was 10 minutes and the average background 14 cpm. The minimum sensitivity of LSC analysis for these samples was $5.19 \text{ E-}4$ ppm, corresponding to 0.0823% AR. When expressed as Lowest Acceptable Gross Count Rate (LAGC) it was 28 cpm, while as Lowest Acceptable Net Count Rate (LANC) – 14 cpm. The greatest probable error GPE = 8.10%.

The LSC analysis of radioactivity liberated from soda lime traps was performed on LKB-Wallac 1219 Spectral counter, using whole 20-mL scintillation-cocktail samples. The counting time for these samples was 10 minutes and the average background 28 cpm. The minimum sensitivity of LSC analysis for these samples was $2.85 \text{ E-}6$ ppm, corresponding to 4.52 E-4% AR. When expressed as Lowest Acceptable Gross Count Rate (LAGC) it was 56 cpm, while as Lowest Acceptable Net Count Rate (LANC) – 28 cpm. The greatest probable error GPE = 5.72%.

The LSC analysis of solid samples was performed using PW 4700 (Philips/Raytest) counter.

The radioactivity retained on paper filters, each weighing ~0.5 g, was determined after their compression to pellets followed by combustion. The resulting $^{14}\text{CO}_2$ was absorbed in 15 mL of Oxysolve C400. The counting time was 10 min and the average background 21 cpm. The minimum sensitivity of LSC analysis for these samples was $2.19 \text{ E-}6$ ppm, corresponding to 0.0347% AR. When expressed as Lowest Acceptable Gross Count Rate (LAGC) it was 42 cpm, while as Lowest Acceptable Net Count Rate (LANC) – 21 cpm. The greatest probable error GPE = 6.64%.

The radioactivity in extracted soil pellets was determined using three 1.0-g aliquots of dried and homogenised material, oxidised by combustion. The resulting $^{14}\text{CO}_2$ was absorbed in 15 mL of Oxysolve C400. The counting time was 10 min and the average background 21 cpm. The minimum sensitivity of LSC analysis for these samples was $6.73 \text{ E-}6$ ppm, corresponding to 1.07 E-3% AR. When expressed as Lowest Acceptable Gross Count Rate (LAGC) it was 42 cpm, while as Lowest Acceptable Net Count Rate (LANC) – 21 cpm. The greatest probable error GPE = 6.64%.

Liquid samples were also analysed using the following instrumental methods:

- TLC – primary quantitation method for the parent compound and its degradation products;
- HPLC conformatory method for checking the purity of the test compound in the stock solution.

The TLC analysis was carried out directly on the obtained samples, without any enrichment or conditioning step. It was performed at ambient temperature, in saturated chamber, on silica gel 60, F₂₅₄, TLC plates. The solvent system used in the analysis was Chloroform/Ethyl acetate 3:1 (v/v).

Two detectors were used:

- UV cabinet (Camag) detector working at wavelength $\lambda = 254 \text{ nm}$;
- Bio-Imaging Analyser Fujix BAS-2000 for analysis of radioactivity.

The LOD for a single peak was determined to be 1% AR, assuming the instrumental LOD = 0.8 Bq.

The HPLC analysis was performed in a gradient mode using Lichrospher 100 RP 18, 250 * 4 mm, 5 μm , chromatographic column, kept at constant temperature $T = 40^\circ\text{C}$. The chromatograph was coupled with Ramona 92 radioactivity flow-through detector.

The HPLC worked in the following gradient regime:

- **Mobile phase A:** 1% mL CH₃COOH in water;
- **Mobile phase B:** CH₃CN;
- **Gradient mode:** from 10% B on 0 min. to 40% B on 10th min., then to 60% B on 30th min. and finally to 90% B on 35th min.;
- The flow rate was set to 1.0 mL/min.;
- Total run time was 35 minutes.

Results and their discussion:

The monitoring of the experimental conditions demonstrated that the samples were incubated at the mean temperature 20.29^oC, ranging from 20.0^oC to 20.8^oC. These values were in line with the assumed constant temperature T = 20^oC. The soil moisture content was demonstrated to be in line with the assumed value of 50% MWHC and no significant losses were observed throughout the study duration.

The results of the verification of the homogeneity of application showed that it was homogenous – on average the application dose was 135.42 kBq/vessel (with range 134.82 kBq/vessel – 135.94 kBq/vessel; n = 3). That value was set to 100% AR. The purity of the test solution in relation to Flufenacet, determined by TLC, was on average 92.32% (range 92.17% - 92.47%; n = 3). The average application dose calculated on that basis was 62.51 µg Flufenacet/vessel, or 97.67% of the anticipated application dose of 64 µg Flufenacet/vessel.

The determination of the soil microbial activity at the beginning and the end of the study demonstrated that the test soil was biologically viable throughout its duration. For details please refer to the table B.8.1.1.2.1.1._CA-1. The determined decrease in soil microbial activity throughout the incubation period was by 41.23% for Replicate 1 and by 49.29% for replicate 2. The Applicant indicated that the initial soil biomass content was in the usual range expected for agricultural soils. Also the decrease in soil microbial activity was attributed, although that was not explicitly stated, to natural causes. It shall be pointed out however that while the determination of soil biomass content in DAT-0 samples was performed for soil not treated with the blank application solution, at the end of the experiment – in DAT-56 samples, it was done in soil treated with blank application solution. Therefore, in RMS's opinion, the would-be influence of the application solution on the soil biomass cannot be fully ruled out.

Never the less it was demonstrated that the soil microbial biomass was throughout the study duration well above the recommended level of 1% OC, so the conclusion on the biological viability of the test soil during the whole incubation period is fully defensible.

The assessment of the distribution of Applied Radioactivity (AR) was based on the initial value of 135.42 kBq/100 g soil (d. w.), set as 100% AR.

It shall be noted that the mass balance in DAT-0 samples was not determined, because it was assumed that at that time point the whole portion of AR should be extractable. Therefore for that time point the reported values represent the concentration of AR in the application solution. As a result the proper mass balance was performed starting for the samples collected on DAT 0.1 (2 hours after application of the test compound).

The recovery of AR was within the recommended limits, although with tendency to decrease with time, and it was in range of 94.8% AR – 99.5% AR.

The amount of AR extracted decreased in time from 93.6% AR on DAT 0.1 to 20.0% AR on DAT 56. That was correlated with the gradual increase of both NER fraction – from 5.9% AR on DAT 0.1 to 56.7% AR (maximum level) on DAT 42, and mineralisation – from 1.6% AR on DAT 0.1 to 19.5% AR on DAT 56. It shall be also noted that the NER fraction reached its maximum before the termination of the incubation – on DAT 42 (penultimate time point). The level recorded on the last sampling point – DAT 56, was slightly lower – 55.2% AR. That was in line with findings of the study by [Kelley et al.; 1995], summarised under the point B.8.1.1.1.1. as **Study 1**.

The identification of the constituents of the extract was limited solely to the active compound – Flufenacet. The degradation products were quantified under one common name – “Origin”. No further attempts to analyse that fraction qualitatively and quantitatively were made. The same concerns other isolated fractions.

For that reason the study, although performed with radiolabelled material, has limited utility as route-of-degradation study.

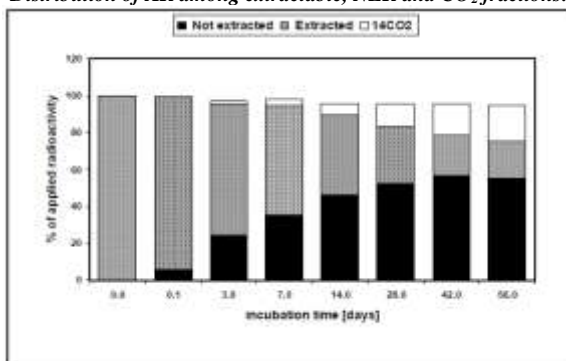
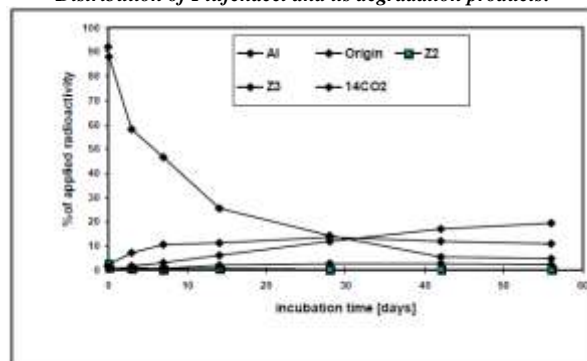
The detailed results are presented below, in numerical form in the table B.8.1.1.2.1.1._CA-2 and in graphical form on figure B.8.1.1.2.1.1._CA-4. The left-hand graph presents the distribution of radioactivity among extracted, not extracted and “mineralised” fractions. On the right-hand graph are presented the concentrations of the constituents of extracts and that of ¹⁴CO₂ (representing the level of mineralisation).

Table B.8.1.2.1.1._CA-4: The detailed results obtained in the study.

% AR		Results obtained for sample collected at DAT ¹⁾ :							
		0 ²⁾	0.1	3	7	14	28	42	56
<i>Extracted as:</i>	Organic extract	100.0	93.6	71.0	59.5	43.3	31.5	21.8	20.0
	Total extracted	100	93.6	71.0	59.5	43.3	31.5	21.8	20.0
<i>In extracts identified as:</i>	Flufenacet	92.3	88.0	58.1	46.7	25.6	14.4	5.3	4.9
	Origin ³⁾	1.9	2.5	7.1	10.7	11.1	13.6	12.0	10.8
	Z2	2.9	1.0	0.7	0.4	0.7	0.3	0.3	0.4
	Z3	1.5	1.1	0.9	0.8	2.2	2.6	2.7	2.5
	Diffuse radioactivity	1.4	1.0	4.2	0.9	3.7	0.6	1.5	1.4
	Total identified	100.0	93.6	71.0	59.5	43.3	31.5	21.8	20.0
<i>Bound residues (NER)</i>	Soil	N. A. ⁵⁾	4.2	23.2	34.2	45.3	51.5	55.8	54.7
	Paper filters	N. A. ⁵⁾	1.7	1.3	1.1	1.0	0.7	0.9	0.5
	Total NER	N. A.⁵⁾	5.9	24.5	35.3	46.2	52.1	56.7	55.2
<i>Volatile compounds</i>	CO ₂	N. A. ⁵⁾	n. a. ⁶⁾	1.6	3.2	6.0	11.8	17.0	19.5
	VOC (PU foam)	N. A. ⁵⁾	n. a. ⁶⁾	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
	Total volatile compounds⁴⁾	N. A.⁵⁾	n. a.⁶⁾	1.6	3.2	6.0	11.8	17.0	19.5
Total recovered AR		100.0	99.5	97.1	98.1	95.5	95.4	95.5	94.8

Footnotes to the table:

- 1) Values presented are the means of the two replicates for each sampling point, with exception of DAT-0 samples (three replicates);
- 2) For that time point the results are those for the application solution;
- 3) "Origin" is sum of all degradation products, detected and quantified in other studies with Flufenacet radiolabelled in phenyl ring;
- 4) Value calculated by adding the results obtained for VOC and those for CO₂
- 5) N. A. = Not Available – fraction by default not analysed at that time point;
- 6) n. a. = not analysed, probably because of the assumption made that at that sampling point neither significant mineralisation nor significant formation of volatile compounds is expected to occur.

Distribution of AR among extractable, NER and CO₂ fractions:*Distribution of Flufenacet and its degradation products:***Figure B.8.1.2.1.1._CA-4:** Graphical presentation of the obtained results (copied from the study report).

The results of the study obtained for Flufenacet were kinetically examined. RMS evaluated that examination and stated that:

- evaluation was performed initially first for 1st order kinetic model using linear regression and MS-Excel tool;
- the refined analysis was performed using Timme&Frehse 2.0 modelling tool for 1st order kinetics and 1.5-order kinetics (best fit).

It does not comply with the current standards of the kinetic analysis set by FOCUS Kinetics Guidance Document (FOCUS, 2006). As such it cannot be considered acceptable. For that reason the RMS decided not to present its results in this summary.

Study 2:

Report: Reinken G., Partsch S., (2014): “Kinetic Evaluation of the Degradation of [phenyl-UL-¹⁴C] flufenacet and its Degradation Products under Aerobic Soil Conditions in Laboratory According to FOCUS Kinetics Using the KinGUI 2 Tool. Flufenacet (FOE 5043); FOE sulfonic acid; FOE oxalate; FOE methylsulfone.”; Bayer CropScience AG, Environmental Safety, Alfred-Nobel-Straße 50, 40789 Monheim, Germany; unpublished Report No. EnSa-12-0575; 2014. 02. 17; study reference number: M-477878-01-1;

Guidelines: The study was declared to be performed to comply with the following guidelines:

- FOCUS (2006): “Guidance Document on Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration.” Report of the FOCUS Work Group on Degradation Kinetics, EC Document Reference SANCO/10058/2005 version 2.0, 434 pp.;
- FOCUS (2011): “Generic guidance for Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration”, version 1.0 (issued on 23 November 2011).

GLP: No, not applicable – this is a modelling study;

RMS comments: RMS verified the study for its compliance with the provisions of the Guidelines listed above. It was stated that the study generally complied with the two evoked Guidance Documents. It was also noted that it was aimed on the derivation of the kinetic endpoints to be used in modelling. For that reason the best fit was not identified and SFO model was generally indicated as returning acceptable fit for parent compound – Flufenacet. As a result when the data for parent and metabolites were kinetically examined only the combination SFO-SFO was tested. RMS summarising the study used the soil names that were provided in the source study reports (in the study report they were slightly altered) to maintain the internal coherence of the document.

Summary:

The aim of the study was to kinetically examine the data obtained in the experiments with [Phenyl-U-¹⁴C] Flufenacet. That was done in order to derive the kinetic parameters suitable for modelling and environmental risk assessment.

The data were taken from three following studies: [Kelley et al.; 1995] (a route-of-degradation study, summarised as **Study 1** under the point B.8.1.1.1.1.), [Pangilinan and Smith; 1994] (a route-of-degradation study, summarised as **Study 2** under the point B.8.1.1.1.1.) and [Hellpointner; 1999] (a rate-of-degradation study, summarised under this point as **Study 1**). The characteristic of the test soils used in each of the experiments is provided below in three following tables: B.8.1.1.2.1.1._CA-5 for the study by [Kelley et al.; 1995], B.8.1.1.2.1.1._CA-6 for the study by [Pangilinan and Smith; 1994] and B.8.1.1.2.1.1._CA-7 for the study by [Hellpointner; 1999]. To maintain the consistency of reporting, only physicochemical properties are reported. The data on soil microbial activity were not given here. To check them please refer to adequate summaries of the source studies.

Table B.8.1.1.2.1.1._CA-5: The characteristic of soils used in the study [Kelley et al.; 1995].

Parameter		Soil		
		BBA 2.2	Laacherhof	Höfchen im Tal
Soil origin		Germany; EU	Germany; EU	Germany; EU
Soil type (in the DAR)		Loamy sand	Silt Loam	Silt Loam
Soil type (USDA; re-assessed)		Loamy sand	Silt Loam	Silt Loam
Particle size distribution	Sand [%]	86.2	36.9	3.6
	Silt [%]	7.7	51.1	80.8
	Clay [%]	6.1	12.0	15.6
pH value (in H ₂ O, CaCl ₂)		6.2	7.3	5.8
Organic carbon content (C _{org}) [%]		2.58	0.90	2.40
Cation Exchange Capacity – CEC [mEq/100g]		9.7	10.0	10.0
Maximum water holding capacity [%]		53.8	48.6	71.6

Table B.8.1.1.2.1.1._CA-6: The characteristic of soil used in the study [Pangilinan and Smith; 1994].

Parameter		Soil:			
		395			
Soil origin		Howe, Indiana, USA			
Batch analysed		A ¹⁾	B ²⁾	C ³⁾	Average
Soil type (USDA)		Sandy loam	Sandy loam	Sandy loam	Sandy loam
Particle size distribution	Sand [%]	72.5	77.5	70.4	73.5
	Silt [%]	20.0	17.2	20.0	19.1
	Clay [%]	7.5	5.3	9.6	7.5
pH value (in water, 1:1)		6.1	6.4	6.2	6.2
pH value in CaCl ₂ ⁴⁾		5.5	5.9	5.6	5.6 ⁵⁾
Organic matter content (OM) [%]		0.2	0.4	1.2	0.6
Organic carbon content (C _{org}) [%] ⁵⁾		0.12	0.23	0.70	0.35
Cation Exchange Capacity – CEC [mEq/100g]		6.9	7.4	5.1	6.5
Bulk density (disturbed) [g/cm ³]		1.31	1.33	1.47	1.37
Moisture holding capacity at ½ bar [%]		14.8	13.1	11.3	13.1

Footnotes to the table:

- 1) Analysis performed by Agvise Inc. on 13 August 1991;
- 2) Analysis performed by Agvise Inc. on 4 February 1992;
- 3) Analysis performed by A&L Great Lakes Laboratories Inc. on 29 March 1993;
- 4) Value recalculated by the RMS using the following equation: $pH_{H_2O} = 0.982 pH_{CaCl_2} + 0.648$;
- 5) Value calculated from the corresponding pH in water;
- 6) Value calculated by RMS using the following relationship: OC = OM/1.724.

Table B.8.1.1.2.1.1._CA-7: The characteristic of soil used in the study [Hellpointner; 1999].

Parameter		Soil:
		Laacherhof AXXa
Soil origin		Monheim/ Rheinland/ North Rhine-Westphalia/ Germany
Soil type (USDA)		Sandy loam
Particle size distribution	Sand (50 µm – 2 mm) [%]	71.77
	Silt (2 – 50 µm) [%]	16.47
	Clay (< 2 µm) [%]	11.76
pH value in distilled water		7.0
pH value in 0.01M CaCl ₂		6.1
Organic carbon content (C _{org}) [%] ¹⁾		1.41
Organic matter content (OM) [%] ²⁾		2.42
Cation Exchange Capacity – CEC [mEq/100g]		9.61
Particle density [g/cm ³]		2.5
Water holding capacity	Maximum [g H ₂ O/100 g soil d. w.]	34.4
	50% MWHC [g H ₂ O/100 g soil d. w.]	17.2

Footnotes to the table:

- 1) Measured value;
- 2) Value calculated by the Applicant using the following equation: OM = 1.724*OC;

The incubation conditions used in each experiment are summarised below in the table B.8.1.1.2.1.1._CA-8.

Table B.8.1.1.2.1.1._CA-8: The incubation conditions used in each experiment.

Study	Test soil		Experimental conditions			
	Name	Type (USDA classification)	Incubation temperature T [°C]	Soil moisture		
				In experiment	Reference value	
					MWHC	at ½ bar
Kelley <i>et al.</i> ; 1995	BBA 2.2	Loamy sand	20 ± 1	40% MWHC	53.8%	----
	Laacherhof	Silt loam	20 ± 1	40% MWHC	48.6%	----
	Höfchen im Tal	Silt loam	20 ± 1	40% MWHC	71.6%	----
Pangilinan and Smith; 1994	Howe, Indiana	Sandy loam	21 ± 1	75% of ½ bar	----	13.1%
Hellpointner; 1999	Laacherhof AXXa	Sandy loam	20	50% MWHC	34.4 [g/100 g soil d. w.]	----

The not-processed input data used in the kinetic analysis are presented below, separately for each test soils, in tables B.8.1.1.2.1.1._CA-9 – B.8.1.1.2.1.1._CA-13. In case of the data obtained in two studies – [Pangilinan and Smith; 1994] and [Hellpointner; 1999], only the averages of two replicates are given. For the data from the study by [Kelley et al.; 1995] the results for each replicate are provided only for the parent compound, while for the degradation products they are given as averages. That format of reporting the values was adopted by the authors of this study report.

Table B.8.1.1.2.1.1._CA-9: The non-processed data obtained in **BBA 2.2** Loamy sand soil (study by [Kelley et al.; 1995]) used as input in kinetic analysis.

Time Point – DAT ¹⁾ [days]	Concentration, expressed as [% AR], of:					
	<i>Flufenacet</i>		<i>FOE Sulfonic acid</i>	<i>FOE Oxalate</i>	<i>FOE Methylsulfoxide</i>	<i>FOE Methylsulfone</i>
	Replicate 1	Replicate 2	average	average	average	average
0	97.0	97.7	0.0	0.0	0.0	0.0
7	70.8	75.4	2.4	3.7	0.0	0.0
14	67.2	65.7	3.9	5.4	0.0	0.2
28	45.2	42.0	9.5	6.6	1.1	1.1
56	27.6	27.8	12.3	4.0	1.4	2.8
70	21.5	18.3	17.8	0.6	0.3	2.6
100	14.7	18.9	25.4	0.0	0.3	6.6
120	10.3	9.7	22.6	0.0	0.0	4.7

Footnotes to the table:

1) DAT stands for “Days After Treatment”;

Table B.8.1.1.2.1.1._CA-10: The non-processed data obtained in **Laacherhof** Silt loam soil (study by [Kelley et al.; 1995]) used as input in kinetic analysis.

Time Point – DAT ¹⁾ [days]	Concentration, expressed as [% AR], of:					
	<i>Flufenacet</i>		<i>FOE Sulfonic acid</i>	<i>FOE Oxalate</i>	<i>FOE Methylsulfoxide</i>	<i>FOE Methylsulfone</i>
	Replicate 1	Replicate 2	average	average	average	average
0	84.7	85.9	0.6	0.0	0.0	0.0
7	56.1	58.2	3.9	7.0	1.0	0.2
14	51.5	42.9	9.0	10.9	1.6	0.5
28	28.0	19.2	14.6	15.6	3.4	1.7
56	7.6	4.7	22.2	10.0	3.5	4.0
70	5.4	3.9	21.0	7.3	3.2	4.1
100	3.0	3.4	26.3	1.6	2.4	3.1
120	2.5	3.1	21.8	0.0	0.7	4.3

Footnotes to the table:

1) DAT stands for “Days After Treatment”;

Table B.8.1.1.2.1.1._CA-11: The non-processed data obtained in **Höfchen im Tal** Silt loam soil (study by [Kelley et al.; 1995]) used as input in kinetic analysis.

Time Point – DAT ¹⁾ [days]	Concentration, expressed as [% AR], of:					
	<i>Flufenacet</i>		<i>FOE Sulfonic acid</i>	<i>FOE Oxalate</i>	<i>FOE Methylsulfoxide</i>	<i>FOE Methylsulfone</i>
	Replicate 1	Replicate 2	average	average	average	average
0	91.9	90.9	0.1	0.0	0.0	0.0
7	80.7	73.2	2.6	4.9	0.8	0.1
14	49.7	59.3	4.3	8.9	0.5	0.2
28	37.0	37.5	8.7	10.0	1.3	1.6
56	14.1	14.0	13.0	6.4	1.5	2.9
70	13.0	9.2	11.2	3.7	1.1	4.1
100	4.9	5.0	13.5	0.9	0.2	3.6
120	6.3	4.9	13.5	0.0	0.2	5.6

Footnotes to the table:

1) DAT stands for “Days After Treatment”;

Table B.8.1.1.2.1.1._CA-12: The non-processed data obtained in **Howe, Indiana**, Sandy loam soil (study by [Pangilinan and Smith; 1994]) used as input in kinetic analysis.

Time Point – DAT ¹⁾ [days]	Concentration, expressed as [% AR], of:		
	<i>Flufenacet</i>	<i>FOE Sulfonic acid</i>	<i>FOE Oxalate</i>
0	93.3	<0.1	0.1
7	76.1	1.0	4.7
14	67.3	2.6	10.1
21	59.7	3.5	10.6
28	51.4	4.7	12.2
44	51.2	5.1	11.9
65	48.0	4.7	14.0
76	51.3	6.0	14.1
91	47.5	5.5	15.2
180	44.6	7.7	14.6
271	38.6	5.8	17.0
365	35.2	5.3	26.5

Footnotes to the table:

1) DAT stands for “Days After Treatment”;

Table B.8.1.1.2.1.1._CA-13: The non-processed data obtained in **Laacherhof AXXA** Sandy loam soil (study by [Hellpointner; 1999]) used as input in kinetic analysis.

Time Point – DAT ¹⁾ [days]	Concentration of Flufenacet, expressed as [% AR]:
0	92.3
0.1	88.0
3	58.1
7	46.7
14	25.6
28	14.4
42	5.3
56	4.9

Footnotes to the table:

1) DAT stands for “Days After Treatment”;

Additionally, in the table B.8.1.1.2.1.1._CA-14 are presented the DAT-0 recoveries, used in processed-data sets as inputs for DAT-0 time points. The averages of two replicates are given, because only these values were provided in source study reports. In the same table are given the LOD values, subsequently used in data-processing procedure.

Table B.8.1.1.2.1.1._CA-14: The DAT-0 recoveries and LOD determined for each experiment.

Study	Test soil		Determined parameter	
	<i>Soil name</i>	<i>Soil type (USDA classification)</i>	<i>DAT-0 recovery [% AR]</i>	<i>LOD [% AR]</i>
<i>Kelley et al.; 1995</i>	BBA 2.2	Loamy sand	99.3	0.1
	Laacherhof	Silt loam	93.2	0.1
	Höfchen im Tal	Silt loam	97.3	0.1
<i>Pangilinan and Smith; 1994</i>	Howe, Indiana	Sandy loam	95.1	0.1
<i>Hellpointner; 1999</i>	Laacherhof AXXa	Sandy loam	100.0	1.0

The data presented in the above tables were subjected to a multistep evaluation procedure performed in line with the recommendations of FOCUS Kinetics Guidelines [FOCUS; 2006]. It consisted of the following steps:

- **Step 1:** Processing of the raw input data;
- **Step 2:** Kinetic evaluation of the processed data using following, 1st order, kinetic models: SFO, FOMC and DFOP, and KinGUI 2 as a modelling tool. That step consisted of the two sub-steps:
 - **Sub-step 1:** kinetic evaluation of the data for parent compound (Flufenacet) only, in order to determine the appropriate kinetic model. At that stage of analysis were tested all three kinetic models listed above;
 - **Sub-step 2:** kinetic evaluation of the data for parent compound (Flufenacet) and its degradation products using for Flufenacet the kinetic model identified as appropriate at previous stage, and SFO model for degradation products;

- **Step 3:** Evaluation of the results of kinetic examination of the data;
- **Step 4:** Reporting of the obtained results, in particular kinetic parameters (not normalised) recommended for modelling.

The raw input data, presented in tables B.8.1.1.2.1.1._CA-9 – B.8.1.1.2.1.1._CA-14, were processes following the recommendations given by FOCUS. In general terms it looked as follows:

- Measured and reported true replicates were taken into account singularly;
- The data sets were checked for their consistency and clear outliers. In case the outliers were found and removed, that was clearly indicated.
- In case of the data from the study by [Pangilinan and Smith; 1994] all data after the time point DAT 28 were removed. That was due to the fact that the collapse of soil microbial activity was observed after that time point. RMS stated that the measure taken by the Applicant was in line with the provisions of FOCUS Kinetics Guidance Document, [FOCUS; 2006].

The particular, measures taken in the processing of the data for the parent compound – Flufenacet, were following:

- The total AR recovery recorded in DAT-0 samples was used as concentration of Flufenacet at that time point, but the M_0 value was allowed to be estimated by the model;
- Values between LOD and LOQ were set to measured values;
- All single values <LOD or the non-detects (n. d.) were set to $\frac{1}{2}$ LOD. The same procedure was applied to the first appearances. However, when the values <LOD/n.d. appeared consecutively for second and next times, the kinetic curve was cut off until the appearance of the first value >LOQ.

The values for degradation products were processed in a following way:

- The initial (DAT-0) concentration was set to 0. That value, unlike the free-fitted M_0 concentration for the parent compound, was a fixed value;
- The values for subsequent time points, if reported as <LOD or non-detects were also set to 0 until the last time point before the first detectable amount was recorded;
- The value reported as <LOD/n.d. appearing just before the first detectable amount was recorded was set to $\frac{1}{2}$ LOD.
- Values between LOD and LOQ were set to measured values;
- In the decline phase the first values <LOD/n.d. were also set $\frac{1}{2}$ LOD. For the consecutive second and next such appearances the kinetic curve was cut off until, eventually, the first value >LOQ appeared.

The processed values used as input data for the kinetic examination are presented below, individually for each test soil, in tables B.8.1.1.2.1.1._CA-15 – B.8.1.1.2.1.1._CA-19. In case of the results obtained in the study by [Kelley et al.; 1995] – in soils **BBA 2.2**, **Laacherhof** and **Höfchen im Tal**, for all compounds the values for two replicates were given. As in case of the degradation products only averages of the two replicates were provided, the measured value was given for the Replicate 1, while for the Replicate 2 it was set to NaN (“Not a Number” – KinGUI default when numbers are not available). In case of the results obtained in two remaining studies – [Pangilinan and Smith; 1994] and [Hellpointner; 1999] the processed values used as input data were the averages of the two replicates, as such were reported in the source study reports.

Table B.8.1.1.2.1.1._CA-15: The processed residue data for **BBA 2.2** Loamy sand soil (study [Kelley et al.; 1995]).

Time Point – DAT ¹⁾ [days]	Concentration, expressed as [% AR], of:									
	<i>Flufenacet</i>		<i>FOE Sulfonic acid</i>		<i>FOE Oxalate</i>		<i>FOE Methylsulfoxide</i>		<i>FOE Methylsulfone</i>	
	Replic. 1	Replic. 2	Replic. 1	Replic. 2	Replic. 1	Replic. 2	Replic. 1	Replic. 2	Replic. 1	Replic. 2
0	99.3	99.3	0.0	NaN	0.0	NaN	0.0	NaN	0.0	NaN
7	70.8	75.4	2.4	NaN	3.7	NaN	NaN	NaN	0.05 ¹⁾	NaN
14	67.2	65.7	3.9	NaN	5.4	NaN	0.05 ¹⁾	NaN	0.2	NaN
28	45.2	42.0	9.5	NaN	6.6	NaN	1.1	NaN	1.1	NaN
56	27.6	27.8	12.3	NaN	4.0	NaN	1.4	NaN	2.8	NaN
70	21.5	18.3	17.8	NaN	0.6	NaN	0.3	NaN	2.6	NaN
100	14.7	18.9	24.5	NaN	0.05 ¹⁾	NaN	0.3	NaN	6.6	NaN
120	10.3	9.7	22.6	NaN	NaN	NaN	0.05 ¹⁾	NaN	4.7	NaN

Footnotes to the table:

1) Value set to $\frac{1}{2}$ LOD.

Table B.8.1.1.2.1.1._CA-16: The processed residue data for **Laacherhof** Silt loam soil (study [Kelley et al.; 1995]).

Time Point – DAT ¹⁾ [days]	Concentration, expressed as [% AR], of:									
	<i>Flufenacet</i>		<i>FOE Sulfonic acid</i>		<i>FOE Oxalate</i>		<i>FOE Methylsulfoxide</i>		<i>FOE Methylsulfone</i>	
	Replic. 1	Replic. 2	Replic. 1	Replic. 2	Replic. 1	Replic. 2	Replic. 1	Replic. 2	Replic. 1	Replic. 2
0	93.2	93.2	0.0	NaN	0.0	NaN	0.0	NaN	0.0	NaN
7	56.1	58.2	3.9	NaN	7.0	NaN	1.0	NaN	0.2	NaN
14	51.5	42.9	9.0	NaN	10.9	NaN	1.6	NaN	0.5	NaN
28	28.0	19.2	14.6	NaN	15.6	NaN	3.4	NaN	1.7	NaN
56	7.6	4.7	22.2	NaN	10.0	NaN	3.5	NaN	4.0	NaN
70	5.4	3.9	21.0	NaN	7.3	NaN	3.2	NaN	4.1	NaN
100	3.0	3.4	26.3	NaN	1.6	NaN	2.4	NaN	3.1	NaN
120	2.5	3.1	21.8	NaN	0.05 ¹⁾	NaN	0.7	NaN	4.3	NaN

Footnotes to the table:

1) Value set to ½LOD.

Table B.8.1.1.2.1.1._CA-17: The processed residue data for **Höfchen im Tal** Silt loam soil (study [Kelley et al.; 1995]).

Time Point – DAT ¹⁾ [days]	Concentration, expressed as [% AR], of:									
	<i>Flufenacet</i>		<i>FOE Sulfonic acid</i>		<i>FOE Oxalate</i>		<i>FOE Methylsulfoxide</i>		<i>FOE Methylsulfone</i>	
	Replic. 1	Replic. 2	Replic. 1	Replic. 2	Replic. 1	Replic. 2	Replic. 1	Replic. 2	Replic. 1	Replic. 2
0	97.3	97.3	0.0	NaN	0.0	NaN	0.0	NaN	0.0	NaN
7	80.7	73.2	2.6	NaN	4.9	NaN	0.8	NaN	0.1	NaN
14	49.7	59.3	4.3	NaN	8.9	NaN	0.5	NaN	0.2	NaN
28	37.0	37.5	8.7	NaN	10.0	NaN	1.3	NaN	1.6	NaN
56	14.1	14.0	13.0	NaN	6.4	NaN	1.5	NaN	2.9	NaN
70	13.0	9.2	11.2	NaN	3.7	NaN	1.1	NaN	4.1	NaN
100	4.9	5.0	13.5	NaN	0.9	NaN	0.2	NaN	3.6	NaN
120	6.3	4.9	13.5	NaN	0.05 ¹⁾	NaN	0.2	NaN	5.6	NaN

Footnotes to the table:

1) Value set to ½LOD.

Table B.8.1.1.2.1.1._CA-18: The processed residue data for **Howe, Indiana**, Sandy loam soil (study [Pangilinan and Smith; 1994]).

Time Point – DAT ¹⁾ [days]	Concentration, expressed as [% AR], of:		
	<i>Flufenacet</i>	<i>FOE Sulfonic acid</i>	<i>FOE Oxalate</i>
0	95.1	0.0	0.0
7	76.1	1.0	4.7
14	67.3	2.6	10.1
21	59.7	3.5	10.6
28	51.4	4.7	12.2

Table B.8.1.1.2.1.1._CA-19: The processed residue data for **Laacherhof AXXa** Sandy loam soil (study [Hellpointner; 1999]).

Time Point – DAT ¹⁾ [days]	Concentration of Flufenacet, expressed as [% AR]:
0	100.0
0.1	88.0
3	58.1
7	46.7
14	25.6
28	14.4
42	5.3
56	4.9

The processed data were kinetically examined using KinGUI ver. 2 modelling tool, developed by Bayer. The optimisation was performed using IRLS (Iteratively Reweighed Nonlinear Least Squares) algorithm. The fitting procedure was a two-stage one. The first step, further called **Step 1**, consisted on the determination of the appropriate kinetic model for the parent compound – Flufenacet. At that stage three 1st-order kinetic models were tested: SFO, FOMC and DFOP. During the next stage, further called **Step 2**, the whole data set – data for the Flufenacet and its degradation products, was kinetically examined. In case of Flufenacet the tested kinetic model was that determined as appropriate at **Step 1**, while for the degradation products the SFO model was used.

The conceptual metabolic pathway built in the modelling tool for the most complex data bases – the data from the study by [Kelley et al.; 1995], is presented below on figure B.8.1.1.2.1.1_CA-5. The following abbreviations were used:

- FFA for Flufenacet (parent compound);
- FOESA for FOE Sulfonic acid;
- FOEOX for FOE Oxalate;
- FOEMSX for FOE Methylsulfoxide;
- FOEMS for FOE Methylsulfone.

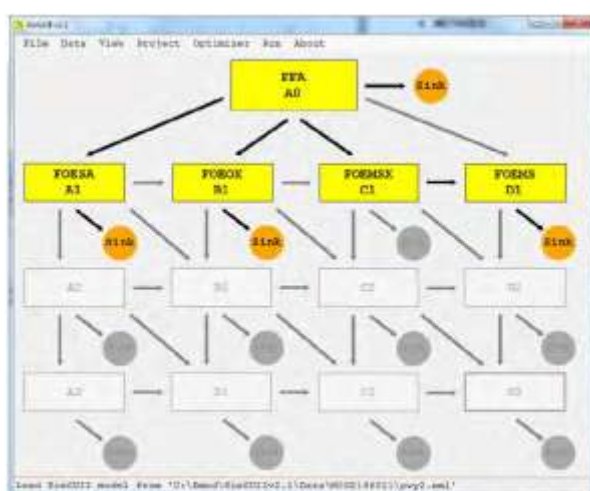


Figure B.8.1.1.2.1.1_CA-5: The conceptual transformation scheme assumed in the modelling tool for the data sets from the study by [Kelley et al.; 1995]
(copied from the study report).

For the data sets from other studies that scheme was adopted, according to the needs, as follows:

- for the data from the study by **[Pangilinan and Smith; 1994]** by removing FOEMSX and FOEMS compartments;
- for the data from the study by **[Hellpointner; 1999]** by removing all compartments representing the degradation products.

The obtained results of the kinetic analysis of the data were evaluated by the Applicant. That was done by means of a detailed statistical analysis, comprising the following components:

- visual assessment of the fit;
- χ^2 -error statistics;
- t-test significance;
- correlation analysis.

Characterising the whole procedure the Applicant stated at the beginning that it is generally preferred to select the simplest kinetic model with a high goodness of fit. That principle was followed when the assessment of the results obtained at the **Step 1** of kinetic analysis of the data was carried out.

Characterising the adopted approach to the visual assessment of the fit, considered to be the first step in the evaluation, the Applicant stated that it focused on the following features:

- the conformity of the fitted decline curve with measured residue concentrations;
- the distribution of the residuals, which should be random and not systematic;
- level of residuals, which should be as small as possible – in such case even if their distribution is rather systematic, the fit may be still qualified as acceptable.

Based on these criteria the fit could be classified as:

- **good fit**, when the conformity of the kinetic curve and measured residues was good, levels of residuals were low, they were randomly scattered and no obvious systematic deviation in residual plot was visible;
- **acceptable fit**, when the conformity of the kinetic curve and measured residues was acceptable, levels of residuals were medium and they were more-or-less randomly scattered, and the absolute level of residuals was low;
- **poor fit**, when the fitted decline curve significantly deviated from the measured residues and did not match the observed pattern, the level of residuals was high and they were clearly not randomly scattered around zero line.

Characterising the next component of the assessment – χ^2 -error statistics, the Applicant indicated that 15% threshold value was not considered to be an absolute cut-off criterion, especially in case of the degradation products. That was indicated to be due to the fact that that threshold value is strictly appropriate for optimal experimental conditions only. It was therefore indicated that in some cases, even though χ^2 -error > 15%, the fit may be acceptable. Additionally, for degradation products it was indicated that for them usually measurements in comparison to the mean of all measurements are low, what strongly influences the χ^2 test.

Finally, characterising the t-test, the Applicant stated that the t-test probability of 0.05 was sufficiently small and should be used as acceptability criterion, in case however of degradation products, or the results of field dissipation studies the *prob* > *t* value of 0.10 or even higher may be still acceptable.

On that basis the following multistep assessment procedure was followed:

- **Step 1:** bearing in mind the aim of the kinetic evaluation of the data – determination of the kinetic parameters used in modelling, the SFO kinetic model was tested as first option and if passed the acceptance criteria (visually acceptable, χ^2 -error not exceeding, or not significantly exceeding, 15%, *prob.* > *t* value in t-test less than 0.05 for parent and 0.10 for the degradation products), it was considered acceptable;
- **Step 2:** in case the χ^2 -error was significantly greater than 15%, model parameters were fixed and fitting repeated using SFO model;
- **Step 3:** if the **Step-2** fitting failed the χ^2 -error test, bi-phasic models were introduced. These were FOMC, DFOP and, possibly HS. The model with smaller error was indicated as the most appropriate;
- **Step 4:** if none of the bi-phasic model returned significantly improved fit, SFO model was selected if visually acceptable. That was done in order to avoid of an over-parameterised model based on a marginally better fit.

Analysing the proposed assessment procedure RMS stated that it complied with the procedure for determination of the kinetic endpoints for modelling, presented in FOCUS Kinetics Guidance Document [FOCUS; 2006].

The results of the kinetic examination of the data and their evaluation are provided below, individually for each test soil.

- 1) The results of the kinetic analysis of the data obtained in **BBA 2.2** Loamy sand soil (study by [Kelley et al.; 1995]):

The analysis for this data-set was a two-step analysis. Its results are presented below, individually for each step.

- a) Results obtained at **Step 1** – fitting of the data for the parent compound (Flufenacet) alone:

The results of the kinetic analysis performed by the Applicant are presented below, in graphical form on figure B.8.1.1.2.1.1_CA-6 and in numerical form in the table B.8.1.1.2.1.1_CA-20. Additionally the table B.8.1.1.2.1.1_CA-21 provides the kinetic endpoints obtained with each of the kinetic models tested.

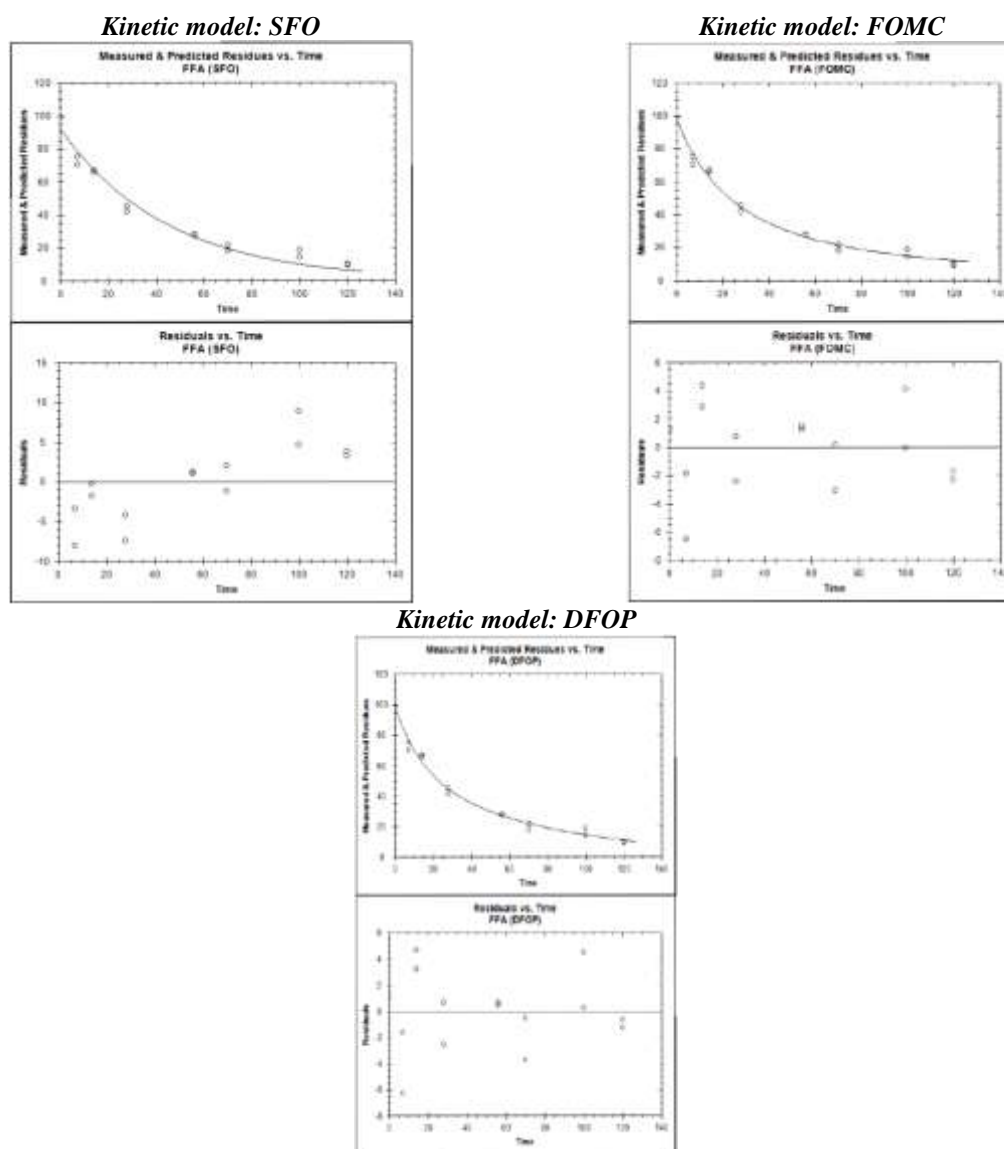


Figure B.8.1.1.2.1.1_CA-6: The graphical results of the kinetic analysis (copied from the study report).

Table B.8.1.1.2.1.1._CA-20: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment ¹⁾
				Lower	Upper			
SFO	M ₀	92.060	2.779	86.613	97.507	5.3 E-15	8.495	0.975; Acceptable fit
	k	0.02224	0.00155	0.0192	0.025	4.39 E-10		
FOMC	M ₀	98.066	2.034	94.079	102.053	2.4 E-16	4.520	0.992; Good fit
	α	1.5660	0.2987	0.9806	2.151	7.93 E-5		
	β	42.5634	12.0661	18.9142	66.212	0.00186		
DFOP	M ₀	98.232	2.174	93.971	102.492	4.5 E-15	4.862	0.992; Good fit
	k ₁	0.06906	0.02590	0.01892	0.120	0.0103		
	k ₂	0.01367	0.00333	0.00714	0.020	0.00073		
	g	0.4258	0.1580	0.1161	0.735	0.00974		

Footnotes to the table:

1) Visual assessment of the kinetic curve as proposed by the Applicant.

Table B.8.1.1.2.1.1._CA-21: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested		
		SFO	FOMC	DFOP
Flufenacet	DT ₅₀ [days]	31.16	23.70	23.55
	DT ₉₀ [days]	103.50	142.60	127.90

The Applicant stated that the fit returned by the SFO model was visually and statistically acceptable, therefore it was selected as appropriate and used at the next step to kinetically examine the data for Flufenacet and its degradation products. RMS accepted that choice.

- b) Results obtained at **Step 2** – fitting of the data for the parent compound (Flufenacet) and its degradation products:

The results of the kinetic analysis performed by the Applicant are presented below, in graphical form on figure B.8.1.1.2.1.1._CA-7 and in numerical form in the table B.8.1.1.2.1.1._CA-22. Additionally, in the table B.8.1.1.2.1.1._CA-23 are presented the kinetic endpoints obtained as a result of the evaluation, which were considered reliable by the Applicant.

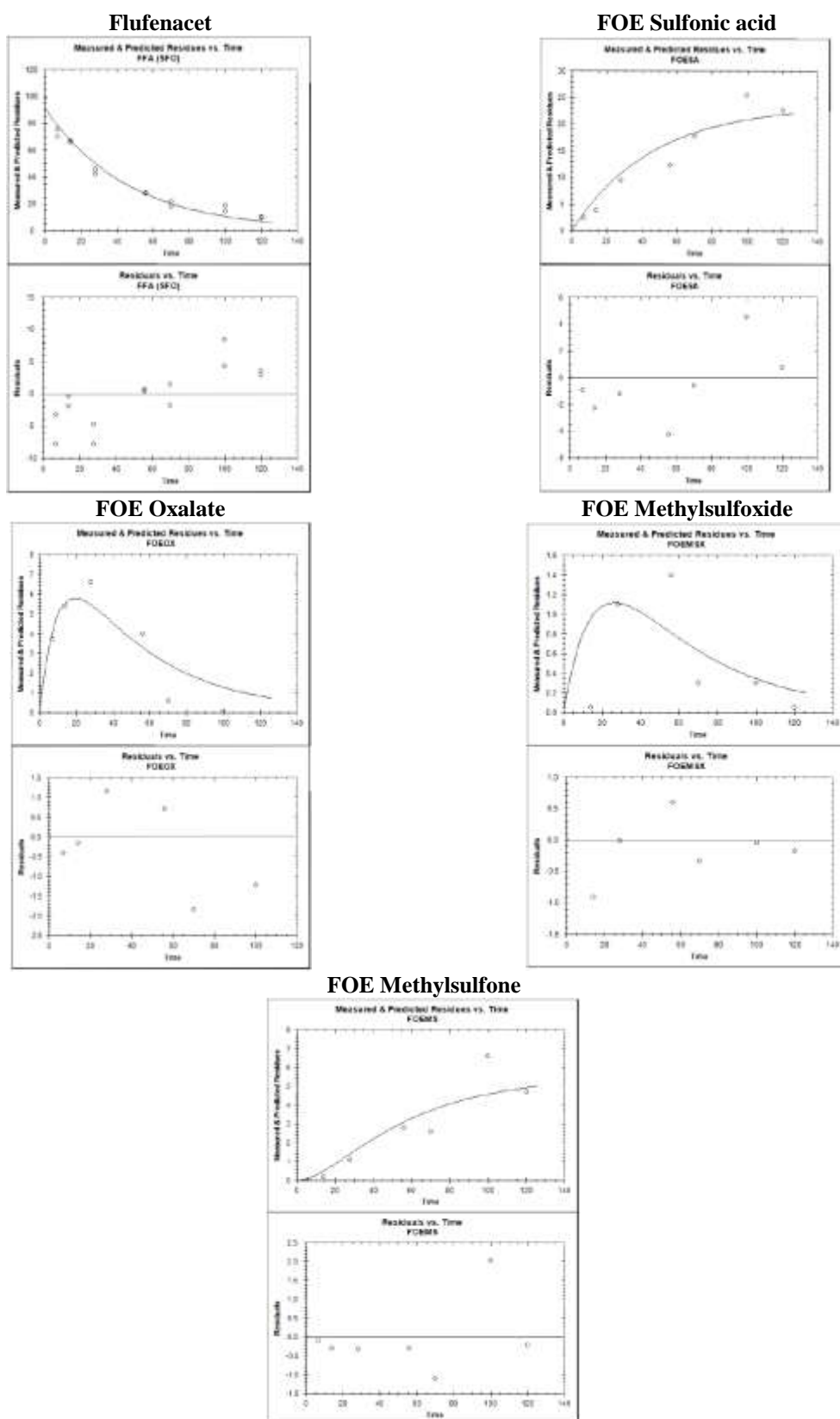


Figure B.8.1.1.2.1.1_CA-7: The graphical results of the kinetic examination of the data for Flufenacet, FOE Sulfonic acid, FOE Oxalate, FOE Methylsulfoxide and FOE Methylsulfone obtained in BBA 2.2 soil (copied from the study report).

Table B.8.1.1.2.1.1._CA-22: The numerical results of the kinetic examination of the data for Flufenacet, FOE Sulfonic acid, FOE Oxalate, FOE Methylsulfoxide and FOE Methylsulfone obtained in BBA 2.2 soil.

Compound	Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
			Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment ¹⁾
					Lower	Upper			
Flufenacet	SFO	M ₀	91.49	2.82	85.97	97.02	<2 E-16	8.53	0.974; fit acceptable
		k	0.02170	0.001506	0.01875	0.025	<2 E-16		
FOE Sulfonic acid	SFO	M ₀	0.0	----	----	----	----	15.40	0.936; fit good
		k	2.3 E-14	+ ∞	- ∞	+ ∞	0.5		
		ff	0.257	0.0214	----	----	----		
FOE Oxalate	SFO	M ₀	0.0	----	----	----	----	25.23	0.879; fit acceptable
		k	0.1011	0.03815	0.002629	0.176	0.0059		
		ff	0.448	0.202	----	----	----		
FOE Methylsulfoxide	SFO	M ₀	0.0	----	----	----	----	69.71	0.377; fit not assessed
		k	0.06102	0.01643	0.02882	0.093	3.35 E-4		
		ff	0.0606	0.114	----	----	----		
FOE Methylsulfone	SFO	M ₀	0.0	----	----	----	----	27.75	0.871; fit good
		k	2.4 E-14	+ ∞	- ∞	+ ∞	0.5		
		ff	1.0	----	----	----	----		

Footnotes to the table:

1) Visual assessment of the kinetic curve as proposed by the Applicant.

Table B.8.1.1.2.1.1._CA-23: The kinetic endpoints determined in the experiment, as reported by the Applicant.

Determined parameter	Compound			
	Flufenacet	FOE Sulfonic acid	FOE Oxalate	FOE Methylsulfone
DT ₅₀ [days]	31.9	1000	6.9	1000
DT ₉₀ [days]	106.1	> 1000	22.8	> 1000
Kinetic formation fraction ff	Not applicable	0.257 ± 0.021	0.448 ± 0.202	0.061 ± 0.114
Precursor	Not applicable	Flufenacet	Flufenacet	FOE Methylsulfoxide
Kinetic model	SFO	SFO	SFO	SFO

The results of the kinetic fitting for Flufenacet and FOE Sulfonic acid are acceptable. RMS however is of the opinion that while the kinetic formation fraction *ff* calculated for that compound may be considered reliable, the proposed for that compound kinetic endpoints – DT₅₀ and DT₉₀ values bear to high level of uncertainty to be considered such. It was also noticed that the kinetic model did not perform the statistical evaluation of the estimated rate constant *k* for FOE Sulfonic acid. All the may be attributed to the fact that neither well-pronounced decline phase, nor even the would-be maximum, were reached. As a result the proposed DT₅₀ and DT₉₀ values, although included into the definitive set of the endpoints derived from this experiment, will be considered informative only.

Applicant stated that the kinetic endpoints determined for FOE Oxalate are acceptable. In the study report it was stated that the fit, similarly to other fits obtained for all degradation products, showed a good conformity of measured residues and fitted decline curve, demonstrating itself in low χ^2 -error and high correlation coefficients. At the same time the Applicant characterised that fit only as “acceptable”, what stands in contrast with the above statement. RMS analysed the conformity of the fitted curve and measured residues and stated that it was good for the formation phase, but much worse for the decline phase. As a result, the kinetic parameters – DT₅₀ and DT₉₀ values, although statistically reliable according to the results of the t-test, bear some level of uncertainty. RMS also noticed that the distribution of the experimental points on the decline part of the kinetic curve and their number – four, may indicate that the repeated fitting of the data using the top-down approach may result in obtaining more reliable kinetic endpoints. The Applicant’s conclusion with regard to the reliability of the kinetic formation fraction for FOE Oxalate is valid.

In order to verify the assumption about the possible improvement of the fitting results for FOE Oxalate using the top-down approach the RMS performed own kinetic assessment of the data. As a starting point was used the DAT-28 time-point, where the measured concentration of FOE Oxalate in the test soil reached its maximum. The fitting was performed for two data sets – one of them consisting of four points (the DAT-120 was omitted, as it was done by the Applicant), the second one consisting of five data points, including DAT-120, for which the residue value was set to 0. The data used in repeated fitting are presented below in the table B.8.1.1.2.1.1._CA-24.

Table B.8.1.1.2.1.1_CA-24: The input data used in the repeated kinetic assessment for FOE Oxalate performed using the top-down approach.

Variant 1: 4-point data set		Variant 2: 5-point data set	
Time point – DAT [days]	Concentration of FOE Oxalate [%AR]	Time point – DAT [days]	Concentration of FOE Oxalate [%AR]
28	6.6	28	6.6
56	4.0	56	4.0
70	0.6	70	0.6
100	0.05	100	0.05
		120	0.0

The kinetic analysis of the data was performed using CAKE 3.1 modelling tool. IRLS (Iteratively Reweighed Nonlinear Least Squares) was used as optimisation algorithm. Due to the limited amount of the experimental points only SFO model was tested. The results are presented below, in graphical form on figure B.8.1.1.2.1.1_CA-8 and in numerical form in the table B.8.1.1.2.1.1_CA-25.

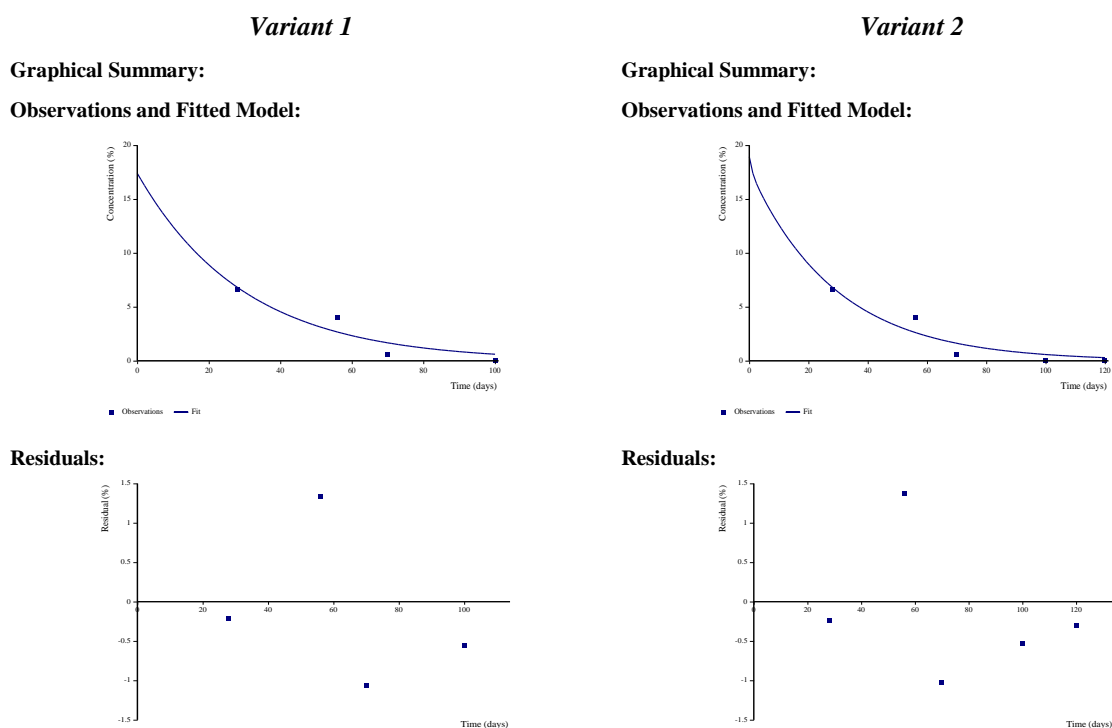


Figure B.8.1.1.2.1.1_CA-8: The graphical results of the kinetic analysis.

Table B.8.1.1.2.1.1_CA-25: The numerical results of the kinetic examination of the data for FOE Oxalate obtained in BBA 2.2 soil using the top-down approach.

Variant of the experiment	Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
			Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment
					Lower	Upper			
Variant 1	SFO	M_0	17.39	8.022	-17.12	51.91	-----	26.3	0.890; fit acceptable
		k	0.03349	0.01259	-0.02068	0.088	0.05852		
Variant 2	SFO	M_0	17.73	6.688	-3.551	39.02	-----	29.2	0.909; fit acceptable
		k	0.03411	0.0103	0.001332	0.067	0.02267		

The kinetic re-examination of the data did not resulted in statistical improvement of the fit – the level of the χ^2 -error even increased for both variants. Visually fit improved, but not significantly. The kinetic endpoints

determined for the Variant-1 fitting were not fully reliable – the *prob. > t* was higher than 0.05. In case of the Variant 2 it was possible to obtain reliable kinetic endpoints. RMS noticed that the kinetic endpoints were about three times higher in comparison to those obtained by the Applicant in fitting of the whole data set – for Variant 1 $DT_{50} = 20.7$ days and for Variant 2 $DT_{50} = 20.3$ days.

Additionally, for Variant-2 data set the RMS performed the fitting using two bi-phasic models – FOMC and DFOP. However, as no improvement of the fit was achieved and the reliability of the kinetic parameters was low, RMS decided not to present these results in order not to overburden the report.

In case of FOE Methylsulfone RMS stated that it was not possible to obtain the reliable kinetic fit. That was due to three factors:

- 1) low concentrations of FOE Methylsulfoxide – the precursor of FOE Methylsulfone, what made not possible to obtain the reliable kinetic fit for that compound;
- 2) low concentrations of FOE Methylsulfone itself, what also made impossible to obtain the acceptable fit for this compound;
- 3) the fact that the kinetic curve for FOE Methylsulfone was still in formation phase at the end of the experiment.

As a result, RMS stated that neither kinetic endpoints for FOE Methylsulfone nor the kinetic fraction *ff* reported for that compound by the Applicant may be considered reliable.

Examining the available data set RMS stated that the possible solution, which may lead to some improvement of the results of the fitting, would be to merge the results for FOE Methylsulfoxide and FOE Methylsulfone into one data set, considered as representative for FOE Methylsulfone, and repeat the kinetic analysis.

The data set used in the fitting exercise is presented below in the table B.8.1.1.2.1.1._CA-26. RMS decided for Flufenacet, FOE Sulfonic acid and FOE Oxalate to use the same data as the Applicant. However, as for Flufenacet two replicates were available, while for the metabolites only the averages of the two replicates, the RMS decided to use for all three degradation products, the average values as both Replicate 1 and Replicate 2.

Table B.8.1.1.2.1.1._CA-26: The input data used by the RMS in repeated kinetic evaluation of the results obtained in **BBA 2.2** Loamy sand soil (study [Kelley et al.; 1995]).

Time Point – DAT ¹⁾ [days]	Concentration, expressed as [% AR], of:							
	Flufenacet		FOE Sulfonic acid		FOE Oxalate		corr. FOE Methylsulfone	
	Replic. 1	Replic. 2	Replic. 1	Replic. 2	Replic. 1	Replic. 2	Replic. 1	Replic. 2
0	99.3	99.3	0.0	0.0	0.0	0.0	0.0	0.0
7	70.8	75.4	2.4	2.4	3.7	3.7	0.05 ¹⁾	0.05 ¹⁾
14	67.2	65.7	3.9	3.9	5.4	5.4	0.25	0.25
28	45.2	42.0	9.5	9.5	6.6	6.6	2.2	2.2
56	27.6	27.8	12.3	12.3	4.0	4.0	4.2	4.2
70	21.5	18.3	17.8	17.8	0.6	0.6	2.9	2.9
100	14.7	18.9	24.5	24.5	0.05 ¹⁾	0.05 ¹⁾	6.9	6.9
120	10.3	9.7	22.6	22.6	0.0	0.0	4.75	4.75

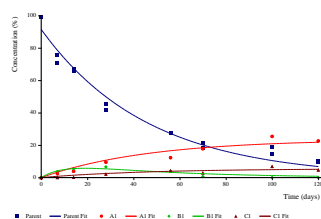
Footnotes to the table:

1) Value set to ½LOD.

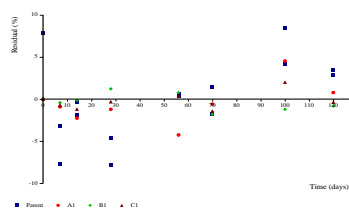
The analysis was carried out using CAKE 3.1 modelling tool, using IRLS (Iteratively Reweighed Nonlinear Least Squares) as optimisation algorithm. To maintain the consistency with the analysis performed by the Applicant RMS decided to perform it only for the SFO model in case of the parent compound. The results of the kinetic analysis performed by the RMS are presented below, in graphical form on figure B.8.1.1.2.1.1._CA-9 and in numerical form in the table B.8.1.1.2.1.1._CA-27. The kinetic endpoints calculated by the model are presented in the table B.8.1.1.2.1.1._CA-28.

Whole fit

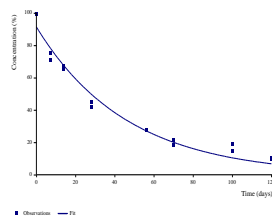
**Graphical Summary:
Observations and Fitted Model:**



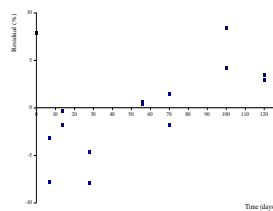
Residuals:

**Flufenacet**

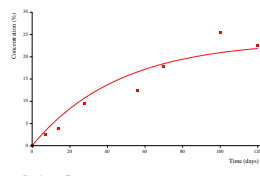
**Graphical Summary:
Observations and Fitted Model:**



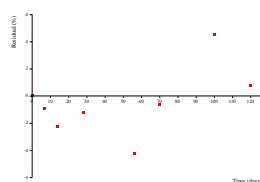
Residuals:

**FOE Sulfonic acid**

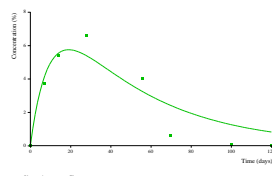
**Graphical Summary:
Observations and Fitted Model:**



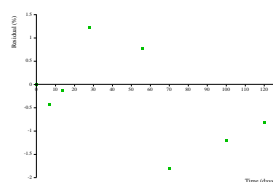
Residuals:

**FOE Oxalate**

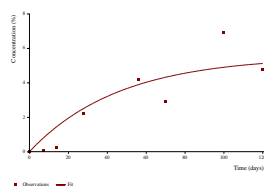
**Graphical Summary:
Observations and Fitted Model:**



Residuals:

**corr. FOE Methylsulfone**

**Graphical Summary:
Observations and Fitted Model:**



Residuals:

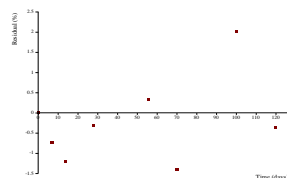


Figure B.8.1.1.2.1.1. CA-9: The graphical results of the kinetic examination of the data for Flufenacet, FOE Sulfonic acid, FOE Oxalate, and corr. FOE Methylsulfone obtained in BBA 2.2 soil.

Table B.8.1.1.2.1.1._CA-27: The numerical results of the kinetic examination of the data for Flufenacet, FOE Sulfonic acid, FOE Oxalate, FOE Methylsulfoxide and FOE Methylsulfone obtained in BBA 2.2 soil.

Compound	Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
			Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment
					Lower	Upper			
Flufenacet	SFO	M ₀	91.43	2.913	85.58	97.28	----	8.54	0.9736; good fit
		k	0.02164	0.001563	0.0185	0.025	4.8 E-19		
FOE Sulfonic acid	SFO	M ₀	0.0	----	----	----	----	15.4	0.9362; good fit
		k	7.5 E-25	0.002099	-0.00422	0.004	0.5		
		ff	0.2579	0.0378	0.182	0.334	----		
FOE Oxalate	SFO	M ₀	0.0	----	----	----	----	28.6	0.8943; acceptable fit
		k	0.104	0.02858	0.04656	0.161	3.25 E-4		
		ff	0.4559	0.1148	0.2253	0.687	----		
corr. FOE Methylsulfone	SFO	M ₀	0.0	----	----	----	----	28.5	0.8415; acceptable fit
		k	1.1 E-24	0.00368	-0.00740	0.007	0.5		
		ff	0.06047	0.01422	0.03191	0.089	----		

Table B.8.1.1.2.1.1._CA-28: The kinetic endpoints calculated by the model.

Determined parameter	Compound			
	Flufenacet	FOE Sulfonic acid	FOE Oxalate	corr. FOE Methylsulfone
DT ₅₀ [days]	32	10000	6.7	10000
DT ₉₀ [days]	106	> 10000	22.2	> 10000
Kinetic formation fraction ff	Not applicable	0.258 ± 0.038	0.456 ± 0.115	0.061 ± 0.014
Precursor	Not applicable	Flufenacet	Flufenacet	FOE Methylsulfoxide
Kinetic model	SFO	SFO	SFO	SFO

The results of the repeated kinetic analysis returned results comparable to those obtained by the Applicant. No significant improvement was achieved for the corrected data for FOE Methylsulfone.

Final assessment:

The kinetic analysis of the data for Flufenacet and its degradation products – FOE Sulfonic acid, FOE Oxalate, FOE Methylsulfoxide and FOE Methylsulfone resulted in good fitting results for the parent compound and FOE Sulfonic acid. In case of FOE Oxalate the fit was visually acceptable but not statistically, most probably due to the low concentrations of that compound in the test soil. It was noted that in case of FOE Sulfonic acid the decline phase was not reached during the experiment, it is even doubtful whether the kinetic curve reached its maximum point. Therefore the kinetic endpoints for that compound should be considered as indicative. The determined kinetic formation fraction *ff* for that compound may be considered reliable.

For FOE Oxalate it may be stated that despite not very good conformity of the kinetic curve in its decline part with the measurable residues the determined kinetic endpoints may be considered reliable, as demonstrated their statistical evaluation, although they bear some uncertainty. Reliable is also the kinetic formation fraction *ff* determined for that compound. It shall be noted that the repeated kinetic analysis of the data for FOE Oxalate performed by the RMS using the top-down approach did not result in obtaining more reliable fits. That may further indicate that the problems with the fitting are related to low concentrations of FOE Oxalate in the test soil, what in turn indicated its low persistence. Therefore the calculated for the whole kinetic curve DT₅₀ and DT₉₀ values may be considered reliable.

In case of FOE Methylsulfoxide and FOE Methylsulfone it was not possible to obtain fully reliable fit. Hence the kinetic endpoints determined for FOE Methylsulfone should be considered indicative, while kinetic formation fraction *ff* conditionally reliable.

- 2) The results of the kinetic analysis of the data obtained in **Laacherhof** Silt loam soil (study by [Kelley et al.; 1995]):

The analysis for this data-set was a two-step analysis. Its results are presented below, individually for each step.

- a) Results obtained at **Step 1** – fitting of the data for the parent compound (Flufenacet) alone:

The results of the kinetic analysis performed by the Applicant are presented below, in graphical form on figure B.8.1.1.2.1.1_CA-10 and in numerical form in the table B.8.1.1.2.1.1_CA-29. Additionally the table B.8.1.1.2.1.1_CA-30 provides the kinetic endpoints obtained with each of the kinetic models tested.

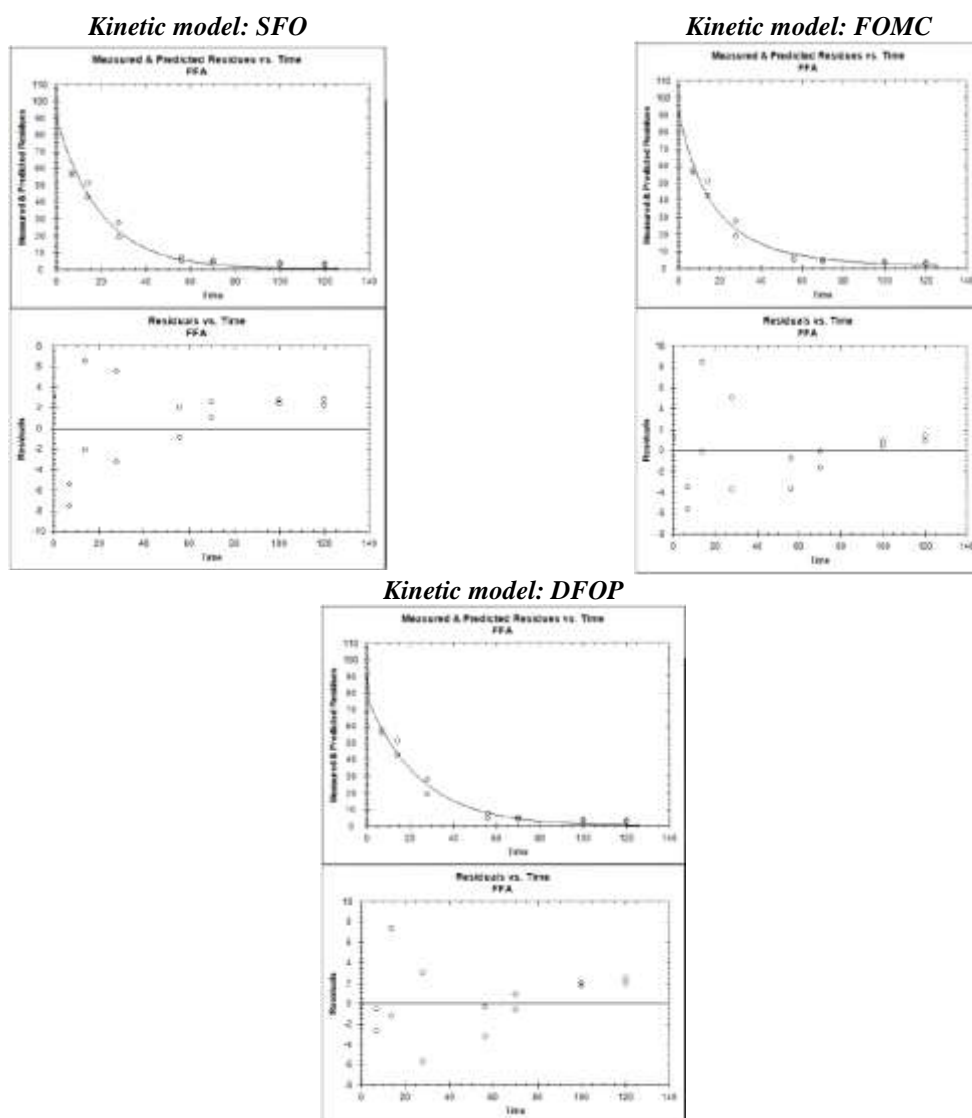


Figure B.8.1.1.2.1.1_CA-10: The graphical results of the kinetic analysis (copied from the study report).

Table B.8.1.1.2.1.1._CA-29: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment ¹⁾
				Lower	Upper			
SFO	M ₀	90.117	2.603	85.015	95.219	2.88 E-15	8.215	0.987; Good fit
	k	0.04965	0.00330	0.04318	0.056	2.43 E-10		
FOMC	M ₀	92.026	2.545	87.038	97.013	9.83 E-15	6.953	0.989; Acceptable fit
	α	3.7022	1.6909	0.3881	7.016	0.0237		
	β	61.4572	33.7177	-4.6283	127.543	0.0457		
DFOP	M ₀	93.200	2.365	88.565	97.835	2.30 E-14	5.496	0.992; Acceptable fit
	k ₁	196.922	n. a. ²⁾	n. a. ²⁾	n. a. ²⁾	n. a. ²⁾		
	k ₂	0.04086	0.00349	0.03402	0.048	3.17 E-8		
	g	0.1610	0.04854	0.06588	0.2562	0.00307		

Footnotes to the table:

- 1) Visual assessment of the kinetic curve as proposed by the Applicant;
 2) Value not calculated by the modelling tool.

Table B.8.1.1.2.1.1._CA-30: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested		
		SFO	FOMC	DFOP
Flufenacet	DT ₅₀ [days]	13.96	12.65	12.67
	DT ₉₀ [days]	46.38	53.01	52.05

On the basis of the obtained results the Applicant proposed to consider SFO as returning reliable and acceptable fit. That model was proposed to be used for the parent compound in kinetic examination of the data for parent compound and degradation products. RMS accepted that proposal noticing that neither FOMC nor DFOP returned fully reliable results.

- b) results obtained at **Step 2** – fitting of the data for the parent compound (Flufenacet) and its degradation products:

The results of the kinetic analysis performed by the Applicant are presented below, in graphical form on figure B.8.1.1.2.1.1._CA-11 and in numerical form in the table B.8.1.1.2.1.1._CA-31. Additionally, in the table B.8.1.1.2.1.1._CA-32 are presented the kinetic endpoints obtained as a result of the evaluation, which the Applicant considered reliable.

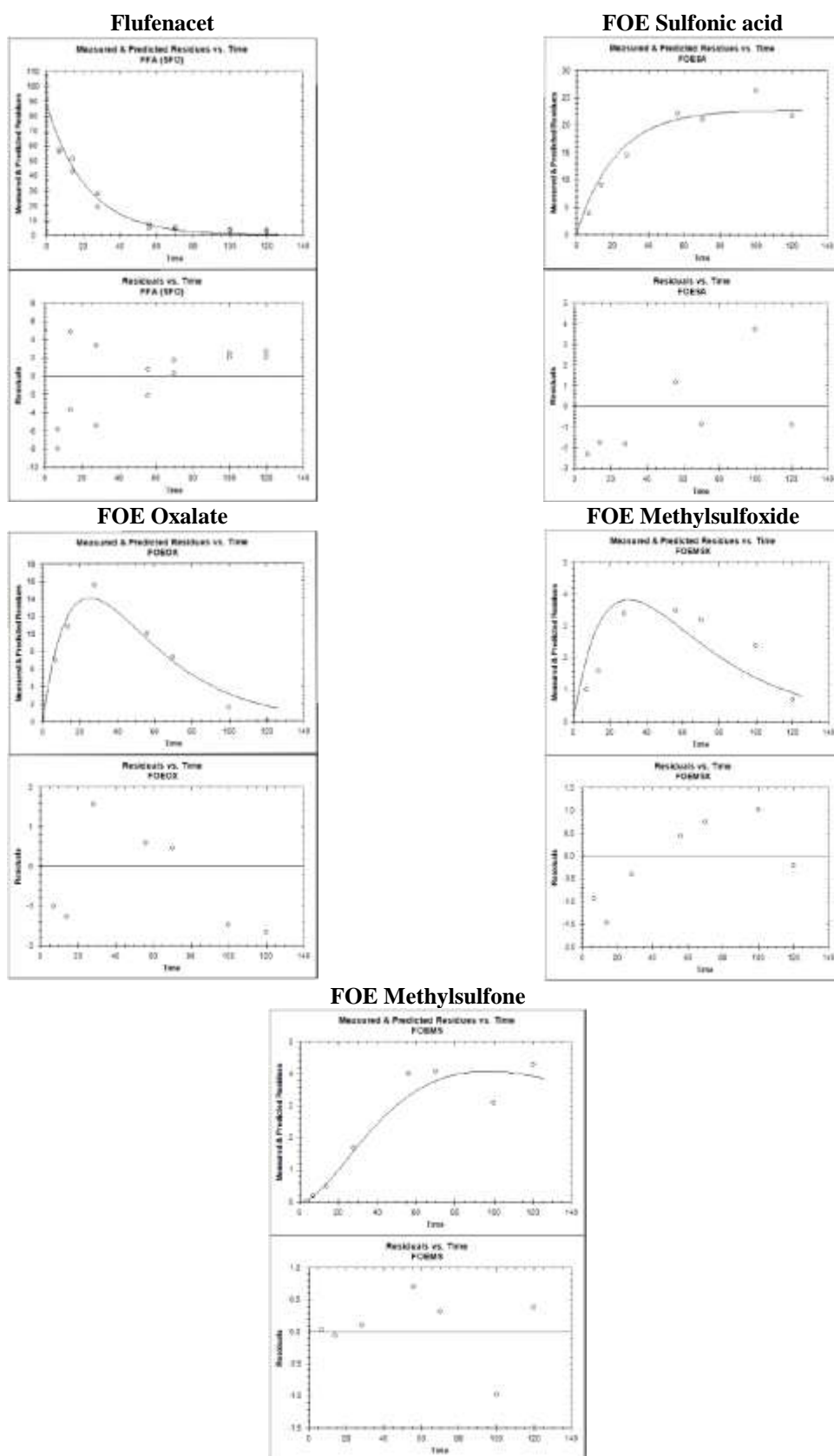


Figure B.8.1.1.2.1.1_CA-11: The graphical results of the kinetic examination of the data for Flufenacet, FOE Sulfonic acid, FOE Oxalate, FOE Methylsulfoxide and FOE Methylsulfone obtained in Laacherhof soil (copied from the study report).

Table B.8.1.1.2.1.1._CA-31: The numerical results of the kinetic examination of the data for Flufenacet, FOE Sulfonic acid, FOE Oxalate, FOE Methylsulfoxide and FOE Methylsulfone obtained in Laacherhof soil.

Compound	Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
			Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment ¹⁾
					Lower	Upper			
Flufenacet	SFO	M_0	88.197	2.738	82.831	93.564	<2 E-16	8.861	0.947; good fit
		k	0.04557	0.00322	0.03927	0.052	< 2 E-16		
FOE Sulfonic acid	SFO	M_0	0.0	----	----	----	----	9.501	0.964; Good fit
		k	0.000	0.00151	-0.00298	0.003	0.500		
		ff	0.2586	0.0294	----	----	----		
FOE Oxalate	SFO	M_0	0.0	----	----	----	----	13.050	0.966; fit acceptable
		k	0.03349	0.00461	0.02445	0.043	4.79 E-9		
		ff	0.375	0.0716	----	----	----		
FOE Methylsulfoxide	SFO	M_0	0.0	----	----	----	----	29.700	0.6343; fit not assessed
		k	0.0232	0.00344	0.01642	0.030	2.51 E-8		
		ff	0.0872	0.0547	----	----	----		
FOE Methylsulfone	SFO	M_0	0.0	----	----	----	----	15.364	0.930; good fit
		k	0.00838	0.00307	0.00236	0.014	0.00475		
		ff	1.0	----	----	----	----		

Table B.8.1.1.2.1.1._CA-32: The kinetic endpoints determined in the experiment, as reported by the Applicant.

Determined parameter	Compound			
	Flufenacet	FOE Sulfonic acid	FOE Oxalate	FOE Methylsulfone
DT ₅₀ [days]	15.21	1000	20.70	82.70
DT ₉₀ [days]	50.53	> 1000	68.76	274.74
Kinetic formation fraction ff	Not applicable	0.259 ± 0.029	0.375 ± 0.072	0.087 ± 0.057
Precursor	Not applicable	Flufenacet	Flufenacet	FOE Methylsulfoxide
Kinetic model	SFO	SFO	SFO	SFO

The results of the kinetic fitting for Flufenacet, FOE Sulfonic acid and FOE Oxalate are acceptable.

The kinetic parameters – DT₅₀ and DT₉₀ values for Flufenacet are reliable, therefore acceptable. Also reliable and therefore acceptable are all kinetic parameters – DT₅₀ and DT₉₀ values as well as kinetic formation fraction ff , obtained for FOE Oxalate. Also the statement with regard to the kinetic fit for that compound – it showed a good conformity of measured residues and fitted decline curve, demonstrating itself in low χ^2 -error and high correlation coefficients may be considered correct. RMS noticed that the Applicant classified the fit for FOE Oxalate, on the basis of the results of its visual inspection, as acceptable. RMS however is of the opinion that that fit should be classified as “good”.

In case of FOE Sulfonic acid RMS however is of the opinion that while the kinetic formation fraction ff calculated for that compound may be considered reliable, the proposed kinetic endpoints – DT₅₀ and DT₉₀ values bear to high level of uncertainty to be considered such. It was also noticed that the kinetic model did not estimate rate constant k for FOE Sulfonic acid. All the may be attributed to the fact that the decline phase was not reached. As a result the proposed DT₅₀ and DT₉₀ values, although included into the definitive set of the endpoints derived from this experiment, will be considered informative only.

In case of FOE Methylsulfone the acceptable fit was obtained, but it cannot be considered as reliable due to the lack of reliability of that for its precursor – FOE Methylsulfoxide. The lack of the reliability of the kinetic fit for FOE Methylsulfoxide is caused by low measurable concentrations of that compound used as input data in the kinetic analysis, what in turn is due to the fact that that compound was classified as minor/transient degradation product.

RMS decided to verify whether it was possible to obtain better, reliable fit for FOE Methylsulfone by merging the data for FOE Methylsulfone and FOE Methylsulfoxide into one data set and repeating kinetic analysis. That was done and the resulting data set is presented below in the table B.8.1.1.2.1.1._CA-33. RMS decided to use the data for Flufenacet, FOE Sulfonic acid and FOE Oxalate not modified in comparison to those proposed by the Applicant. However, as for Flufenacet two replicates were available, while for the metabolites only the averages of the two replicates, the RMS decided to use average values as Replicate 1 and Replicate 2. The same approach was adopted in case of FOE Methylsulfone.

Table B.8.1.1.2.1.1_CA-33: The input data used by the RMS in repeated kinetic evaluation of the results obtained in **Laacherhof** Silt loam soil (study [Kelley et al.; 1995]).

Time Point – DAT ¹⁾ [days]	Concentration, expressed as [% AR], of:							
	<i>Flufenacet</i>		<i>FOE Sulfonic acid</i>		<i>FOE Oxalate</i>		<i>corr. FOE Methylsulfone</i>	
	Replic. 1	Replic. 2	Replic. 1	Replic. 2	Replic. 1	Replic. 2	Replic. 1	Replic. 2
0	93.2	93.2	0.0	0.0	0.0	0.0	0.0	0.0
7	56.1	58.2	3.9	3.9	7.0	7.0	1.2	1.2
14	51.5	42.9	9.0	9.0	10.9	10.9	2.1	2.1
28	28.0	19.2	14.6	14.6	15.6	15.6	5.1	5.1
56	7.6	4.7	22.2	22.2	10.0	10.0	7.5	7.5
70	5.4	3.9	21.0	21.0	7.3	7.3	7.3	7.3
100	3.0	3.4	26.3	26.3	1.6	1.6	5.5	5.5
120	2.5	3.1	21.8	21.8	0.05 ¹⁾	0.05 ¹⁾	5.0	5.0

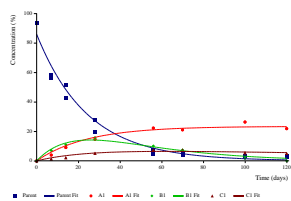
Footnotes to the table:

1) Value set to ½LOD.

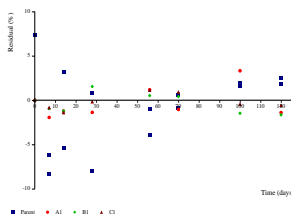
The analysis was carried out using CAKE 3.1 modelling tool, using IRLS (Iteratively Reweighed Nonlinear Least Squares) as optimisation algorithm. To maintain the consistency with the analysis performed by the Applicant RMS decided to perform it only for the SFO model in case of the parent compound. The results of the kinetic analysis performed by the RMS are presented below, in graphical form on figure B.8.1.1.2.1.1_CA-12 and in numerical form in the table B.8.1.1.2.1.1_CA-34. The kinetic endpoints calculated by the model are presented in the table B.8.1.1.2.1.1_CA-35.

Whole fit

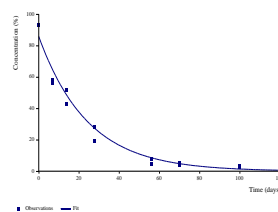
**Graphical Summary:
Observations and Fitted Model:**



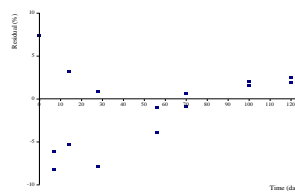
Residuals:

**Flufenacet**

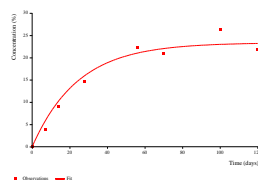
**Graphical Summary:
Observations and Fitted Model:**



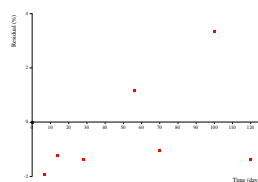
Residuals:

**FOE Sulfonic acid**

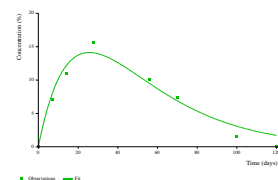
**Graphical Summary:
Observations and Fitted Model:**



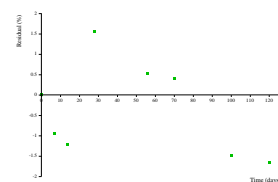
Residuals:

**FOE Oxalate**

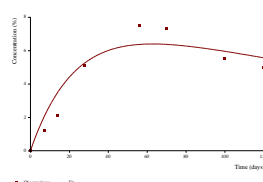
**Graphical Summary:
Observations and Fitted Model:**



Residuals:



**Graphical Summary:
Observations and Fitted Model:**

corr. FOE Methylsulfone

Residuals:

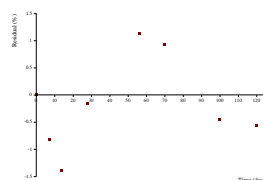


Figure B.8.1.2.1.1_CA-12: The graphical results of the kinetic examination of the data for Flufenacet, FOE Sulfonic acid, FOE Oxalate, and corr. FOE Methylsulfone obtained in Laacherhof soil.

Table B.8.1.1.2.1.1._CA-34: The numerical results of the kinetic examination of the data for Flufenacet, FOE Sulfonic acid, FOE Oxalate, FOE Methylsulfoxide and FOE Methylsulfone obtained in Laacherhof soil.

Compound	Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
			Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment
					Lower	Upper			
Flufenacet	SFO	M_0	85.85	3.188	79.45	92.26	----	11.0	0.9777; good fit
		k	0.04113	0.003421	0.03425	0.048	1.2 E-16		
FOE Sulfonic acid	SFO	M_0	0.0	----	----	----	----	8.42	0.9701; good fit
		k	2.8 E-27	0.001085	-0.00218	0.002	0.5		
		ff	0.2721	0.0264	0.219	0.325	----		
FOE Oxalate	SFO	M_0	0.0	----	----	----	----	12.7	0.9688; good fit
		k	0.03663	0.00438	0.02783	0.045	2.3 E-11		
		ff	0.422	0.0522	0.3172	0.527	----		
corr. FOE Methylsulfone	SFO	M_0	0.0	----	----	----	----	14.4	0.9227; good fit
		k	0.003995	0.00180	3.85 E-4	0.008	0.01539		
		ff	0.09566	0.01185	0.07186	0.119	----		

Table B.8.1.1.2.1.1._CA-35: The kinetic endpoints calculated by the model.

Determined parameter	Compound			
	Flufenacet	FOE Sulfonic acid	FOE Oxalate	corr. FOE Methylsulfone
DT ₅₀ [days]	16.9	10000	18.9	174
DT ₉₀ [days]	56	> 10000	62.9	576
Kinetic formation fraction ff	Not applicable	0.272 ± 0.026	0.422 ± 0.052	0.096 ± 0.012
Precursor	Not applicable	Flufenacet	Flufenacet	FOE Methylsulfoxide
Kinetic model	SFO	SFO	SFO	SFO

The results of the repeated kinetic analysis returned results comparable to those obtained by the Applicant. It was noted that for all compounds the calculated ff values increased. Also increased the DT₅₀ and DT₉₀ values for Flufenacet and FOE Methylsulfone. While in case of Flufenacet that increase was not significant, it was substantial for FOE Methylsulfone – the values increased by the factor of two.

In case of FOE Oxalate was observed a slight decrease of both DT₅₀ and DT₉₀ values.

Final assessment:

The kinetic analysis of the data for Flufenacet and its degradation products – FOE Sulfonic acid, FOE Oxalate, and FOE Methylsulfone performed by the Applicant resulted in good fitting results for all examined compounds. In case however of FOE Methylsulfone it cannot be considered fully acceptable, as the not reliable was the kinetic analysis for its immediate precursor – FOE Methylsulfoxide.

RMS repeated the kinetic analysis for the whole data set, correcting the input values for FOE Methylsulfone, obtaining the reliable fits for all evaluated compounds – Flufenacet, FOE Sulfonic acid, FOE Oxalate and FOE Methylsulfone. The obtained results, with exception of those for FOE Methylsulfone, differed slightly from those obtained by the Applicant, so it was possible to keep the Applicant's results at least for Flufenacet, FOE Sulfonic acid and FOE Oxalate. RMS however decided, in order to maintain the internal consistency of the data, to fully rely on the results of the repeated kinetic assessment in the further evaluation.

- 3) The results of the kinetic analysis of the data obtained in **Höfchen im Tal** Silt loam soil (study by [Kelley et al.; 1995]):

The analysis for this data-set was a two-step analysis. Its results are presented below, individually for each step.

- a) Results obtained at **Step 1** – fitting of the data for the parent compound (Flufenacet) alone:

The results of the kinetic analysis performed by the Applicant are presented below, in graphical form on figure B.8.1.1.2.1.1_CA-13 and in numerical form in the table B.8.1.1.2.1.1_CA-36. Additionally the table B.8.1.1.2.1.1_CA-37 provides the kinetic endpoints obtained with each of the kinetic models tested.

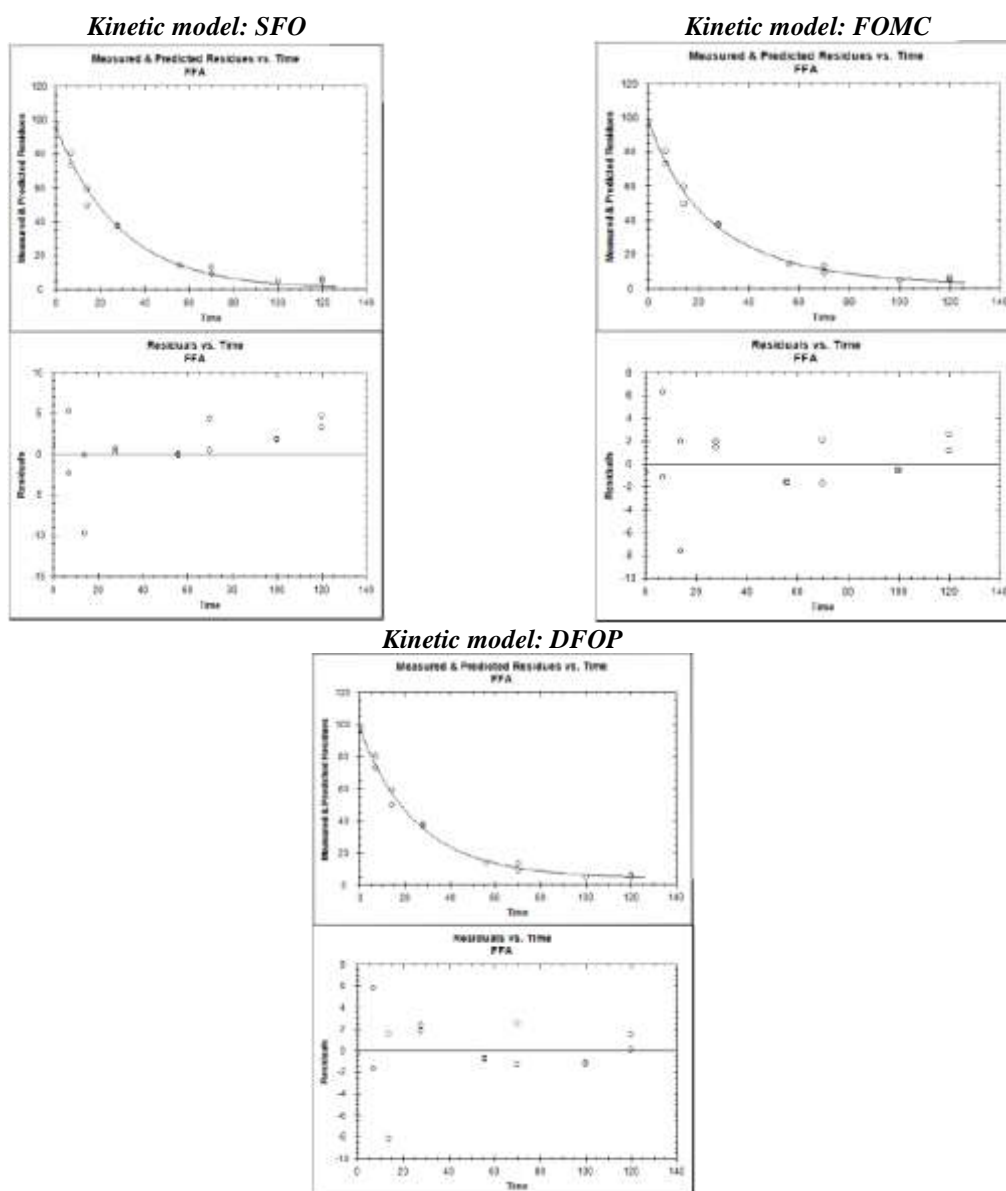


Figure B.8.1.1.2.1.1_CA-13: The graphical results of the kinetic analysis (copied from the study report).

Table B.8.1.1.2.1.1._CA-36: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment ¹⁾
				Lower	Upper			
SFO	M_0	95.960	2.153	91.740	100.180	<2 E-16	5.459	0.991; Good fit
	k	0.03428	0.00179	0.03077	0.038	9.65 E-12		
FOMC	M_0	98.039	2.116	93.892	102.190	4.02 E-16	3.957	0.993; Good fit
	α	4.3379	1.8430	0.7256	7.95	0.0175		
	β	106.3129	53.3219	1.8039	210.82	0.0338		
DFOP	M_0	97.582	2.145	93.582	101.787	4.16 E-15	4.072	0.993; Good fit
	k_1	0.0409	0.00851	0.02427	0.058	0.000212		
	k_2	0.00496	0.02116	-0.03652	0.046	0.4094		
	g	0.9225	0.1853	0.5593	1.286	0.000161		

Footnotes to the table:

1) Visual assessment of the kinetic curve as proposed by the Applicant.

Table B.8.1.1.2.1.1._CA-37: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested		
		SFO	FOMC	DFOP
Flufenacet	DT ₅₀ [days]	20.22	18.42	18.68
	DT ₉₀ [days]	67.17	74.45	73.19

On the basis of the obtained results the Applicant proposed to consider SFO as returning reliable and acceptable fit. That model was proposed to be used for the parent compound in kinetic examination of the data for parent compound and degradation products. RMS accepted that proposal.

- b) Results obtained at **Step 2** – fitting of the data for the parent compound (Flufenacet) and its degradation products:

The results of the kinetic analysis performed by the Applicant are presented below, in graphical form on figure B.8.1.1.2.1.1._CA-14 and in numerical form in the table B.8.1.1.2.1.1._CA-38. Additionally, in the table B.8.1.1.2.1.1._CA-39 are presented the kinetic endpoints obtained as a result of the evaluation, which were considered reliable by the Applicant.

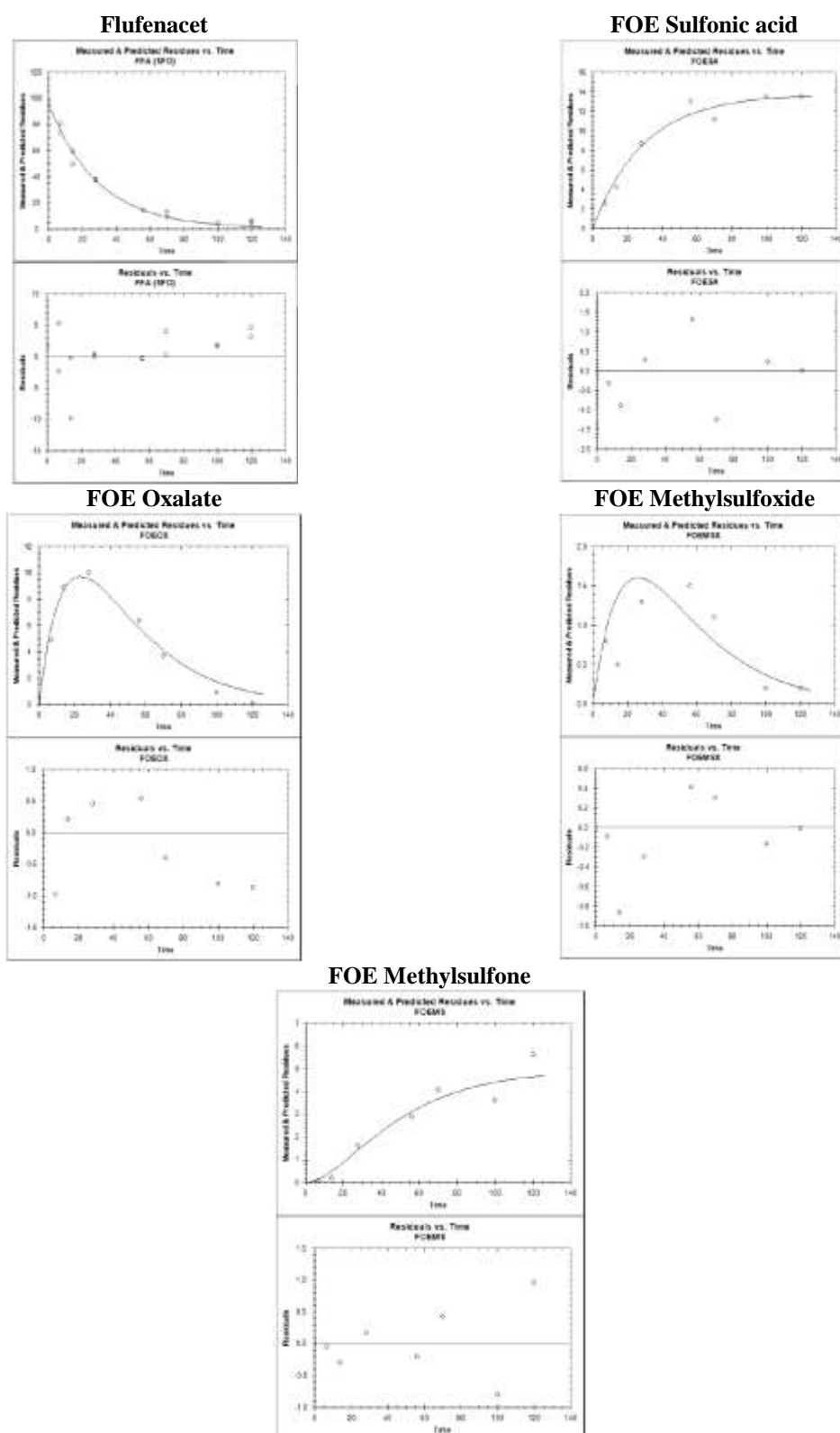


Figure B.8.1.1.2.1.1_CA-14: The graphical results of the kinetic examination of the data for Flufenacet, FOE Sulfonic acid, FOE Oxalate, FOE Methylsulfoxide and FOE Methylsulfone obtained in Höfchen im Tal soil (copied from the study report).

Table B.8.1.1.2.1.1._CA-38: The numerical results of the kinetic examination of the data for Flufenacet, FOE Sulfonic acid, FOE Oxalate, FOE Methylsulfoxide and FOE Methylsulfone obtained in Höfchen im Tal soil.

Compound	Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
			Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment ¹⁾
					Lower	Upper			
Flufenacet	SFO	M ₀	95.700	2.143	91.500	99.901	< 2 E-16	5.473	0.990; Good fit
		k	0.03391	0.001691	0.03060	0.0370	< 2 E-16		
FOE Sulfonic acid	SFO	M ₀	0.0	----	----	----	----	6.560	0.979; Good fit
		k	2.3 E-14	+ ∞	- ∞	+ ∞	0.5		
		ff	0.143	0.00626	----	----	----		
FOE Oxalate	SFO	M ₀	0.0	----	----	----	----	10.553	0.983; Good fit
		k	0.05296	0.006093	0.04102	0.065	5.8 E-11		
		ff	0.350	0.0451	----	----	----		
FOE Methylsulfoxide	SFO	M ₀	0.0	----	----	----	----	39.894	0.942; fit not assessed
		k	0.04327	0.007845	0.02789	0.059	1.22 E-6		
		ff	0.051	0.017	----	----	----		
FOE Methylsulfone	SFO	M ₀	0.0	----	----	----	----	16.038	0.942; Good fit
		k	0.00	0.002659	-0.00521	0.005	0.5		
		ff	1.0	----	----	----	----		

Table B.8.1.1.2.1.1._CA-39: The kinetic endpoints determined in the experiment, as reported by the Applicant.

Determined parameter	Compound			
	Flufenacet	FOE Sulfonic acid	FOE Oxalate	FOE Methylsulfone
DT ₅₀ [days]	20.44	1000	13.09	1000
DT ₉₀ [days]	67.90	> 1000	43.48	> 1000
Kinetic formation fraction ff	Not applicable	0.143 ± 0.006	0.350 ± 0.045	0.051 ± 0.018
Precursor	Not applicable	Flufenacet	Flufenacet	FOE Methylsulfoxide
Kinetic model	SFO	SFO	SFO	SFO

The results of the kinetic fitting for Flufenacet, FOE Sulfonic acid and FOE Oxalate are acceptable.

The kinetic parameters – DT₅₀ and DT₉₀ values for Flufenacet are reliable, therefore acceptable. Also reliable and therefore acceptable are all kinetic parameters – DT₅₀ and DT₉₀ values as well as kinetic formation fraction ff, obtained for FOE Oxalate. Also the statement with regard to the kinetic fit for that compound – it showed a good conformity of measured residues and fitted decline curve, demonstrating itself in low χ^2 -error and high correlation coefficients may be considered correct.

In case of FOE Sulfonic acid RMS however is of the opinion that while the kinetic formation fraction ff calculated for that compound may be considered reliable, the proposed kinetic endpoints – DT₅₀ and DT₉₀ values bear to high level of uncertainty to be considered such. It was also noticed that the kinetic model although it estimated rate constant k for FOE Sulfonic acid was not able to provide its statistical evaluation. All the may be attributed to the fact that the decline phase was not reached. As a result the proposed DT₅₀ and DT₉₀ values, although included into the definitive set of the endpoints derived from this experiment, will be considered informative only.

In case of FOE Methylsulfone the acceptable fit was obtained, but it cannot be considered reliable due to the lack of reliability of that for its precursor – FOE Methylsulfoxide. The lack of the reliability of the kinetic fit for FOE Methylsulfoxide is caused by low measurable concentrations of that compound used as input data in the kinetic analysis, what in turn is due to the fact that that compound was classified as minor/transient degradation product.

RMS decided to verify whether it was possible to obtain, better, reliable fit for FOE Methylsulfone by merging the data for FOE Methylsulfone and FOE Methylsulfoxide into one data set and repeating kinetic analysis. That was done and the resulting data set is presented below in the table B.8.1.1.2.1.1._CA-40. RMS decided to use the data for Flufenacet, FOE Sulfonic acid and FOE Oxalate not modified in comparison to those proposed by the Applicant. However, as for Flufenacet two replicates were available, while for the metabolites only the averages of the two replicates, the RMS decided to use average values as Replicate 1 and Replicate 2. The same approach was adopted in case of FOE Methylsulfone.

Table B.8.1.1.2.1.1._CA-40: The input data used by the RMS in repeated kinetic evaluation of the results obtained in **Höfchen im Tal** Silt loam soil (study [Kelley et al.; 1995]).

Time Point – DAT ¹⁾ [days]	Concentration, expressed as [% AR], of:							
	<i>Flufenacet</i>		<i>FOE Sulfonic acid</i>		<i>FOE Oxalate</i>		<i>corr. FOE Methylsulfone</i>	
	Replic. 1	Replic. 2	Replic. 1	Replic. 2	Replic. 1	Replic. 2	Replic. 1	Replic. 2
0	97.3	97.3	0.0	0.0	0.0	0.0	0.0	0.0
7	80.7	73.2	2.6	2.6	4.9	4.9	0.9	0.9
14	49.7	59.3	4.3	4.3	8.9	8.9	0.7	0.7
28	37.0	37.5	8.7	8.7	10.0	10.0	2.9	2.9
56	14.1	14.0	13.0	13.0	6.4	6.4	4.4	4.4
70	13.0	9.2	11.2	11.2	3.7	3.7	5.2	5.2
100	4.9	5.0	13.5	13.5	0.9	0.9	3.8	3.8
120	6.3	4.9	13.5	13.5	0.05 ¹⁾	0.05 ¹⁾	5.8	5.8

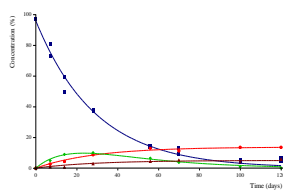
Footnotes to the table:

1) Value set to ½LOD.

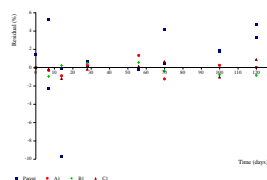
The analysis was carried out using CAKE 3.1 modelling tool, using IRLS (Iteratively Reweighed Nonlinear Least Squares) as optimisation algorithm. To maintain the consistency with the analysis performed by the Applicant RMS decided to perform it only for the SFO model in case of the parent compound. The results of the kinetic analysis performed by the RMS are presented below, in graphical form on figure B.8.1.1.2.1.1._CA-15 and in numerical form in the table B.8.1.1.2.1.1._CA-41. The kinetic endpoints calculated by the model are presented in the table B.8.1.1.2.1.1._CA-42.

Whole fit

Graphical Summary:
Observations and Fitted Model:

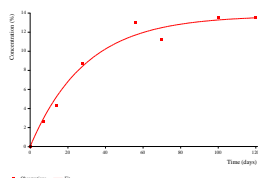


Residuals:

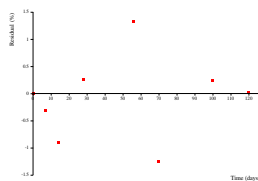


FOE Sulfonic acid

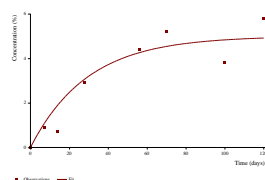
Graphical Summary:
Observations and Fitted Model:



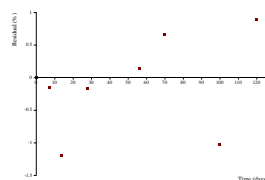
Residuals:



Graphical Summary: Observations and Fitted Model:

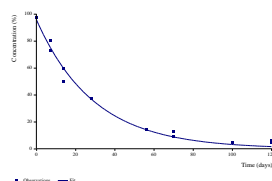


Residuals:

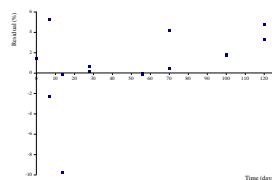


Flufenacet

Graphical Summary: Observations and Fitted Model:

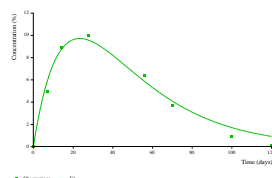


Residuals:



FOE Oxalate

Graphical Summary: Observations and Fitted Model:



Residuals:

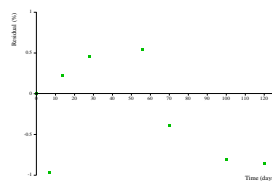


Figure B.8.1.1.2.1.1_CA-15: The graphical results of the kinetic examination of the data for Flufenacet, FOE Sulfonic acid, FOE Oxalate, and corr. FOE Methylsulfone obtained in Höfchen im Tal.

Table B.8.1.1.2.1.1._CA-41: The numerical results of the kinetic examination of the data for Flufenacet, FOE Sulfonic acid, FOE Oxalate, FOE Methylsulfoxide and FOE Methylsulfone obtained in Höfchen im Tal soil.

Compound	Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
			Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment
					Lower	Upper			
Flufenacet	SFO	M ₀	95.84	2.256	91.31	100.4	----	5.46	0.9905; good fit
		k	0.03411	0.001833	0.03042	0.038	2.0 E-24		
FOE Sulfonic acid	SFO	M ₀	0.0	----	----	----	----	6.57	0.9794; good fit
		k	1.1 E-16	8.66 E-4	-0.00174	0.002	0.5		
		ff	0.1431	0.0103	0.1224	0.164	----		
FOE Oxalate	SFO	M ₀	0.0	----	----	----	----	10.5	0.9827; good fit
		k	0.05267	0.00500	0.04262	0.063	1.4 E-14		
		ff	0.3474	0.0337	0.2797	0.415	----		
corr. FOE Methylsulfone	SFO	M ₀	0.0	----	----	----	----	17.3	0.8995; acceptable fit
		k	1.5 E-16	0.00205	-0.00412	0.004	0.5		
		ff	0.05214	0.00723	0.03762	0.067	----		

Table B.8.1.1.2.1.1._CA-42: The kinetic endpoints calculated by the model.

Determined parameter	Compound			
	Flufenacet	FOE Sulfonic acid	FOE Oxalate	corr. FOE Methylsulfone
DT ₅₀ [days]	20.3	10000	13.2	10000
DT ₉₀ [days]	67.5	> 10000	43.7	> 10000
Kinetic formation fraction ff	Not applicable	0.143 ± 0.010	0.347 ± 0.034	0.052 ± 0.007
Precursor	Not applicable	Flufenacet	Flufenacet	FOE Methylsulfoxide
Kinetic model	SFO	SFO	SFO	SFO

The results of the repeated kinetic analysis returned results comparable to those obtained by the Applicant, with no significant differences observed.

Final assessment:

The kinetic analysis of the data for Flufenacet and its degradation products – FOE Sulfonic acid, FOE Oxalate, and FOE Methylsulfone resulted in good fitting results for all examined compounds.

It can be therefore stated that:

- the kinetic parameters – DT₅₀ and DT₉₀ values, determined by the Applicant for Flufenacet are reliable and acceptable;
- the kinetic parameters – DT₅₀ and DT₉₀ values as well as kinetic formation fraction ff determined by the Applicant for FOE Oxalate are reliable and acceptable;
- for FOE Sulfonic acid the determined kinetic formation fraction ff may be considered reliable and acceptable, but other kinetic parameters – DT₅₀ and DT₉₀ values should be considered indicative only due to significant level of uncertainty;
- For FOE Methylsulfoxide the determined kinetic formation fraction ff may be considered reliable and acceptable, but other kinetic parameters – DT₅₀ and DT₉₀ values should be considered indicative only due to significant level of uncertainty.

- 4) The results of the kinetic analysis of the data obtained in **Howe, Indiana**, Sandy loam soil (study by [Pangilinan and Smith; 1994]):

The analysis for this data-set was a two-step analysis. Its results are presented below, individually for each step.

- a) Results obtained at **Step 1** – fitting of the data for the parent compound (Flufenacet) alone:

The results of the kinetic analysis performed by the Applicant are presented below, in graphical form on figure B.8.1.1.2.1.1_CA-16 and in numerical form in the table B.8.1.1.2.1.1_CA-43. Additionally the table B.8.1.1.2.1.1_CA-44 provides the kinetic endpoints obtained with each of the kinetic models tested.

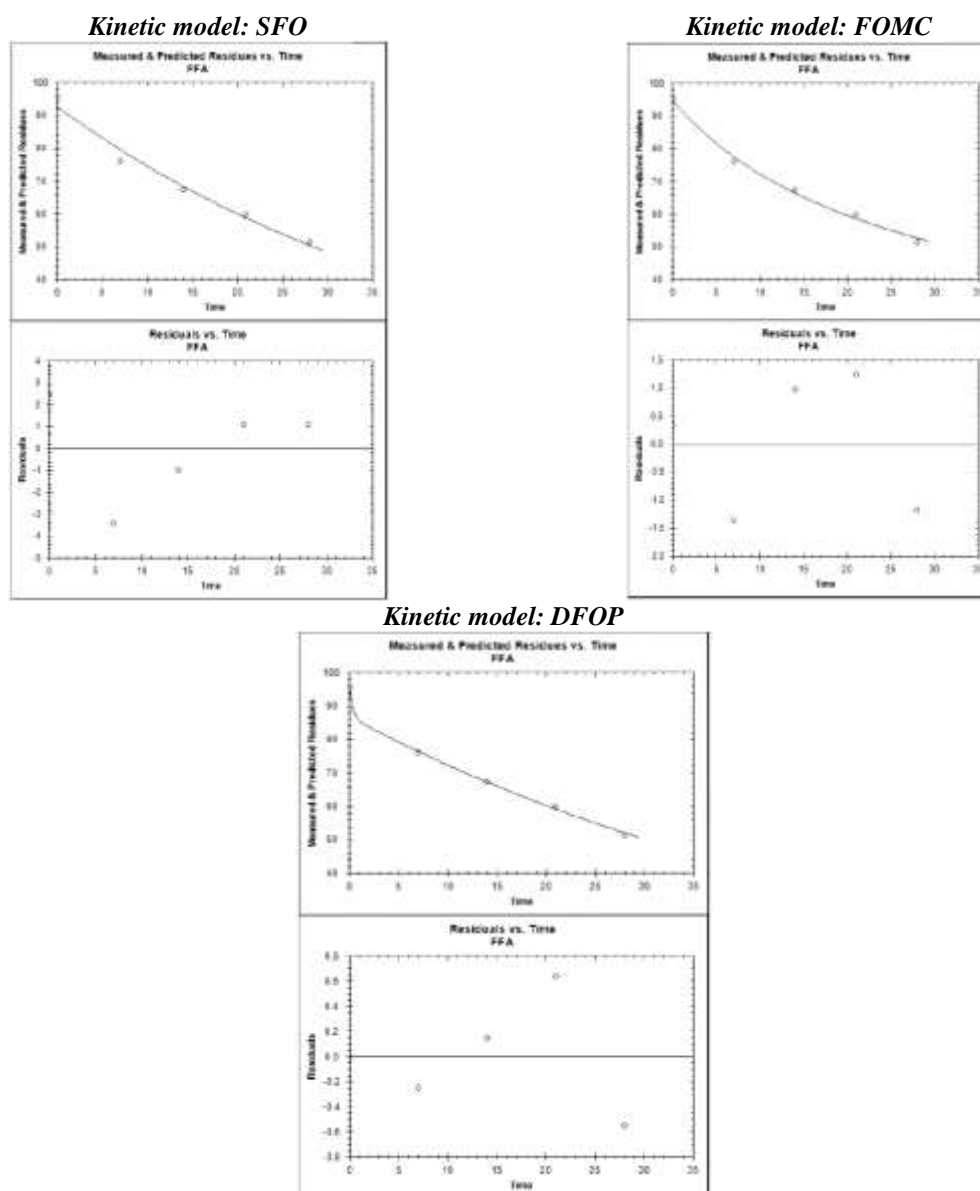


Figure B.8.1.1.2.1.1_CA-16: The graphical results of the kinetic analysis.

Table B.8.1.1.2.1.1._CA-43: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment ¹⁾
				Lower	Upper			
SFO	M ₀	92.683	2.241	88.291	97.075	1.56 E-5	2.351	0.981; Good fit
	k	0.02182	0.001778	0.01833	0.025	0.000583		
FOMC	M ₀	94.780	1.686	91.474	98.085	1.58 E-4	1.407	0.995; Good fit
	α	0.6735	0.2870	0.1111	1.2360	0.07174		
	β	20.0267	12.1999	-3.8846	43.938	0.1212		
DFOP	M ₀	95.100	0.889	93.360	96.840	0.00298	0.649	0.999; Acceptable fit
	k ₁	2.980	n. a. ²⁾	n. a. ²⁾	n. a. ²⁾	n. a. ²⁾		
	k ₂	0.01834	9.084 E-4	0.01656	0.02	0.01575		
	g	0.08718	0.01654	0.05477	0.120	0.05967		

Footnotes to the table:

- 1) Visual assessment of the kinetic curve as proposed by the Applicant;
 2) Value not calculated by the modelling tool.

Table B.8.1.1.2.1.1._CA-44: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested		
		SFO	FOMC	DFOP
Flufenacet	DT ₅₀ [days]	31.77	36.02	32.82
	DT ₉₀ [days]	105.50	591.40	120.60

On the basis of the obtained results the Applicant proposed to consider SFO as returning reliable and acceptable fit. That model was proposed to be used for the parent compound in kinetic examination of the data for parent compound and degradation products. RMS accepted that proposal noticing that neither FOMC nor DFOP returned fully reliable results.

- b) Results obtained at **Step 2** – fitting of the data for the parent compound (Flufenacet) and its degradation products:

The results of the kinetic analysis performed by the Applicant are presented below, in graphical form on figure B.8.1.1.2.1.1._CA-17 and in numerical form in the table B.8.1.1.2.1.1._CA-45. Additionally, in the table B.8.1.1.2.1.1._CA-46 are presented the kinetic endpoints obtained as a result of the evaluation, which Applicant considered reliable.

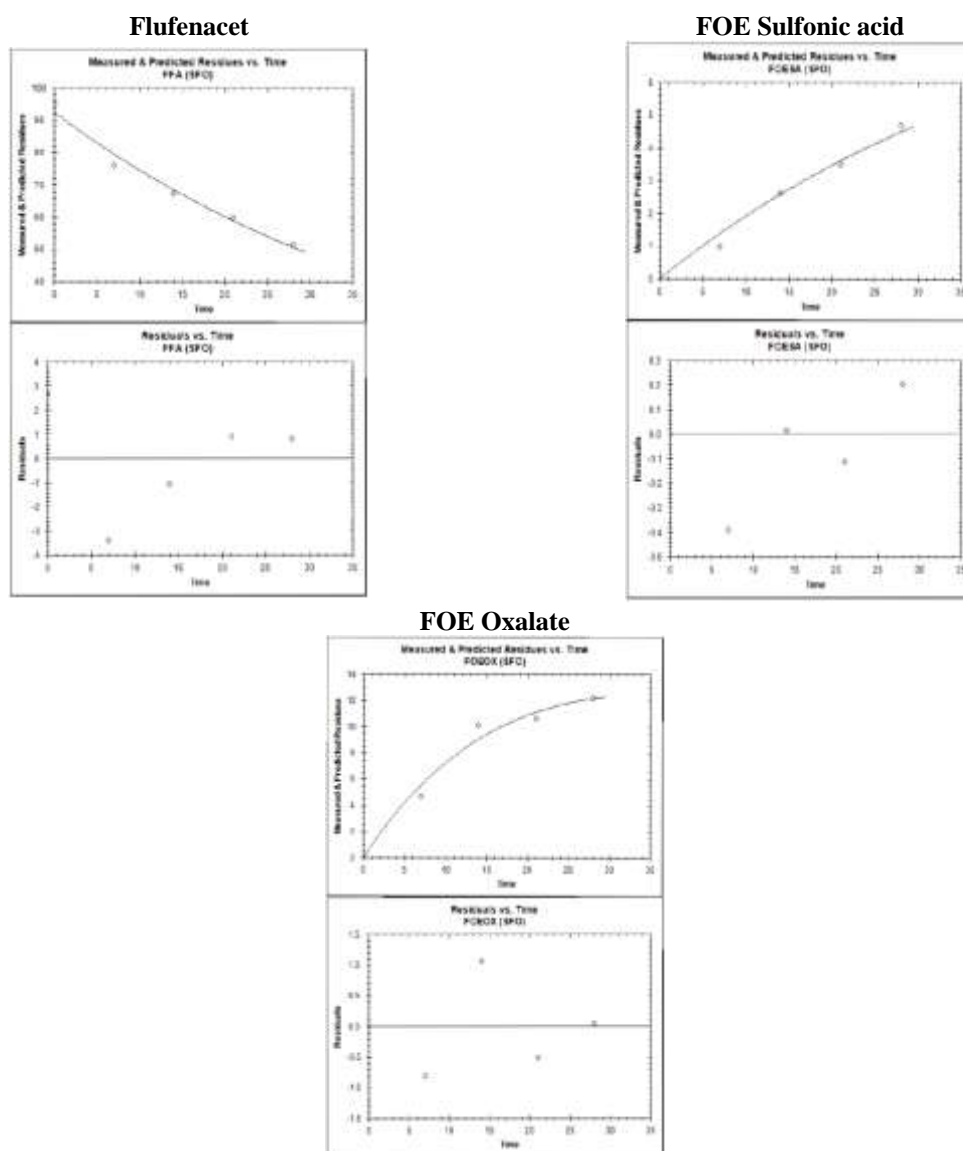


Figure B.8.1.1.2.1.1_CA-17: The graphical results of the kinetic examination of the data for Flufenacet, FOE Sulfonic acid and FOE Oxalate obtained in Howe, Indiana, soil (copied from the study report).

Table B.8.1.1.2.1.1_CA-45: The numerical results of the kinetic examination of the data for Flufenacet, FOE Sulfonic acid and FOE Oxalate obtained in Howe, Indiana, soil.

Compound	Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
			Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment ¹⁾
					Lower	Upper			
Flufenacet	SFO	M_0	92.410	2.273	87.950	96.864	8.2 E-12	2.362	0.981; Good fit
		k	0.02152	0.001796	0.0180	0.025	3.91 E-7		
FOE Sulfonic acid	SFO	M_0	0.0	----	----	----	----	6.283	0.989; Good fit
		k	2.3 E-14	n. a. ¹⁾	n. a. ¹⁾	n. a. ¹⁾	n. a. ¹⁾		
		ff	0.108	0.001	----	----	----		
FOE Oxalate	SFO	M_0	0.0	----	----	----	----	6.240	0.980; Good fit
		k	0.03579	0.01426	0.007853	0.064	0.0166		
		ff	0.484	0.101	----	----	----		

Footnotes to the table:

1) Value not calculated by the modelling tool.

Table B.8.1.1.2.1.1._CA-46: The kinetic endpoints determined in the experiment, as reported by the Applicant.

Determined parameter	Compound		
	<i>Flufenacet</i>	<i>FOE Sulfonic acid</i>	<i>FOE Oxalate</i>
DT ₅₀ [days]	32.21	1000	19.37
DT ₉₀ [days]	107.00	> 1000	64.33
Kinetic formation fraction <i>ff</i>	Not applicable	0.108 ± 0.010	0.484 ± 0.101
Precursor	Not applicable	Flufenacet	Flufenacet
Kinetic model	SFO	SFO	SFO

The results of the kinetic fitting for Flufenacet, FOE Sulfonic acid and FOE Oxalate are acceptable.

The kinetic parameters – DT₅₀ and DT₉₀ values for Flufenacet are reliable, therefore acceptable.

In case of FOE Sulfonic acid RMS is of the opinion that while the kinetic formation fraction *ff* calculated for that compound may be considered reliable, the proposed kinetic endpoints – DT₅₀ and DT₉₀ values bear to high level of uncertainty to be considered such. It was also noticed that the kinetic model, although it estimated rate constant *k* for FOE Sulfonic acid, was not able to provide its statistical evaluation. All the may be attributed to the fact that the decline phase was not reached. As a result the proposed DT₅₀ and DT₉₀ values, although included into the definitive set of the endpoints derived from this experiment, will be considered informative only.

Also for FOE Oxalate RMS stated that while the kinetic formation fraction *ff* calculated for that compound may be considered reliable, the proposed kinetic endpoints – DT₅₀ and DT₉₀ values cannot be considered as such. That conclusion was drawn despite the fact that the model estimated seemingly reliable rate constant *k* for FOE Oxalate and from it calculated the kinetic endpoints – DT₅₀ and DT₉₀. It shall be pointed out however that the decline phase for that compound was not reached. Moreover, careful examination of the full data base, including the later time points cut-off by the Applicant because of the collapse of soil microbial activity, showed that the compound was still forming at the end of the experiment. As a results neither the estimated rate constant *k* nor resulting from it kinetic endpoints – DT₅₀ and DT₉₀ values, may be considered reliable. It is probable that what the modelling tool in fact calculated was the rate constant of the formation of FOE Oxalate in the test soil.

Final assessment:

The kinetic analysis of the data for Flufenacet and its degradation products – FOE Sulfonic acid and FOE Oxalate resulted in good fitting results for all examined compounds.

It can be therefore stated that:

- the kinetic parameters – DT₅₀ and DT₉₀ values, determined by the Applicant for Flufenacet are reliable and acceptable;
- for FOE Sulfonic acid the determined kinetic formation fraction *ff* may be considered reliable and acceptable, but other kinetic parameters – DT₅₀ and DT₉₀ values should be considered indicative only due to significant level of uncertainty;
- For FOE Oxalate the determined kinetic formation fraction *ff* may be considered reliable and acceptable, but other kinetic parameters – DT₅₀ and DT₉₀ values cannot be considered even indicative due to significant level of uncertainty.

- 5) The results of the kinetic analysis of the data obtained in **Laacherhof AXXa** Sandy loam soil (study by [Hellpointner; 1999]):

The results of the kinetic analysis performed by the Applicant are presented below, in graphical form on figure B.8.1.1.2.1.1._CA-18 and in numerical form in the table B.8.1.1.2.1.1._CA-47. Additionally the table B.8.1.1.2.1.1._CA-48 provides the kinetic endpoints obtained with each of the kinetic models tested.

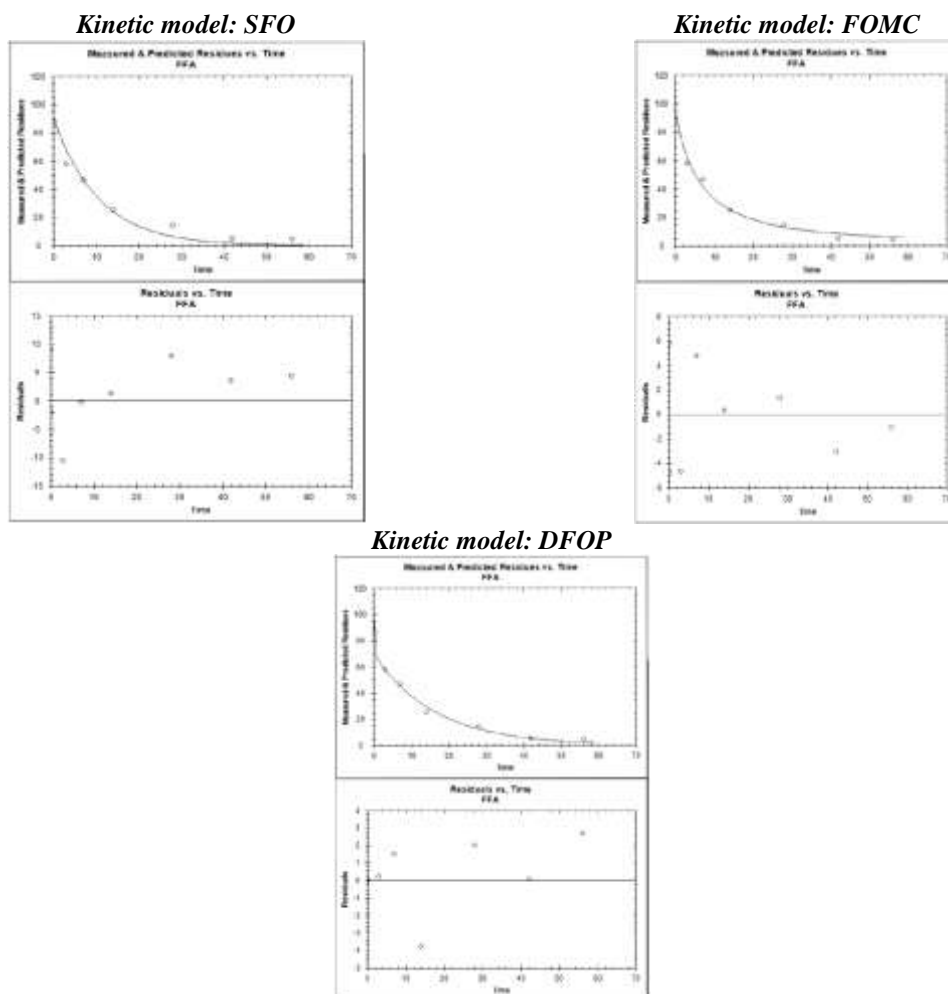


Figure B.8.1.1.2.1.1._CA-18: The graphical results of the kinetic analysis.

Table B.8.1.1.2.1.1._CA-47: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment ¹⁾
				Lower	Upper			
SFO	M_0	90.935	4.640	81.840	100.030	5.72 E-7	11.230	0.975; Acceptable fit
	k	0.09431	0.01429	0.06630	0.122	2.91 E-3		
FOMC	M_0	94.236	3.427	87.518	100.953	5.95 E-7	7.457	0.988; Acceptable fit
	α	1.3745	0.5089	0.3770	2.372	0.0214		
	β	8.725	4.942	-0.9619	18.411	0.0689		
DFOP	M_0	100.000	2.635	94.840	105.164	1.44 E-6	3.990	0.997; Good fit
	k_1	4.798	1.784	1.302	8.294	0.02733		
	k_2	0.06166	0.005786	0.05032	0.073	2.20 E-4		
	g	0.3036	0.03943	0.2264	0.381	7.65 E-4		

Footnotes to the table:

- 1) Visual assessment of the kinetic curve as proposed by the Applicant.

Table B.8.1.1.2.1.1._CA-48: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested		
		<i>SFO</i>	<i>FOMC</i>	<i>DFOP</i>
<i>Flufenacet</i>	DT ₅₀ [days]	7.35	5.72	5.37
	DT ₉₀ [days]	24.42	37.86	31.48

On the basis of the obtained results the Applicant proposed to consider SFO as returning reliable and acceptable fit, therefore being appropriate for deriving modelling endpoints for Flufenacet. RMS accepted that proposal, noticing that FOMC did not return fully reliable results. On the other hand the results obtained with DFOP were fully reliable, however the shape of the kinetic curve was unusual, indicating that probably M₀ value was overestimated by the modelling tool.

Conclusions of the study:

On the basis of the performed kinetic analysis, there were identified the kinetic endpoints that may be considered reliable and recommended to be used as persistence and modelling endpoints. It shall be noted however that the DT₅₀ values require normalisation before being used to calculate the geomean values to be used in FOCUS GW and FOCUS SW modelling. All they are presented below in the table B.8.1.1.2.1.1._CA-49.

Table B.8.1.1.2.1.1._CA-49: The final set of reliable kinetic endpoints determined in the study.

Study	Test soil	Compound	Determined parameter				
			<i>Kinetic model</i>	<i>Rate constant k</i>	<i>DT₅₀ [days]</i>	<i>DT₉₀ [days]</i>	<i>Kinetic formation fraction ff</i>
Kelley et al.; 1995	<i>BBA 2.2</i>	Flufenacet	SFO	0.0217	31.9	106.1	Not applicable
		FOE Sulfonic acid	SFO	not determined	1000	> 1000	0.257
		FOE Oxalate	SFO	0.1011	6.9	22.78	0.448
		FOE Methylsulfone	SFO	not determined	1000	> 1000	0.061
	<i>Laacherhof</i>	Flufenacet	SFO	0.04113	16.9	56.0	Not applicable
		FOE Sulfonic acid	SFO	not determined	1000	> 1000	0.272
		FOE Oxalate	SFO	0.03663	18.9	62.9	0.422
		FOE Methylsulfone	SFO	0.00399	174.0	576.0	0.096
	<i>Höfchen im Tal</i>	Flufenacet	SFO	0.03391	20.44	67.90	Not applicable
		FOE Sulfonic acid	SFO	not determined	1000	> 1000	0.143
		FOE Oxalate	SFO	0.05269	13.09	43.48	0.350
		FOE Methylsulfone	SFO	not determined	1000	> 1000	0.051
Pangilinan and Smith; 1994	<i>Howe, Indiana</i>	Flufenacet	SFO	0.02152	32.21	107.00	Not applicable
		FOE Sulfonic acid	SFO	not determined	1000	> 1000	0.108
		FOE Oxalate	SFO	not determined	1000	> 1000	0.484
Hellpointner; 1999	<i>Laacherhof AXXa</i>	Flufenacet	SFO	0.09431	7.35	24.42	Not applicable

Study 3:

Report: Reinken G., Maassen K., (2014): „Trigger evaluation for the Degradation of Flufenacet Degradation Product FOE oxalate under Aerobic Soil Conditions in Laboratory According to FOCUS Kinetics Using the KinGUI 2 Tool. FOE oxalate.”; Bayer CropScience AG, Environmental Safety, Alfred-Nobel-Strasse 50, 40789 Monheim, Germany; unpublished report No. En-Sa-13-1009; 2014. 02. 18; ; study reference number: M-478440-01-1;

Guidelines: The study was declared to be performed to comply with the following guidelines:

- FOCUS (2006): “Guidance Document on Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration.” Report of the FOCUS Work Group on Degradation Kinetics, EC Document Reference SANCO/10058/2005 version 2.0, 434 pp.;
- FOCUS (2011): “Generic guidance for Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration”, version 1.0 (issued on 23 November 2011).

GLP: No, not applicable – this is a modelling study;

RMS comments: RMS verified the study for its compliance with the provisions of the Guidelines listed above. It was stated that the study generally complied with the two evoked Guidance Documents. The aim of the study was to identify the best-fit kinetic model for Flufenacet and one of its major degradation products – FOE Oxalate. Therefore the study should be considered complementary to the summarised above another study – **Study 2** ([Reinken and Partsch; 2014]), that examined the same data base in order to determine kinetic endpoints for these compounds to be subsequently used in modelling. RMS summarising the study used the soil names as they were provided in the source study reports (in the study report they were slightly altered) to maintain the internal coherence of the Renewal Assessment Report.

Summary:

The aim of the study was to perform the kinetic analysis of the data obtained for Flufenacet and its degradation product FOE Oxalate in two laboratory studies examining degradation of [Phenyl-U-¹⁴C] Flufenacet in aerobic soil – by [Kelley et al.; 1995] and by [Pangilinan and Smith; 1994], both summarised under the point B.8.1.1.1.1. of this report as, respectively, **Study 1** and **Study 2**. It was done in order to identify the best kinetic fit for both compounds in each test soil and derive half-lives for FOE Oxalate (and Flufenacet) suitable for trigger evaluation.

The analysis was performed for the results obtained in four test soils – three EU soils (study by [Kelley et al.; 1995]) and one US soil (study by [Pangilinan and Smith; 1994]). The characteristic of the test soils and the experimental conditions are provided in the summary of the related **Study 2**, in the tables B.8.1.1.2.1.1._CA-6 and B.8.1.1.2.1.1._CA-7 (characterisation of the test soils), and B.8.1.1.2.1.1._CA-8 (characterisation of the experimental conditions). RMS decided not to repeat those data in this summary in order not to overburden the Assessment Report.

The data provided by the source studies are presented below in two separate tables – B.8.1.1.2.1.1._CA-50 for the study by [Kelley et al.; 1995] and B.8.1.1.2.1.1._CA-51 for the study by [Pangilinan and Smith; 1994].

Table B.8.1.1.2.1.1._CA-50: The concentrations of Flufenacet and FOE Oxalate reported in the study by [Kelley et al.; 1995].

Time point – DAT [days]	Results – concentration of the given compound in [%AR], obtained in the test soil:								
	BBA 2.2			Laacherhof			Höfchen im Tal		
	Flufenacet	FOE Oxalate		Flufenacet	FOE Oxalate		Flufenacet	FOE Oxalate	
	Rep. 1	Rep. 2	Average	Rep. 1	Rep. 2	Average	Rep. 1	Rep. 2	Average
0	97.0	97.7	0.0	84.7	85.9	0.0	91.9	90.9	0.0
7	70.8	75.4	3.7	56.1	58.2	7.0	80.7	73.2	4.9
14	67.2	65.7	5.4	51.5	42.9	10.9	49.7	59.3	8.9
28	45.2	42.0	6.6	28.0	19.2	15.6	37.0	37.5	10.0
56	27.6	27.8	4.0	7.6	4.7	10.0	14.1	14.0	6.4
70	2.15	18.3	0.6	5.4	3.9	7.3	13.0	9.2	3.7
100	14.7	18.9	0.0	3.0	3.4	1.6	4.9	5.0	0.9
120	10.3	9.7	0.0	2.5	3.1	0.0	6.3	4.9	0.0

Table B.8.1.1.2.1.1._CA-51: The concentrations of Flufenacet and FOE Oxalate reported in the study by [Pangilinan and Smith; 1994].

Time point – DAT [days]	Concentration in [%AR] obtained in the test soil – Howe, Indiana, for the compound:	
	<i>Flufenacet (average value)</i>	<i>FOE Oxalate (average value)</i>
0	93.3	0.1
7	76.1	4.7
14	76.3	10.1
21	59.7	10.6
28	51.4	12.2
44	51.2	11.9
65	48.0	14.0
76	51.3	14.1
91	47.5	15.2
180	44.6	14.6
271	38.6	17.0
365	35.2	26.5

The data presented above were subjected to a multistep evaluation procedure, already presented in the summary of the **Study 2**. For convenience it is repeated below.

The kinetic-fitting procedure consisted of the following steps:

- **Step 1:** Processing of the raw input data;
- **Step 2:** Kinetic evaluation of the processed data using the following 1st – order kinetic models: SFO, FOMC and DFOP, and KinGUI 2 as a modelling tool. That step consisted of the two sub-steps:
 - **Sub-step 1:** kinetic evaluation of the data for parent compound (Flufenacet) only, in order to determine the appropriate kinetic model. At that stage of analysis all three kinetic models listed above were tested;
 - **Sub-step 2:** kinetic evaluation of the data for parent compound (Flufenacet) and its degradation products using for Flufenacet the kinetic model identified at previous stage as appropriate, and SFO model for degradation products;
- **Step 3:** Evaluation of the results of kinetic examination of the data;
- **Step 4:** Reporting of the obtained results, in particular kinetic parameters recommended for modelling.

The data-processing to obtain the input values for kinetic analysis (**Step 1**) was identical to the procedure described in the summary of the **Study 2** on page 166. The DAT-0 and LOD values used in this activity are provided below, in the table B.8.1.1.2.1.1._CA-52.

Table B.8.1.1.2.1.1._CA-52: The DAT-0 recoveries and LOD determined for each experiment.

Study	Test soil		Determined parameter	
	<i>Soil name</i>	<i>Soil type (USDA classification)</i>	<i>DAT-0 recovery [% AR]</i>	<i>LOD [% AR]</i>
<i>Kelley et al.; 1995</i>	BBA 2.2	Loamy sand	99.3	0.1
	Laacherhof	Silt loam	93.2	0.1
	Höfchen im Tal	Silt loam	97.3	0.1
<i>Pangilinan and Smith; 1994</i>	Howe, Indiana	Sandy loam	95.1	0.1

The processed data used as input in the kinetic examination are presented below, separately for each source study, in tables B.8.1.1.2.1.1._CA-53 and B.8.1.1.2.1.1._CA-54. In case of the data set originating from the study by [Pangilinan and Smith; 1994], the results obtained after the time point DAT 28 were not included, because at that time point a collapse of soil microbial activity was recorded.

Table B.8.1.1.2.1.1._CA-53: The processed residue data originating from the study by [Kelley et al.; 1995].

Data obtained in BBA 2.2 Loamy sand soil:				
Time Point – DAT [days]	Concentration, expressed as [% AR], of:			
	<i>Flufenacet</i>		<i>FOE Oxalate</i>	
	Replicate 1	Replicate 2	Replicate 1	Replicate 2
0	99.3	99.3	0.0	NaN
7	70.8	75.4	3.7	NaN
14	67.2	65.7	5.4	NaN
28	45.2	42.0	6.6	NaN
56	27.6	27.8	4.0	NaN
70	21.5	18.3	0.6	NaN
100	14.7	18.9	0.05 ¹⁾	NaN
120	10.3	9.7	NaN	NaN
Data obtained in Laacherhof Silt loam soil:				
Time Point – DAT [days]	Concentration, expressed as [% AR], of:			
	<i>Flufenacet</i>		<i>FOE Oxalate</i>	
	Replicate 1	Replicate 2	Replicate 1	Replicate 2
0	93.2	93.2	0.0	NaN
7	56.1	58.2	7.0	NaN
14	51.5	42.9	10.9	NaN
28	28.0	19.2	15.6	NaN
56	7.6	4.7	10.0	NaN
70	5.4	3.9	7.3	NaN
100	3.0	3.4	1.6	NaN
120	2.5	3.1	0.05 ¹⁾	NaN
Data obtained in Höfchen im Tal Silt loam soil:				
Time Point – DAT [days]	Concentration, expressed as [% AR], of:			
	<i>Flufenacet</i>		<i>FOE Oxalate</i>	
	Replicate 1	Replicate 2	Replicate 1	Replicate 2
0	97.3	97.3	0.0	NaN
7	80.7	73.2	4.9	NaN
14	49.7	59.3	8.9	NaN
28	37.0	37.5	10.0	NaN
56	14.1	14.0	6.4	NaN
70	13.0	9.2	3.7	NaN
100	4.9	5.0	0.9	NaN
120	6.3	4.9	0.05 ¹⁾	NaN

Footnotes to the table:

1) Value set to ½LOD.

Table B.8.1.1.2.1.1._CA-54: The processed residue data originating from the study by [Pangilinan and Smith; 1994].

Time Point – DAT ¹⁾ [days]	Concentration, expressed as [% AR], of:	
	<i>Flufenacet</i>	<i>FOE Oxalate</i>
0	95.1	0.0
7	76.1	4.7
14	67.3	10.1
21	59.7	10.6
28	51.4	12.2

The processed data were kinetically examined using KinGUI ver. 2 modelling tool, developed by Bayer. The optimisation was performed using IRLS (Iteratively Reweighed Nonlinear Least Squares) algorithm. The fitting procedure was a two-stage one. The first step, further called **Step 1**, consisted on the determination of the best-fit kinetic model for the parent compound – Flufenacet. At that stage three 1st-order kinetic models were tested: SFO, FOMC and DFOP. During the next stage, further called **Step 2**, the whole data set – data for the Flufenacet and FOE Oxalate, was kinetically examined. In case of Flufenacet the tested kinetic model was that determined as appropriate at **Step 1**, while for the degradation products the SFO model was used.

The conceptual metabolic pathway built in the modelling tool is presented below on figure B.8.1.1.2.1.1._CA-19. The following abbreviations were used:

- FFA for Flufenacet (parent compound);
- FOEOX for FOE Oxalate.

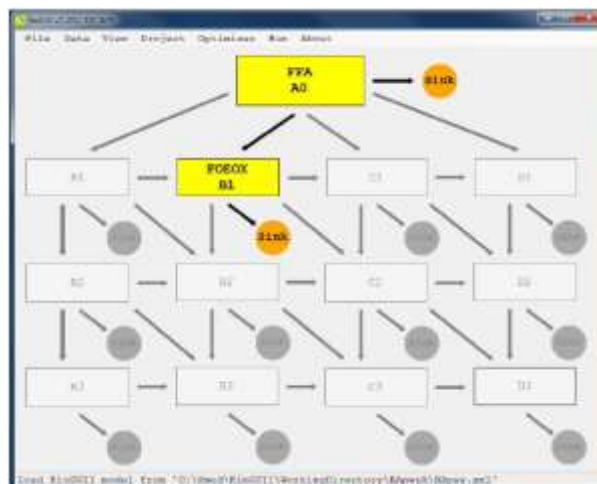


Figure B.8.1.1.2.1.1_CA-19: The conceptual transformation scheme assumed in the modelling tool (copied from the study report).

The obtained results of the kinetic analysis were evaluated by the Applicant. That was done by means of a detailed statistical analysis comprising the following components:

- visual assessment of the fit;
- χ^2 -error statistics;
- t-test significance;
- correlation analysis.

The detailed characteristic of that evaluation is provided in the summary of the **Study 2**, on pages 168 – 169.

The whole assessment was carried out as a multistep procedure, similar to that outlined in the presented above summary of the **Study 2**, on page 169. However, as they differed, mainly due to different goals of the kinetic evaluation of the data, the assessment procedure used here is presented below.

It consisted of the following steps:

- **Step 1:** the data for the parent compound were fitted using two kinetic models: SFO and FOMC and verified for passing the acceptance criteria (χ^2 -error and distribution of residuals); in case the SFO fit was found visually acceptable and statistically more appropriate than FOMC, it was selected as the best-fit model;
- **Step 2:** in case the SFO model was found not to be more appropriate than FOMC, it was refined in three-step procedure, by removing the outliers, fixing model parameters and data weighing, until the best fit was achieved;
- **Step 3:** if the **Step-2** fitting for SFO model still failed the χ^2 -error test, and FOMC was demonstrated to be more appropriate, the DFOP model was tested in order to determine if bi-phasic model is acceptable and if so, which one should be selected as returning the best fit;
- **Step 4:** once the best-fit model was identified, the data for the FOE Oxalate were added to the data set and the kinetic analysis repeated using the identified best-fit model for Flufenacet (parent compound) and SFO for FOE Oxalate.

Analysing the proposed assessment procedure RMS stated that it complied with the procedure for determination of the trigger kinetic endpoints presented in FOCUS Kinetics Guidance Document [FOCUS; 2006].

The results of the kinetic examination of the data and their evaluation are provided below, individually for each test soil.

- 1) The results of the kinetic analysis of the data obtained in **BBA 2.2** Loamy sand soil (study by [Kelley et al.; 1995]):

The analysis for this data-set was a two-step analysis. Its results are presented below, individually for each step.

- a) Results obtained at **Step 1** – fitting of the data for the parent compound (Flufenacet) alone:

The results of the kinetic analysis performed by the Applicant are presented below, in graphical form on figure B.8.1.1.2.1.1_CA-19 and in numerical form in the table B.8.1.1.2.1.1_CA-55. Additionally the table B.8.1.1.2.1.1_CA-56 provides the kinetic endpoints obtained with each of the kinetic models tested.

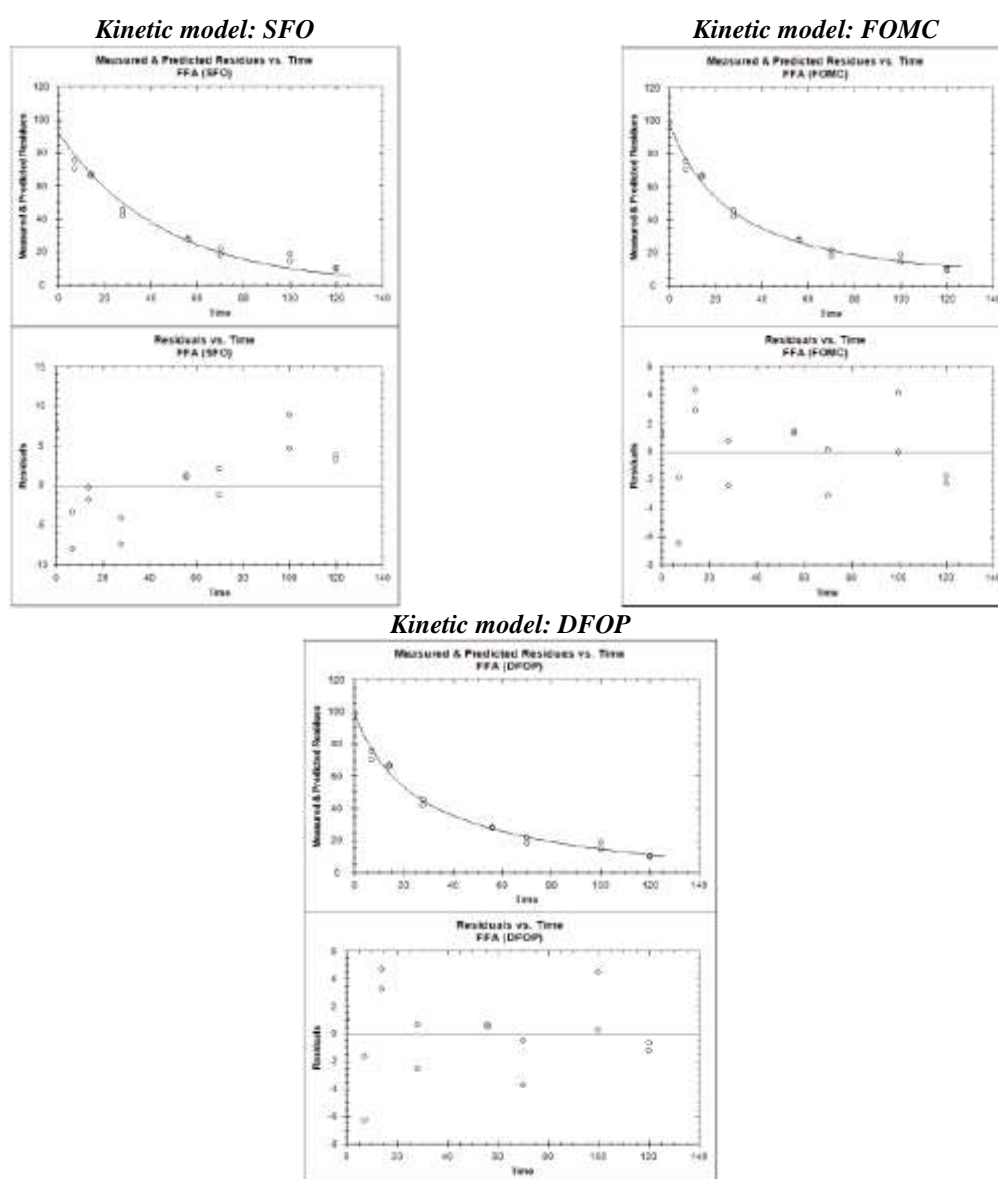


Figure B.8.1.1.2.1.1_CA-19: The graphical results of the kinetic analysis (copied from the study report).

Table B.8.1.2.1.1._CA-55: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment ¹⁾
				Lower	Upper			
SFO	M ₀	92.059	2.851	86.472	97.647	7.54 E-15	8.495	0.98; Good fit
	k	0.02224	0.00167	0.01896	0.026	1.24 E-9		
FOMC	M ₀	98.066	2.059	94.030	102.102	2.82 E-16	4.520	0.99; Good fit
	α	1.5659	0.3067	0.9647	2.167	0.00010		
	β	42.5627	12.3870	18.2846	66.841	0.00221		
DFOP	M ₀	98.237	2.940	92.475	103.999	1.64 E-13	4.862	0.99; Good fit
	k ₁	0.06909	0.09018	-0.1077	0.246	0.2292		
	k ₂	0.01367	0.00824	-0.00248	0.030	0.0615		
	g	0.4257	0.4835	-0.5220	1.373	0.1980		

Footnotes to the table:

1) Visual assessment of the kinetic curve as proposed by the Applicant.

Table B.8.1.2.1.1._CA-56: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested		
		SFO	FOMC	DFOP
Flufenacet	DT ₅₀ [days]	31.16	23.70	23.54
	DT ₉₀ [days]	103.50	142.60	127.90

On the basis of the obtained results the Applicant proposed to consider FOMC model as returning the best fit. That model was proposed to be used for the parent compound in kinetic examination of the data for Flufenacet and FOE Oxalate. RMS accepted that proposal.

- b) Results obtained at **Step 2** – fitting of the data for the parent compound (Flufenacet) and its degradation products:

The results of the kinetic analysis performed by the Applicant are presented below, in graphical form on figure B.8.1.2.1.1._CA-20 and in numerical form in the table B.8.1.2.1.1._CA-57.

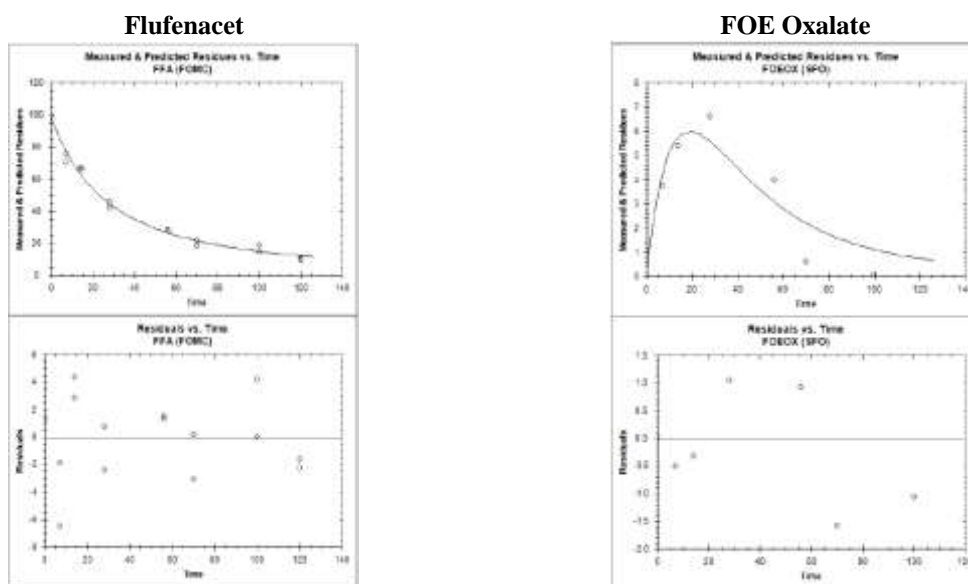


Figure B.8.1.2.1.1._CA-20: The graphical results of the kinetic examination of the data for Flufenacet and FOE Oxalate obtained in BBA 2.2 soil (copied from the study report).

Table B.8.1.1.2.1.1._CA-57: The numerical results of the kinetic examination of the data for Flufenacet and FOE Oxalate obtained in BBA 2.2 soil.

Compound	Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
			Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment ¹⁾
					Lower	Upper			
Flufenacet	FOMC	M ₀	98.054	2.084	93.969	102.139	<2 E-16	4.52	Not provided
		α	1.5831	0.3152	0.9653	2.201	4.42 E-5		
		β	43.1786	12.7565	18.1763	68.181	0.00165		
FOE Oxalate	SFO	M ₀	0.0	----	----	----	----	23.28	0.89; Good fit
		k	0.0582	0.0144	0.0299	0.086	0.00038		
		ff	0.2496	0.0515	----	----	----		

The kinetic endpoints derived from the study are presented below in the table B.8.1.1.2.1.1._CA-58.

Table B.8.1.1.2.1.1._CA-58: The kinetic parameters determined in the experiment.

Determined parameter	Compound	
	Flufenacet	FOE Oxalate
DT ₅₀ [days]	23.72	11.91
DT ₉₀ [days]	141.73	39.58
Kinetic formation fraction ff	Not applicable – parent compound	0.250 ± 0.052
Precursor	Not applicable – parent compound	Flufenacet
Kinetic model	FOMC	SFO

The results of the kinetic fitting for Flufenacet and FOE Oxalate are acceptable.

Applicant proposed to consider the kinetic parameters for FOE Oxalate resulting from the kinetic examination of the data for that compound and Flufenacet using the combination of kinetic models FOMC-SFO as acceptable. Although that was not explicitly said, the kinetic endpoints determined for Flufenacet in that fitting exercise using FOMC kinetic model should be considered as trigger kinetic endpoints for that compound.

Evaluation of the fitting exercise:

The proposal made by the Applicant to consider the kinetic endpoints obtained for Flufenacet and its metabolite FOE Oxalate in the kinetic examination of the data using the combination FOMC-SFO as reliable trigger endpoints is acceptable.

However, that conclusion is contradictory to the proposal made by the Applicant in the previously summarised study – **Study 2**.

- 2) The results of the kinetic analysis of the data obtained in **Laacherhof** Silt loam soil (study by [Kelley et al.; 1995]):

The analysis for this data-set was a two-step analysis. Its results are presented below, individually for each step.

- a) Results obtained at **Step 1** – fitting of the data for the parent compound (Flufenacet) alone:

The results of the kinetic analysis performed by the Applicant are presented below, in graphical form on figure B.8.1.1.2.1.1_CA-21 and in numerical form in the table B.8.1.1.2.1.1_CA-59. Additionally the table B.8.1.1.2.1.1_CA-60 provides the kinetic endpoints obtained with each of the kinetic models tested.

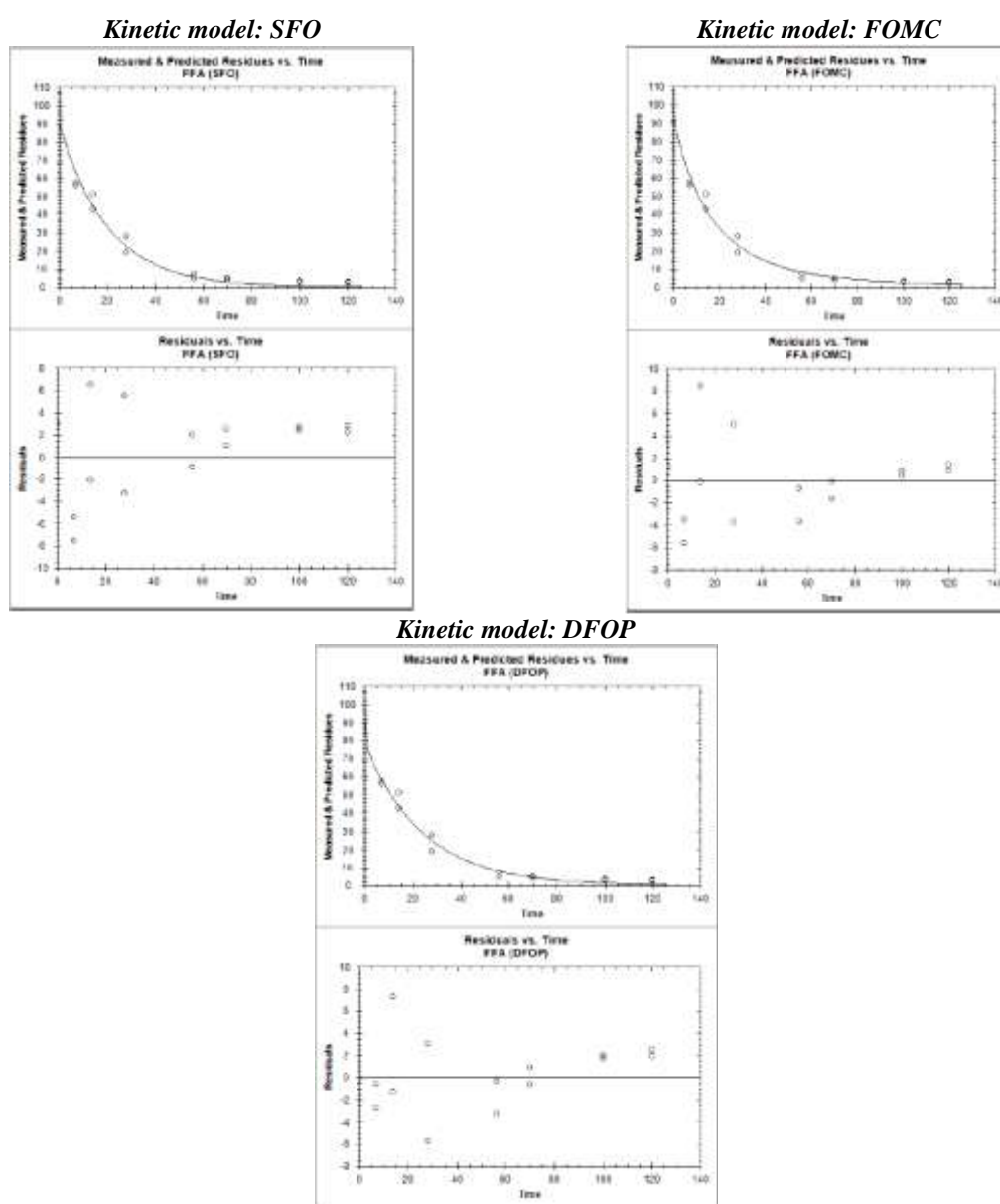


Figure B.8.1.1.2.1.1_CA-21: The graphical results of the kinetic analysis (copied from the study report).

Table B.8.1.2.1.1._CA-59: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment ¹⁾
				Lower	Upper			
SFO	M ₀	90.116	2.648	84.927	95.306	3.65 E-15	8.215	0.99; Good fit
	k	0.04964	0.00351	0.04277	0.057	5.50 E-10		
FOMC	M ₀	92.036	2.388	87.356	96.716	4.32 E-15	6.953	0.99; Good fit
	α	3.684	0.326	3.045	4.323	2.14 E-8		
	β	61.095	5.240	50.824	71.365	1.48 E-8		
DFOP	M ₀	93.200	2.100	89.083	97.316	5.58 E-15	5.496	0.99; Poor fit
	k ₁	2.0510	44.8611	-85.8751	89.977	0.4821		
	k ₂	0.04086	0.00353	0.03395	0.048	3.56 E-8		
	g	0.1610	0.0511	0.0609	0.261	0.0042		

Footnotes to the table:

1) Visual assessment of the kinetic curve as proposed by the Applicant.

Table B.8.1.2.1.1._CA-60: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested		
		SFO	FOMC	DFOP
Flufenacet	DT ₅₀ [days]	13.96	12.65	12.67
	DT ₉₀ [days]	46.38	53.04	52.05

On the basis of the obtained results the Applicant proposed to consider FOMC model as returning the best fit. That model was proposed to be used for the parent compound in kinetic examination of the data for Flufenacet and FOE Oxalate. RMS accepted that proposal.

- b) Results obtained at **Step 2** – fitting of the data for the parent compound (Flufenacet) and its degradation products:

The results of the kinetic analysis performed by the Applicant are presented below, in graphical form on figure B.8.1.2.1.1._CA-21 and in numerical form in the table B.8.1.2.1.1._CA-61.

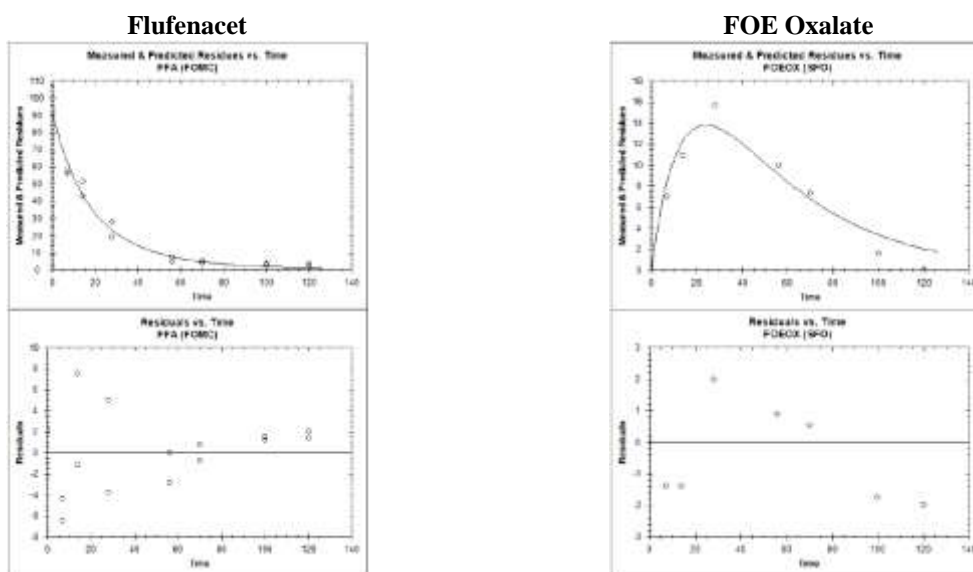


Figure B.8.1.2.1.1._CA-21: The graphical results of the kinetic examination of the data for Flufenacet and FOE Oxalate obtained in Laacherhof soil (copied from the study report).

Table B.8.1.1.2.1.1._CA-61: The numerical results of the kinetic examination of the data for Flufenacet and FOE Oxalate obtained in Laacherhof soil.

Compound	Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
			Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment ¹⁾
					Lower	Upper			
Flufenacet	FOMC	M ₀	91.077	2.664	85.855	96.299	< 2 E-16	7.265	Not provided
		α	5.9561	4.9163	-3.6797	15.592	0.120		
		β	107.7708	99.8100	-87.8531	303.395	0.147		
FOE Oxalate	SFO	M ₀	0.0	----	----	----	----	15.977	0.95; Good fit
		k	0.02962	0.00457	0.02067	0.039	1.63 E-6		
		ff	0.3285	0.0423	----	----	----		

The kinetic endpoints derived from the study are presented below in the table B.8.1.1.2.1.1._CA-62.

Table B.8.1.1.2.1.1._CA-62: The kinetic parameters determined in the experiment.

Determined parameter	Compound	
	Flufenacet	FOE Oxalate
DT ₅₀ [days]	13.30	23.40
DT ₉₀ [days]	50.86	77.74
Kinetic formation fraction ff	Not applicable – parent compound	0.329 ± 0.042
Precursor	Not applicable – parent compound	Flufenacet
Kinetic model	FOMC	SFO

The results of the kinetic fitting for Flufenacet and FOE Oxalate cannot be considered acceptable. That is due to the fact that the estimated kinetic parameters for Flufenacet in FOMC fit are not reliable – for both α and β the CI values contain zero.

Evaluation of the fitting exercise:

The proposal made by the Applicant to consider the kinetic endpoints obtained for Flufenacet and its metabolite FOE Oxalate in the kinetic examination of the data using the combination FOMC-SFO as reliable trigger endpoints cannot be considered acceptable. That is due to the fact that both kinetic parameters estimated for Flufenacet in FOMC fit – α and β are not reliable because their CI values contain zero.

- 3) The results of the kinetic analysis of the data obtained in **Höfchen im Tal** Silt loam soil (study by [Kelley et al.; 1995]):

The analysis for this data-set was a two-step analysis. Its results are presented below, individually for each step.

- a) Results obtained at **Step 1** – fitting of the data for the parent compound (Flufenacet) alone:

The results of the kinetic analysis performed by the Applicant are presented below, in graphical form on figure B.8.1.1.2.1.1_CA-22 and in numerical form in the table B.8.1.1.2.1.1_CA-63. Additionally the table B.8.1.1.2.1.1_CA-64 provides the kinetic endpoints obtained with each of the kinetic models tested.

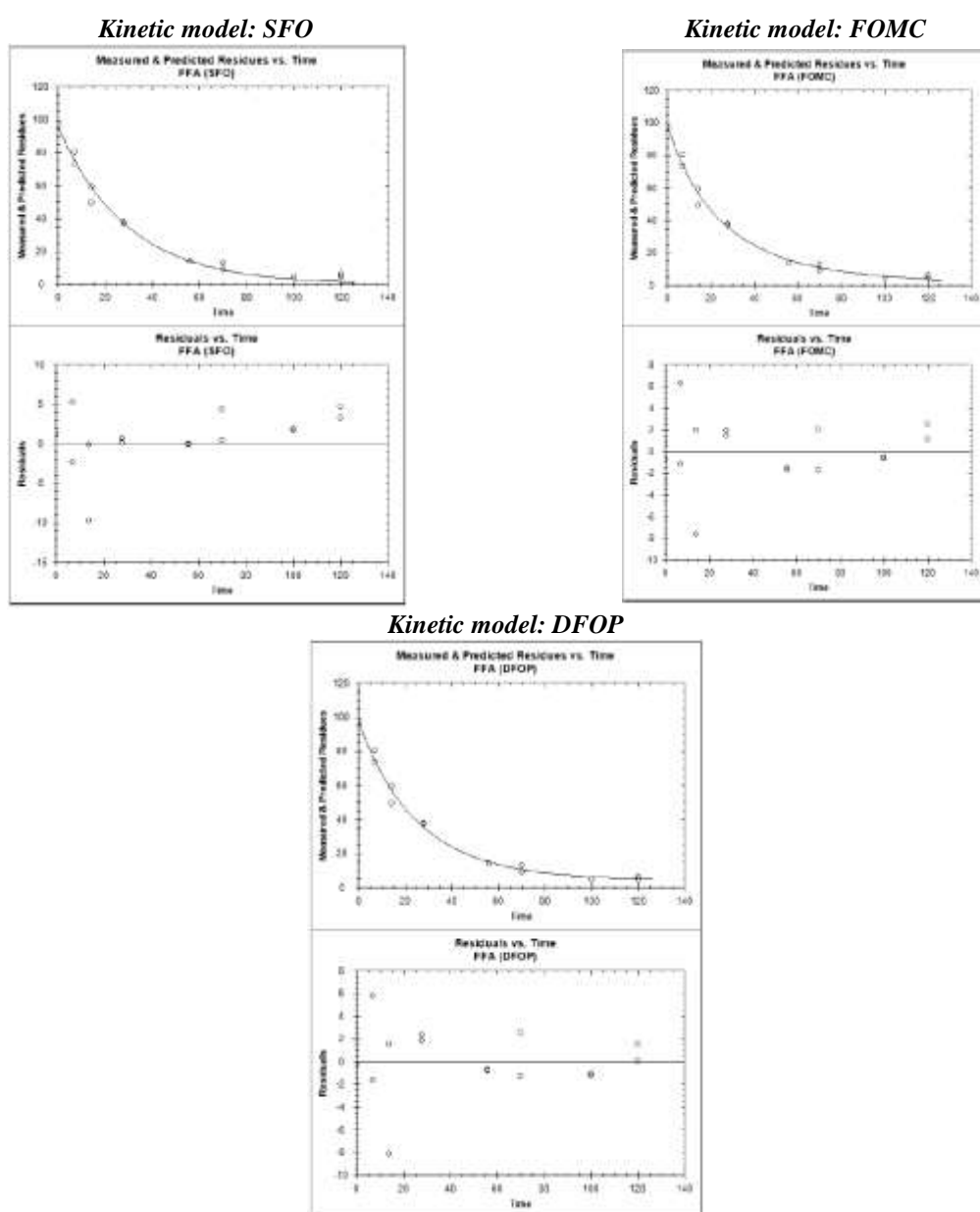


Figure B.8.1.1.2.1.1_CA-22: The graphical results of the kinetic analysis (copied from the study report).

Table B.8.1.2.1.1._CA-63: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment ¹⁾
				Lower	Upper			
SFO	M ₀	95.960	2.191	91.665	100.254	< 2 E-16	5.459	0.99; Good fit
	k	0.03428	0.00189	0.03059	0.038	1.94 E-11		
FOMC	M ₀	98.041	1.894	94.330	101.752	< 2 E-16	3.957	0.99; Good fit
	α	4.3348	0.2414	3.8617	4.808	7.36 E-11		
	β	106.2230	4.577	97.252	115.194	2.89 E-12		
DFOP	M ₀	97.580	2.172	93.322	101.838	4.83 E-15	4.072	0.99; Good fit
	k ₁	0.04092	0.00957	0.02216	0.060	0.00054		
	k ₂	0.00492	0.02403	-0.04218	0.052	0.4206		
	g	0.9229	0.2113	0.5087	1.337	0.00046		

Footnotes to the table:

1) Visual assessment of the kinetic curve as proposed by the Applicant.

Table B.8.1.2.1.1._CA-64: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested		
		SFO	FOMC	DFOP
Flufenacet	DT ₅₀ [days]	20.22	18.42	18.68
	DT ₉₀ [days]	67.17	74.46	73.17

On the basis of the obtained results the Applicant proposed to consider SFO model as returning the best fit. That model was proposed to be used for the parent compound in kinetic examination of the data for Flufenacet and FOE Oxalate. RMS accepted that proposal. It shall be noted however that fully reliable and better fit was obtained for FOMC model. For that reason RM is of the opinion that at Step 2 also the combination FOMC-SFO should be tested.

- b) Results obtained at **Step 2** – fitting of the data for the parent compound (Flufenacet) and its degradation products:

The results of the kinetic analysis performed by the Applicant are presented below, in graphical form on figure B.8.1.2.1.1._CA-23 and in numerical form in the table B.8.1.2.1.1._CA-65.

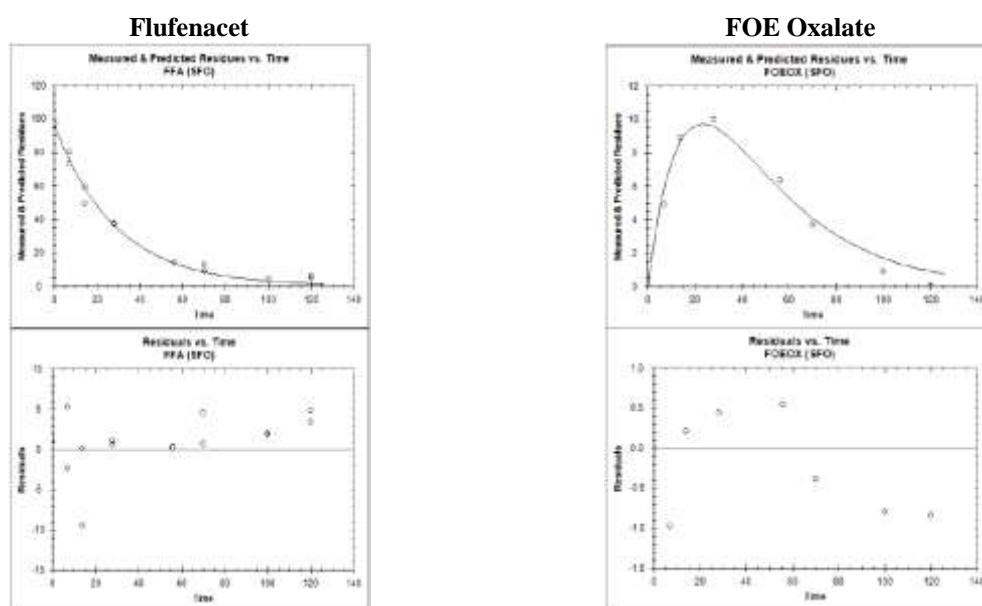
**Figure B.8.1.2.1.1._CA-22:** The graphical results of the kinetic examination of the data for Flufenacet and FOE Oxalate obtained in Höfchen im Tal soil (copied from the study report).

Table B.8.1.1.2.1.1._CA-65: The numerical results of the kinetic examination of the data for Flufenacet and FOE Oxalate obtained in Höfchen im Tal soil.

Compound	Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
			Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment ¹⁾
					Lower	Upper			
Flufenacet	SFO	M ₀	96.248	2.228	91.881	100.614	< 2 E-16	5.476	Not provided
		k	0.03470	0.00190	0.03098	0.038	3.0 E-14		
FOE Oxalate	SFO	M ₀	0.0	----	----	----	----	10.408	0.98; Good fit
		k	0.05179	0.00558	0.03098	0.063	5.47 E-9		
		ff	0.3395	0.0356	----	----	----		

The kinetic endpoints derived from the study are presented below in the table B.8.1.1.2.1.1._CA-66.

Table B.8.1.1.2.1.1._CA-66: The kinetic endpoints determined in the experiment.

Determined parameter	Compound	
	Flufenacet	FOE Oxalate
DT ₅₀ [days]	19.98	13.38
DT ₉₀ [days]	66.36	44.46
Kinetic formation fraction ff	Not applicable – parent compound	0.400 ± 0.036
Precursor	Not applicable – parent compound	Flufenacet
Kinetic model	SFO	SFO

The results of the kinetic fitting for Flufenacet and FOE Oxalate are acceptable.

Applicant proposed to consider the kinetic parameters for FOE Oxalate resulting from the kinetic examination of the data for that compound and Flufenacet using the combination of kinetic models SFO-SFO as acceptable. RMS however has to indicate, that thorough analysis of the Step-1 results showed that FOMC returned fit statistically better than that obtained with SFO. Therefore it is possible that the combination FOMC-SFO may return the best fit and hence appropriate trigger endpoints.

Evaluation of the fitting exercise:

The proposal made by RMS to consider the kinetic endpoints obtained for Flufenacet and its metabolite FOE Oxalate in the kinetic examination of the data using the combination SFO-SFO as reliable trigger endpoints is acceptable, although the results indicated that the option FOMC-SFO should have been tested. RMS noticed that they the results do not differ significantly from those obtained in summarised previously similar study – **Study 2**.

Therefore RMS proposes to consider this fitting as conformatory for that presented for full data set in mentioned **Study 2**.

- 4) The results of the kinetic analysis of the data obtained in **Howe, Indiana**, Sandy loam soil (study by [Pangilinan and Smith; 1994]):

The analysis for this data-set was a two-step analysis. Its results are presented below, individually for each step.

- a) Results obtained at **Step 1** – fitting of the data for the parent compound (Flufenacet) alone:

The results of the kinetic analysis performed by the Applicant are presented below, in graphical form on figure B.8.1.1.2.1.1_CA-23 and in numerical form in the table B.8.1.1.2.1.1_CA-67. Additionally the table B.8.1.1.2.1.1_CA-68 provides the kinetic endpoints obtained with each of the kinetic models tested.

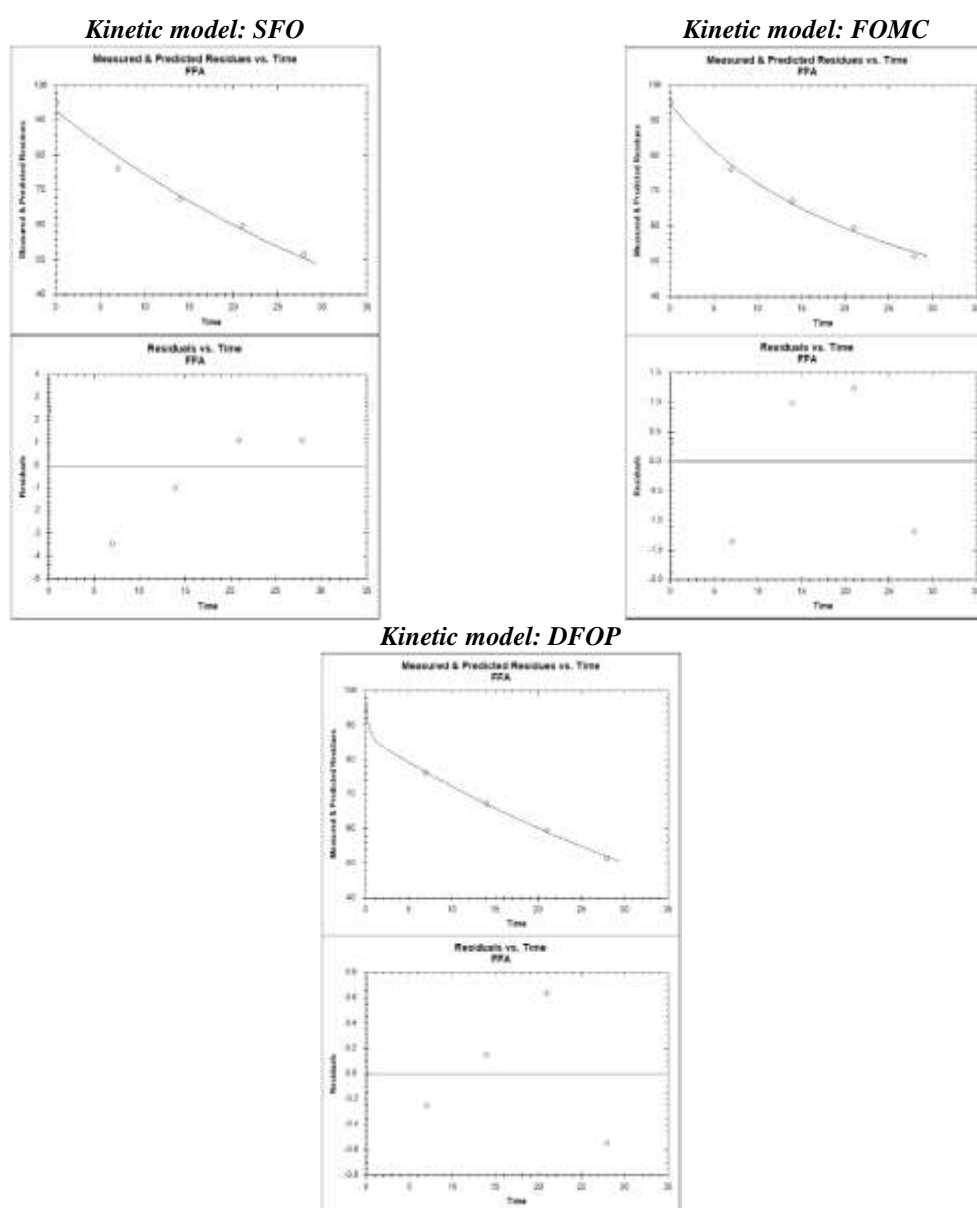


Figure B.8.1.1.2.1.1_CA-23: The graphical results of the kinetic analysis (copied from the study report).

Table B.8.1.2.1.1._CA-67: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment ¹⁾
				Lower	Upper			
SFO	M ₀	92.683	2.250	88.273	97.094	1.57 E-5	2.351	0.98; Good fit
	k	0.02182	0.00177	0.01836	0.025	0.00057		
FOMC	M ₀	94.780	1.605	91.634	97.926	0.00014	1.407	0.99; Acceptable fit
	α	0.6734	0.3022	0.0811	1.266	0.07784		
	β	20.0232	12.8427	-5.1482	45.194	0.1297		
DFOP	M ₀	95.100	0.890	93.355	96.845	0.00298	0.6487	0.993; Poor fit
	k ₁	2.2100	1.2572	-0.2541	4.674	0.1646		
	k ₂	0.01834	0.00091	0.01656	0.020	0.0157		
	g	0.0872	0.0165	0.0548	0.120	0.0596		

Footnotes to the table:

1) Visual assessment of the kinetic curve as proposed by the Applicant.

Table B.8.1.2.1.1._CA-68: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested		
		SFO	FOMC	DFOP
Flufenacet	DT ₅₀ [days]	31.77	36.02	32.82
	DT ₉₀ [days]	105.50	591.50	120.60

On the basis of the obtained results the Applicant proposed to consider SFO model as returning the best fit. That model was proposed to be used for the parent compound in kinetic examination of the data for Flufenacet and FOE Oxalate. RMS accepted that proposal.

- b) Results obtained at **Step 2** – fitting of the data for the parent compound (Flufenacet) and its degradation products:

The results of the kinetic analysis performed by the Applicant are presented below, in graphical form on figure B.8.1.2.1.1._CA-24 and in numerical form in the table B.8.1.2.1.1._CA-69.

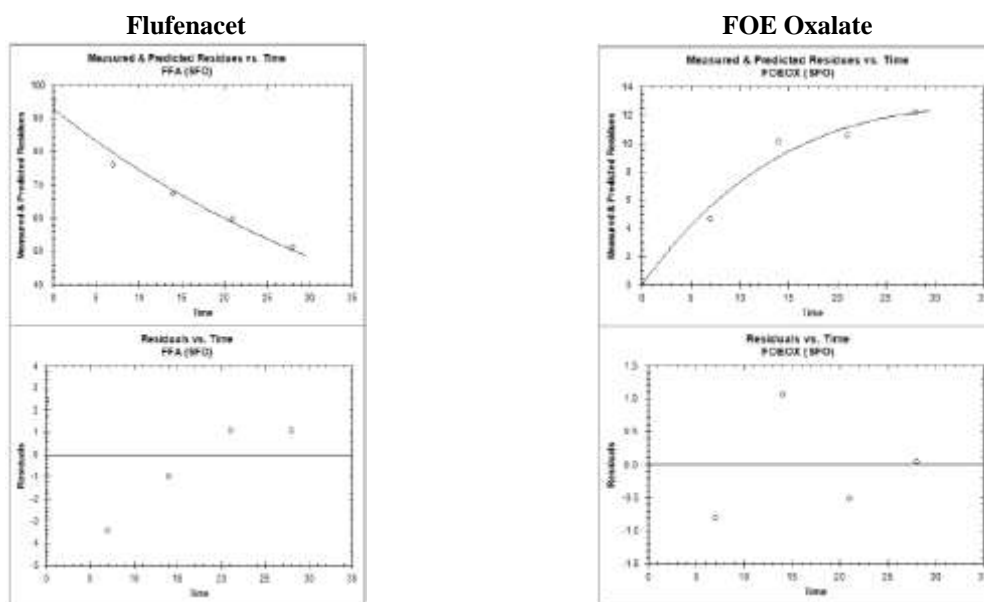


Figure B.8.1.2.1.1._CA-24: The graphical results of the kinetic examination of the data for Flufenacet and FOE Oxalate obtained in Howe, Indiana, soil (copied from the study report).

Table B.8.1.1.2.1.1._CA-69: The numerical results of the kinetic examination of the data for Flufenacet and FOE Oxalate obtained in Howe, Indiana, soil.

Compound	Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
			Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment ¹⁾
					Lower	Upper			
Flufenacet	SFO	M ₀	92.686	2.253	88.271	97.101	6.89 E-9	2.351	Not provided
		k	0.02182	0.00180	0.01830	0.025	9.43 E-6		
FOE Oxalate	SFO	M ₀	0.0	----	----	----	----	6.239	0.98; Good fit
		k	0.03543	0.01377	0.00844	0.062	0.0211		
		ff	0.4756	0.0834	----	----	----		

The kinetic endpoints derived from the study are presented below in the table B.8.1.1.2.1.1._CA-70.

Table B.8.1.1.2.1.1._CA-70: The kinetic endpoints determined in the experiment.

Determined parameter	Compound	
	Flufenacet	FOE Oxalate
DT ₅₀ [days]	31.76	19.56
DT ₉₀ [days]	105.52	64.99
Kinetic formation fraction ff	Not applicable – parent compound	0.476 ± 0.083
Precursor	Not applicable – parent compound	Flufenacet
Kinetic model	SFO	SFO

The results of the kinetic fitting for Flufenacet and FOE Oxalate are acceptable.

Applicant proposed to consider the kinetic parameters for FOE Oxalate resulting from the kinetic examination of the data for that compound and Flufenacet using the combination of kinetic models SFO-SFO as acceptable.

Evaluation of the fitting exercise:

The proposal made by RMS to consider the kinetic endpoints obtained for Flufenacet and its metabolite FOE Oxalate in the kinetic examination of the data using the combination SFO-SFO as reliable trigger endpoints is acceptable only in case of Flufenacet. It cannot be considered such for FOE Oxalate due to the fact that for that compound the decline phase was not reached. Therefore although the modelling tool was able to calculate the rate constant *k* and resulting from it kinetic endpoints – DT₅₀ and DT₉₀ values, their reliability is very limited. It is possible that the calculated kinetic endpoints, and the rate constant in particular, represent the kinetic rate of the formation of FOE Oxalate in the test soil.

As the results obtained for Flufenacet do not differ significantly from those obtained in summarised previously similar study – **Study 2**, RMS proposes to consider this fitting as conformatory for that presented for full data set in mentioned **Study 2**.

Conclusions of the study:

The kinetic analysis aimed on the determination of the trigger endpoints resulted in reliable kinetic endpoints for both Flufenacet and FOE Oxalate for only two experiments – that on BBA 2.2 soil and on Höfchen im Tal soil. The results obtained for the experiment on Laacherhof soil cannot be considered reliable because the kinetic parameters determined for the parent compound – α and β were not reliable. In case of the fourth experiment – on Howe, Indiana, soil, only the kinetic endpoints for Flufenacet may be considered reliable. The kinetic endpoints for FOE Oxalate determined in that experiment, due to the fact that the decline phase was not reached, bear much too high level of uncertainty to be considered credible, unless it is stated that they represent the rate of formation, not degradation of FOE Oxalate in their test soil.

It was also noted that in case of the experiment with BBA 2.2 soil FOMC was identified as the kinetic model returning the best fit for the parent compound. That makes the results of the fitting contradictory to the conclusions of the previously summarised **Study 2**. Finally, it shall be pointed out that the fitting was performed for partial data base in comparison to what was done in already mentioned **Study 2**. As a result, RMS proposes to consider the results of this study as conformatory for those of the **Study 2**, whenever they display similarity, and not to be used to derive the regulatory endpoints.

Study 4:

Report: Hein E.-M., (2012): “[Thiadiazole-5-¹⁴C] Flufenacet: Aerobic Degradation/Metabolism in One European Soil.”; Bayer CropScience AG, BCS-D-EnSa-Testing, 40789 Monheim, Germany, Study M1251994-1; unpublished Study Report No. MEF-11/937; 2012. 09. 19, amended (Amendment No 1) 2013. 04. 10; ; study reference number: M-439105-02-1;

Guidelines: The study was performed to comply with the following Guidelines:

- Commission Directive 95/36/EC amending Council Directive 91/414/EEC (Annexes II and III, Fate and Behaviour in the Environment), 1995;
- OECD Guideline for the Testing of Chemicals, No. 307, Aerobic and Anaerobic Transformation in Soil, 2002;
- US. EPA OCSPP Fate, Transport and Transformation Test Guidelines, OPPTS 835.4100 and OPPTS 835.4200, Aerobic and Anaerobic Soil Metabolism, 2008.

No deviations were stated in the study report.

GLP: Yes

RMS comments: This is a new study submitted specifically for purpose of this assessment. It was verified by the RMS and found acceptable. No deviations from the declared Guidelines were stated. Its summary was provided under the point B.8.1.1.1. of this document (**Study 5**). Presently it was verified for compliance, in the area of kinetic analysis, with the following Guidelines:

- FOCUS (2006): “Guidance Document on Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration.” Report of the FOCUS Work Group on Degradation Kinetics, EC Document Reference SANCO/10058/2005 version 2.0, 434 pp.;
- FOCUS (2011): “Generic guidance for Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration”, version 1.0 (issued on 23 November 2011).

The kinetic analysis provided in the study was found acceptable and its results are presented below.

Summary:

The aim of the study was to investigate the fate – route and rate of degradation, of Flufenacet in aerobic soil incubated under controlled (laboratory) conditions. The experiment was performed using one European soil originating from Germany (Hoefchen am Hohenseh). Its characteristic is provided below in the table B.8.1.1.2.1.1._CA-72. To maintain the consistency of reporting, only physicochemical properties are reported. The data on soil microbial activity were not given here. To check them please refer to adequate summary of the source study.

Table B.8.1.1.2.1.1._CA-72: The characteristic of soil used in the study.

Parameter		Soil:
Soil origin		<i>Hoefchen am Hohenseh 4a</i>
Soil type (USDA)		<i>Burscheid/ North Rhine-Westphalia/ Germany</i>
Particle size distribution		Silt loam
	Sand (50 µm – 2 mm) [%]	29
	Silt (2 – 50 µm) [%]	56
	Clay (< 2 µm) [%]	15
pH value in water (soil:water ratio 1:1)		7.0
pH value in 1N KCl		6.3
pH value in 0.01M CaCl ₂ (soil:solution ratio 1:2)		6.7
Organic carbon content (C _{org}) [%] ¹⁾		2.5
Organic matter content (OM) [%] ²⁾		4.3
Cation Exchange Capacity – CEC [mEq/100g]		12.9
Bulk density (disturbed) [g/cm ³]		1.04
Water holding capacity	Maximum [g H ₂ O/100 g soil d. w.]	61.1
	at ½ bar (pF 2.5) [%]	23.7
	at 0.1 bar (pF 2.0) [%]	29.8

Footnotes to the table:

1) Measured value;

2) Value calculated by the Applicant using the following equation: OM = 1.724*OC;

The summary of the study is provided under the point B.8.1.1.1.1. as **Study 5**. This summary contains only the results the kinetic evaluation of the data obtained for Flufenacet, carried out in line with the provisions of the FOCUS Kinetics Guidance Document [FOCUS; 2006], to identify the best-fit model.

Kinetic analysis was performed using KinGUI 2 software. Three kinetic models were tested: SFO, FOMC and DFOP. Applicant stated that the model input data sets were the residual amounts found in each replicate test system at each sampling interval. It was also declared that, instead of the measured DAT-0 concentrations of Flufenacet, the total AR recovery at that time point was used. Finally, it was stated that the M_0 value was allowed to be estimated by the model.

For the purpose of the kinetic analysis the input values were processed according to the recommendations given by FOCUS. In particular:

- values between LOD and LOQ were set to measured values;
- All single values <LOD or single non-detects (n.d.) were set to 50% LOD determined for HPLC method;
- The consecutive values <LOD or non-detects were not taken into account until the appearance of a value > LOQ.

The raw and processed data for Flufenacet used in kinetic fitting are presented below in the table B.8.1.1.2.1.1._CA-73.

Table B.8.1.1.2.1.1._CA-73: The raw and processed data for Flufenacet used in the kinetic analysis.

The raw data for Flufenacet obtained in the study			The processed data for Flufenacet obtained in the study		
Time point	Concentration of Flufenacet in [%AR]		Time point	Concentration of Flufenacet in [%AR]	
	Replicate 1	Replicate 2		Replicate 1	Replicate 2
DAT 0 – total AR recovered	99.5	100.9	DAT 0	99.5	100.9
DAT 0 – amount of Flufenacet	99.1	100.4			
DAT 2	93.3	91.2	DAT 2	93.3	91.2
DAT 4	87.4	88.3	DAT 4	87.4	88.3
DAT 7	74.8	76.3	DAT 7	74.8	76.3
DAT 10	61.8	66.3	DAT 10	61.8	66.3
DAT 14	52.8	56.8	DAT 14	52.8	56.8
DAT 35	13.4	14.2	DAT 35	13.4	14.2
DAT 60	4.1	3.4	DAT 60	4.1	3.4
DAT 87	1.7	1.6	DAT 87	1.7	1.6
DAT 120	0.9	0.9	DAT 120	0.9	0.9

The results of the kinetic analysis performed by the Applicant are presented below, in graphical form on figure B.8.1.1.2.1.1._CA-25 and in numerical form in the table B.8.1.1.2.1.1._CA-74. Additionally the table B.8.1.1.2.1.1._CA-75 provides the kinetic endpoints obtained with each of the kinetic models tested.

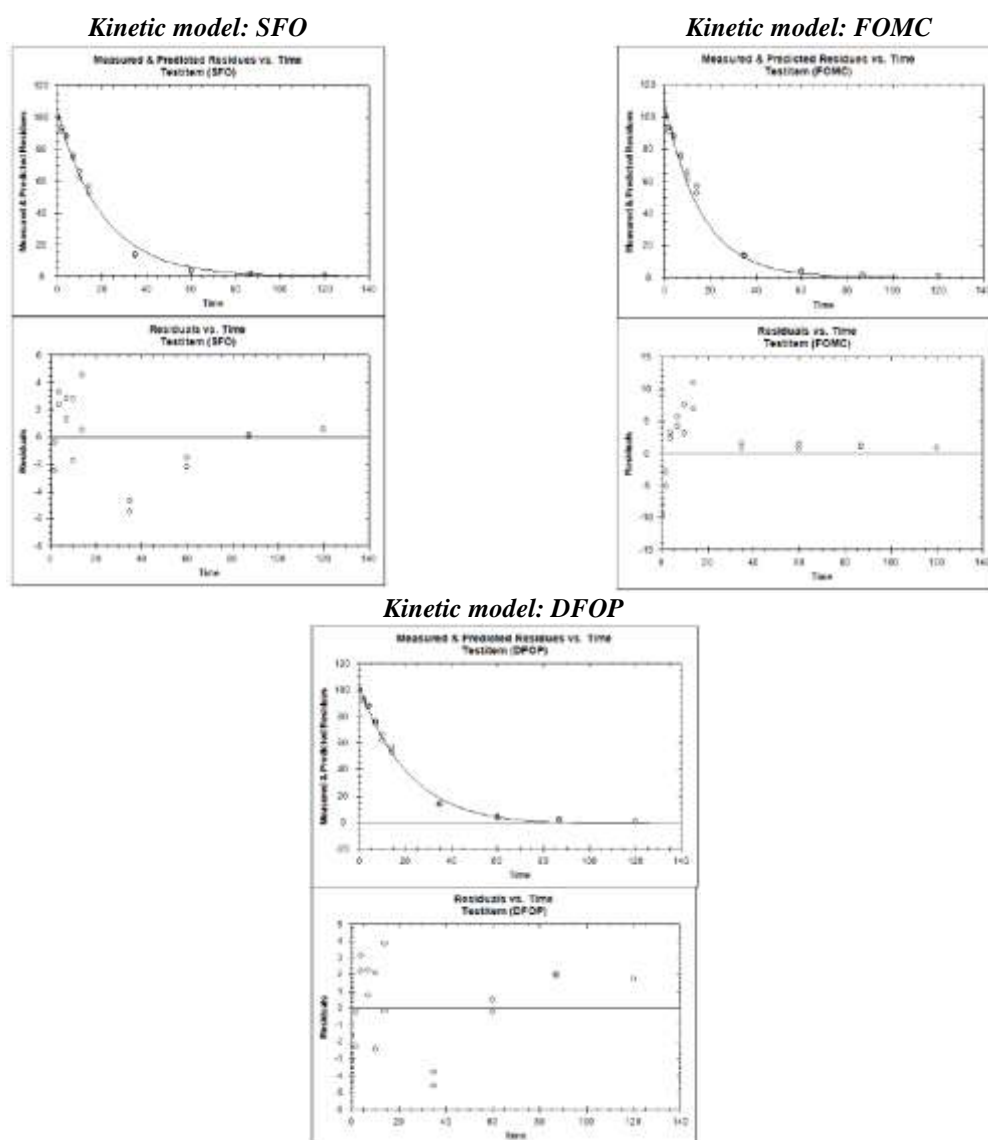


Figure B.8.1.1.2.1.1_CA-25: The graphical results of the kinetic analysis (copied from the study report).

Table B.8.1.1.2.1.1_CA-74: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	Visual assessment ¹⁾
				Lower	Upper			
SFO	M_0	103.3	1.33	100.6	105.86	<2 E-16	3.960	Good fit
	k	0.04858	1.794 E-3	0.04507	0.052	2.44 E-16		
FOMC	M_0	108.944	2.247	104.540	113.3	<2 E-16	8.349	Good fit
	α	7868.97	4583.33	-1114.19	16852.1	0.0521		
	β	127071.8	74020.9	-18006.5	272150.2	0.05221		
DFOP	M_0	102.52	1.171	100.22	104.82	<2 E-16	3.794	Good fit
	k_1	0.03511	0.00386	0.02754	0.043	5.08 E-8		
	k_2	0.03233	0.00328	0.02591	0.039	1.67 E-8		
	g	4.920	7.459	-9.700	19.541	0.259		

Footnotes to the table:

1) Visual assessment of the kinetic curve as proposed by the Applicant.

Table B.8.1.1.2.1.1._CA-75: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested		
		<i>SFO</i>	<i>FOMC</i>	<i>DFOP</i>
<i>Flufenacet</i>	DT ₅₀ [days]	14.27	11.19	14.67
	DT ₉₀ [days]	47.40	37.19	44.74

The obtained results show that all three models returned visually and statistically acceptable fits. The FOMC however was poorest of them and in addition returned statistically unreliable kinetic parameters.

SFO and DFOP returned comparable results, however DFOP was slightly better visually and statistically, so that fit was proposed by the Applicant to be considered as the best fit. RMS however, having analysed the reliability of the kinetic parameters stated that the *g* parameter in DFOP fit was not reliable. For that reason also DFOP model cannot be considered as returning the best fit.

As a result for [Thiadiazole-5-¹⁴C] Flufenacet in Hoefchen am Hohenseh silt loam soil **SFO shall be considered as returning the best fit.**

Study 5:

Report: Hein E.-M., (2012): “[Thiadiazole-5-¹⁴C] Flufenacet: Aerobic Degradation/Metabolism in Three European Soils.”; Bayer CropScience AG, BCS-D-EnSa-Testing, 40789 Monheim, Germany, Study M1252037-0; unpublished Study Report No. MEF-11/938; 2012. 10. 18, amended (Amendment No 1) 2013. 01. 28; ; study reference number: M-440348-02-1;

Guidelines: The study was performed to comply with the following Guidelines:

- OECD Guideline for the Testing of Chemicals, No. 307, Aerobic and Anaerobic Transformation in Soil, 2002;
- US. EPA OCSPP Fate, Transport and Transformation Test Guidelines, OPPTS 835.4100 and OPPTS 835.4200, Aerobic and Anaerobic Soil Metabolism, 2008.

GLP: Yes

RMS comments: This is a new study submitted specifically for purpose of this assessment. It was verified by the RMS and found acceptable. No deviations from the declared Guidelines were stated. Its summary was provided under the point B.8.1.1.1. of this document (**Study 6**). Presently it was verified for compliance, in the area of kinetic analysis of the data, with the following Guidelines:

- FOCUS (2006): “Guidance Document on Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration.” Report of the FOCUS Work Group on Degradation Kinetics, EC Document Reference SANCO/10058/2005 version 2.0, 434 pp.;
- FOCUS (2011): “Generic guidance for Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration”, version 1.0 (issued on 23 November 2011).

The kinetic analysis provided in the study was found acceptable and its results are presented below.

Summary:

The aim of the study was to investigate the fate – route and rate of degradation, of Flufenacet in aerobic soil incubated under controlled (laboratory) conditions. The experiment was performed using three European soils. Their characteristic is provided below in the table B.8.1.1.2.1.1._CA-76. To maintain the consistency of reporting, only physicochemical properties are reported. The data on soil microbial activity were not given here. To check them please refer to adequate summary of the source study.

Table B.8.1.1.2.1.1._CA-76: The characteristic of soils used in the study.

Parameter	Soil		
	<i>Laacherhof AXx</i> (AX)	<i>Dollendorf II</i> (DD)	<i>Laacherhof Wurmwiess</i> (WW)
Soil origin	Monheim/North Rhine-Westphalia/Germany	Blankenheim/North Rhine-Westphalia/Germany	Monheim/North Rhine-Westphalia/Germany
Soil type (USDA)	Loamy sand	Clay Loam	Loam
Particle size distribution	Sand (50 µm – 2 mm) [%]	75	29
	Silt (2 – 50 µm) [%]	20	38
	Clay (< 2 µm) [%]	5	33
pH value in 0.01M CaCl ₂ (soil/solution ratio 1:2)	6.1	7.2	5.4
pH value in H ₂ O (soil/solution ratio 1:1)	6.4	7.4	5.7
pH value in 1N KCl	5.9	7.0	5.2
Organic carbon content (OC) [%]	2.4	5.3	2.2
Organic matter content (OM) [%] ¹⁾	4.1	9.1	3.8
Cation Exchange Capacity – CEC [mEq/100g]	9.9	20.9	10.8
Water holding capacity	Maximum [g H ₂ O/100 g soil]	49.1	79.8
	at 0.1 bar (pF 2.0) [%]	18.7	46.0
	at ½ bar (pF 2.5) [%]	12.0	35.9
Bulk density (disturbed) [g/cm ³]	1.19	0.95	1.12

Footnotes to the table:

1) Value calculated by the RMS using the following equation: OM = 1.724 * OC;

The summary of the study is provided under the point B.8.1.1.1.1. as **Study 6**. This summary contains only the results the kinetic evaluation of the data obtained for Flufenacet, carried out in line with the provisions of the FOCUS Kinetics Guidance Document [FOCUS; 2006], to identify the best-fit model.

Kinetic analysis was performed using KinGUI 2 software. Three kinetic models were tested: SFO, FOMC and DFOP. Applicant stated that the model input data sets were the residual amounts found in each replicate test system at each sampling interval. It was also declared that, instead of the measured DAT-0 concentrations of Flufenacet, the total AR recovery at that time point was used. Finally, it was stated that the M_0 value was allowed to be estimated by the model.

For the purpose of the kinetic analysis the input values were processed according to the recommendations given by FOCUS. In particular:

- values between LOD and LOQ were set to measured values;
- All single values <LOD or single non-detects (n.d.) were set to 50% LOD determined for HPLC method;
- The consecutive values <LOD or non-detects were not taken into account until the appearance of a value > LOQ.

The input data and results of their kinetic analysis are presented below, individually for each test soil.

- a) Results of the kinetic examination of the data obtained for [Thiadiazole-5-¹⁴C] Flufenacet in **Laacherhof AXXa** Loamy sand soil:

The raw and processed data for Flufenacet used in kinetic fitting are presented below in the table B.8.1.1.2.1.1._CA-77.

Table B.8.1.1.2.1.1._CA-77: The raw and processed data for Flufenacet used in the kinetic analysis.

The raw data for Flufenacet obtained in the study			The processed data for Flufenacet obtained in the study		
Time point	Concentration of Flufenacet in [%AR]		Time point	Concentration of Flufenacet in [%AR]	
	Replicate 1	Replicate 2		Replicate 1	Replicate 2
DAT 0 – total AR recovered	99.3	98.9	DAT 0	99.3	98.9
DAT 0 – amount of Flufenacet	98.9	98.5			
DAT 1	97.9	96.2	DAT 1	97.9	96.2
DAT 2	92.3	91.3	DAT 2	92.3	91.3
DAT 4	89.7	90.0	DAT 4	89.7	90.0
DAT 7	80.6	82.2	DAT 7	80.6	82.2
DAT 10	70.7	70.5	DAT 10	70.7	70.5
DAT 14	60.2	59.6	DAT 14	60.2	59.6
DAT 35	29.0	22.4	DAT 35	29.0	22.4
DAT 63	5.1	10.0	DAT 63	5.1	10.0
DAT 91	3.0	3.3	DAT 91	3.0	3.3
DAT 121	1.6	1.3	DAT 121	1.6	1.3

The results of the kinetic analysis performed by the Applicant are presented below, in graphical form on figure B.8.1.1.2.1.1._CA-26 and in numerical form in the table B.8.1.1.2.1.1._CA-78. Additionally the table B.8.1.1.2.1.1._CA-79 provides the kinetic endpoints obtained with each of the kinetic models tested.

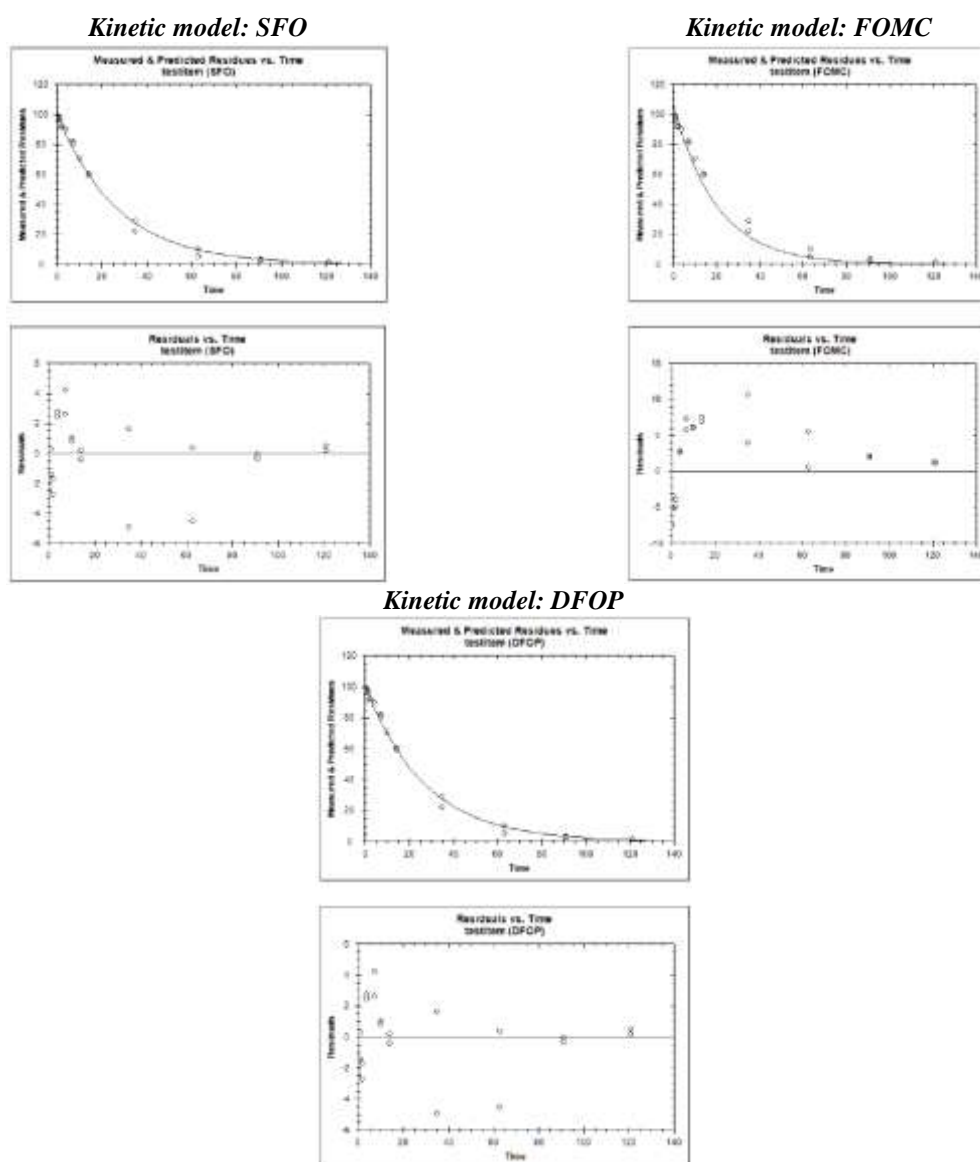


Figure B.8.1.1.2.1.1_CA-26: The graphical results of the kinetic analysis (copied from the study report).

Table B.8.1.1.2.1.1_CA-78: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	Visual assessment ¹⁾
				Lower	Upper			
SFO	M_0	101.3	0.906	99.54	103.09	<2 E-16	2.578	Good fit
	k	0.03741	1.143 E-3	0.03517	0.04	<2 E-16		
FOMC	M_0	106.496	1.965	102.644	110.3	<2 E-16	7.715	Good fit
	α	764.221	1207.331	-1602.10	3130.5	0.267		
	β	15207.23	24049.32	-31928.57	62343.0	0.267		
DFOP	M_0	101.3	0.967	99.42	103.21	<2 E-16	2.828	Good fit
	k_1	0.03741	5.390 E-3	0.02684	0.048	8.72 E-7		
	k_2	0.03741	6.788 E-3	0.0241	0.051	1.65 E-5		
	g	0.563	0.08834	0.3892	0.735	2.69 E-6		

Footnotes to the table:

1) Visual assessment of the kinetic curve as proposed by the Applicant.

Table B.8.1.1.2.1.2._CA-79: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested		
		<i>SFO</i>	<i>FOMC</i>	<i>DFOP</i>
<i>Flufenacet</i>	DT ₅₀ [days]	18.53	13.80	18.53
	DT ₉₀ [days]	61.56	45.89	61.56

The obtained results show that all three models returned visually and statistically acceptable fits. The FOMC however was poorest of them and in addition returned statistically unreliable kinetic parameters.

SFO and DFOP returned comparable results, SFO being superior to DFOP. RMS also noticed that the rate constants k_1 and k_2 in DFOP fit were identical.

Applicant proposed to consider SFO as returning the best fit. RMS accepted that proposal.

As a result for [Thiadiazole-5-¹⁴C] Flufenacet in Laacherhof AXXa sandy loam soil **SFO shall be considered as returning the best fit.**

- b) Results of the kinetic examination of the data obtained for [Thiadiazole-5-¹⁴C] Flufenacet in **Dollendorf II** Clay loam soil:

The raw and processed data for Flufenacet used in kinetic fitting are presented below in the table B.8.1.1.2.1.1._CA-80.

Table B.8.1.1.2.1.1._CA-80: The raw and processed data for Flufenacet used in the kinetic analysis.

The raw data for Flufenacet obtained in the study			The processed data for Flufenacet obtained in the study		
Time point	Concentration of Flufenacet in [%AR]		Time point	Concentration of Flufenacet in [%AR]	
	Replicate 1	Replicate 2		Replicate 1	Replicate 2
DAT 0 – total AR recovered	102.4	99.6	DAT 0	102.4	99.6
DAT 0 – amount of Flufenacet	101.2	98.6			
DAT 1	97.7	96.0	DAT 1	97.7	96.0
DAT 2	88.0	88.4	DAT 2	88.0	88.4
DAT 4	86.9	88.5	DAT 4	86.9	88.5
DAT 7	75.1	78.9	DAT 7	75.1	78.9
DAT 10	62.7	67.5	DAT 10	62.7	67.5
DAT 14	57.6	54.3	DAT 14	57.6	54.3
DAT 35	15.9	14.8	DAT 35	15.9	14.8
DAT 63	2.4	2.6	DAT 63	2.4	2.6
DAT 91	0.9	1.5	DAT 91	0.9	1.5
DAT 121	1.0	0.9	DAT 121	1.0	0.9

The results of the kinetic analysis performed by the Applicant are presented below, in graphical form on figure B.8.1.1.2.1.1._CA-27 and in numerical form in the table B.8.1.1.2.1.1._CA-81. Additionally the table B.8.1.1.2.1.1._CA-82 provides the kinetic endpoints obtained with each of the kinetic models tested.

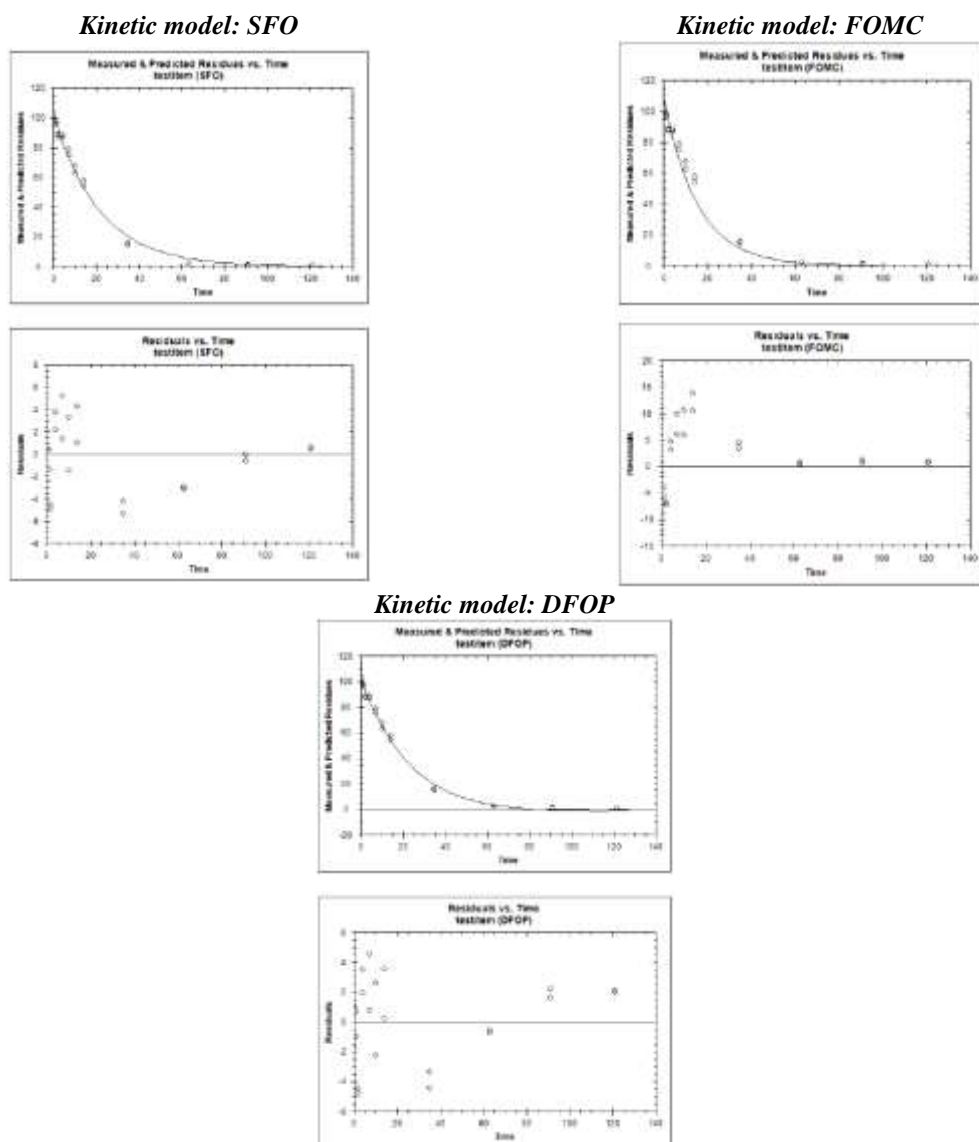


Figure B.8.1.1.2.1.1_CA-27: The graphical results of the kinetic analysis (copied from the study report).

Table B.8.1.1.2.1.1_CA-81: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	Visual assessment ¹⁾
				Lower	Upper			
SFO	M ₀	102.0	1.275	99.48	104.47	<2 E-16	4.13	Good fit
	k	0.04638	1.875 E-3	0.0427	0.05	<2 E-16		
FOMC	M ₀	108.4	2.815	102.90	113.9	<2 E-16	9.944	Good fit
	α	18940	1958	14650	22323.3	6.61 E-9		
	β	285700	30270	226400	345043.1	6.62 E-9		
DFOP	M ₀	101.30	0.989	99.36	103.24	<2 E-16	3.935	Good fit
	k ₁	0.03254	3.977 E-3	0.02475	0.040	8.87 E-8		
	k ₂	0.03002	3.25 E-3	0.02365	0.036	1.5 E-8		
	g	5.412	9.557	-13.320	24.145	0.289		

Footnotes to the table:

1) Visual assessment of the kinetic curve as proposed by the Applicant.

Table B.8.1.1.2.1.1._CA-82: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested		
		<i>SFO</i>	<i>FOMC</i>	<i>DFOP</i>
<i>Flufenacet</i>	DT ₅₀ [days]	14.95	10.71	15.40
	DT ₉₀ [days]	49.65	35.59	46.38

The obtained results show that all three models returned visually and statistically acceptable fits. The FOMC however was poorest of them.

SFO and DFOP returned comparable results, but DFOP fit was better visually and statistically, so that fit was proposed by the Applicant to be considered as the best fit. RMS however, having analysed the reliability of the kinetic parameters stated that the *g* parameter in DFOP fit was not reliable. It was also noticed that the rate constants *k*₁ and *k*₂ in DFOP fit were very similar. For these reasons in RMS's opinion also DFOP model cannot be considered as returning the best fit.

As a result for [Thiadiazole-5-¹⁴C] Flufenacet in Dollendorf II clay loam soil **SFO shall be considered as returning the best fit.**

- c) Results of the kinetic examination of the data obtained for [Thiadiazole-5-¹⁴C] Flufenacet in **Laacherhof Wurmwiese** Loam soil:

The raw and processed data for Flufenacet used in kinetic fitting are presented below in the table B.8.1.1.2.1.1._CA-83.

Table B.8.1.1.2.1.1._CA-83: The raw and processed data for Flufenacet used in the kinetic analysis.

The raw data for Flufenacet obtained in the study			The processed data for Flufenacet obtained in the study		
Time point	Concentration of Flufenacet in [%AR]		Time point	Concentration of Flufenacet in [%AR]	
	Replicate 1	Replicate 2		Replicate 1	Replicate 2
DAT 0 – total AR recovered	98.1	100.6	DAT 0	98.1	100.6
DAT 0 – amount of Flufenacet	97.4	99.9			
DAT 1	96.8	96.8	DAT 1	96.8	96.8
DAT 2	89.5	91.4	DAT 2	89.5	91.4
DAT 4	87.5	85.0	DAT 4	87.5	85.0
DAT 7	74.6	74.2	DAT 7	74.6	74.2
DAT 10	64.3	62.6	DAT 10	64.3	62.6
DAT 14	46.5	48.3	DAT 14	46.5	48.3
DAT 35	13.8	12.8	DAT 35	13.8	12.8
DAT 63	3.4	3.8	DAT 63	3.4	3.8
DAT 91	1.3	1.4	DAT 91	1.3	1.4
DAT 121	1.2	0.8	DAT 121	1.2	0.8

The results of the kinetic analysis performed by the Applicant are presented below, in graphical form on figure B.8.1.1.2.1.1._CA-28 and in numerical form in the table B.8.1.1.2.1.1._CA-84. Additionally the table B.8.1.1.2.1.1._CA-85 provides the kinetic endpoints obtained with each of the kinetic models tested.

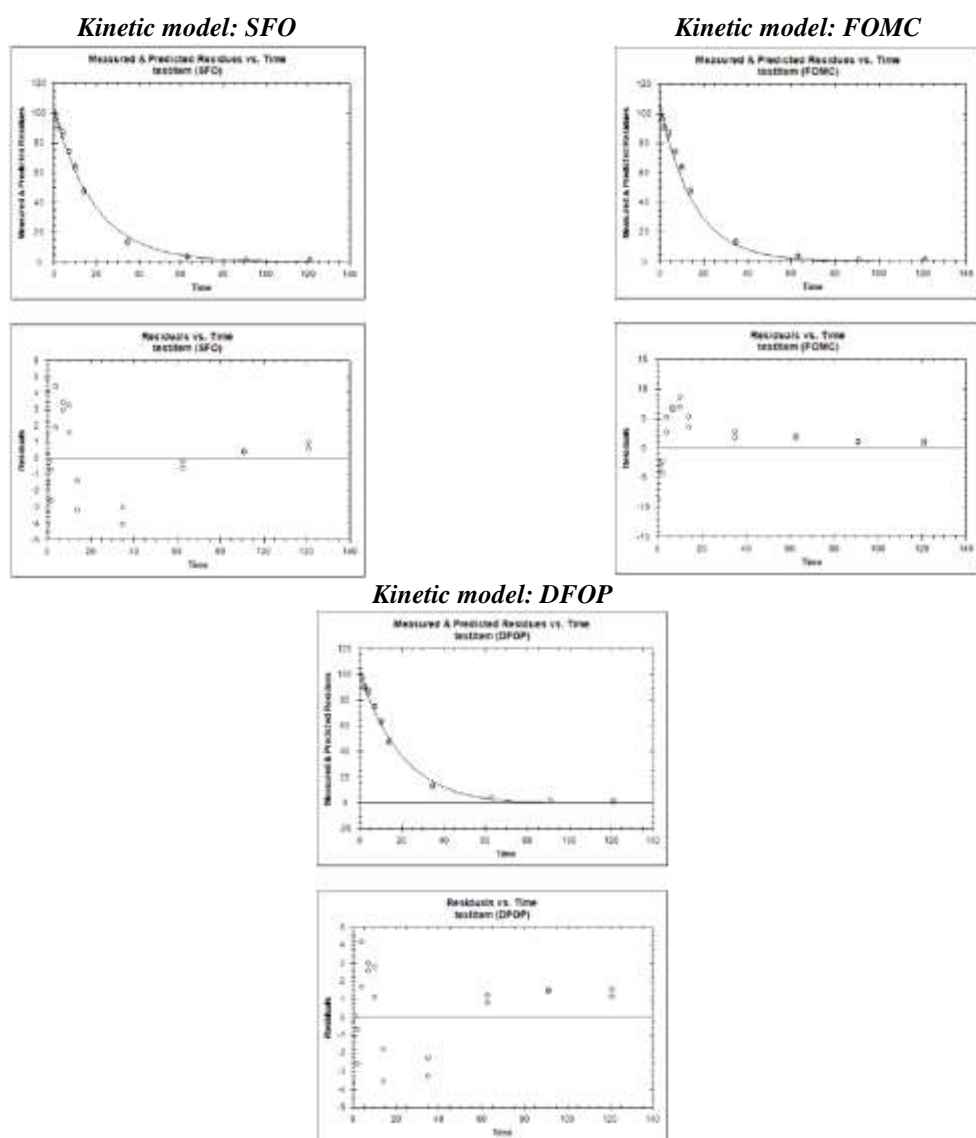


Figure B.8.1.1.2.1.1_CA-28: The graphical results of the kinetic analysis (copied from the study report).

Table B.8.1.1.2.1.1_CA-84: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	Visual assessment ¹⁾
				Lower	Upper			
SFO	M ₀	102.1	1.045	100.1	104.16	<2 E-16	3.436	Good fit
	k	0.05144	1.665 E-3	0.04818	0.055	<2 E-16		
FOMC	M ₀	106.717	1.837	103.117	110.3	<2 E-16	7.236	Good fit
	α	1051.773	1521.424	-1930.162	4033.7	0.249		
	β	16200.365	23452.02	-29764.75	62.165.5	0.249		
DFOP	M ₀	101.712	0.884	99.980	103.445	<2 E-16	3.524	Good fit
	k ₁	0.03958	3.543 E-3	0.03263	0.047	7.94 E-10		
	k ₂	0.03671	3.928 E-3	0.02901	0.044	1.25 E-8		
	g	4.498	6.726	-8.685	17.682	0.256		

Footnotes to the table:

1) Visual assessment of the kinetic curve as proposed by the Applicant.

Table B.8.1.1.2.1.1_CA-85: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested		
		<i>SFO</i>	<i>FOMC</i>	<i>DFOP</i>
<i>Flufenacet</i>	DT ₅₀ [days]	13.48	10.68	13.70
	DT ₉₀ [days]	44.76	35.51	42.78

The obtained results show that all three models returned visually and statistically acceptable fits. The FOMC however was poorest of them and in addition returned statistically unreliable kinetic parameters.

SFO and DFOP returned comparable results, SFO being superior to DFOP. RMS also noticed that the g parameter in DFOP fit was not reliable, and that the rate constants k_1 and k_2 were similar.

Applicant proposed to consider SFO as returning the best fit. RMS accepted that proposal.

As a result for [Thiadiazole-5-¹⁴C] Flufenacet in Laacherhof Wurmwiese loam soil **SFO shall be considered as returning the best fit.**

Final conclusion of the study:

The kinetic analysis of the data obtained for [Thiadiazole-5-¹⁴C] Flufenacet in three experimental soils enabled to identify the following kinetic models as returning the best fit:

- in Laacherhof AXXa loamy sand soil: SFO with DT₅₀ = 18.53 days and DT₉₀ = 61.56 days;
- in Dollendorf III clay loam soil: SFO with DT₅₀ = 14.45 days and DT₉₀ = 49.56 days;
- in Laacherhof Wurmwiese loam soil: SFO with DT₅₀ = 13.48 days and DT₉₀ = 44.76 days.

Study 6:

Report: Reinken G., Partsch S., (2014): “Trigger evaluation for the Degradation of Flufenacet Degradation Product FOE 5043 trifluoroethanesulfonic acid under Aerobic Conditions in Laboratory According to FOCUS Kinetics Using the KinGUI 2 Tool. FOE 5043-trifluoroethane sulfonic acid, Trifluoroacetic acid.”; Bayer Crop Science AG, Environmental Safety, Alfred-Nobel-Strasse 50, 40789 Monheim, Germany; unpublished Study Report No. En-Sa-13-1010; 2014. 02. 18; study reference number: M-478444-01-1;

Guidelines: The study was declared to be performed to comply with the following guidelines:

- FOCUS (2006): “Guidance Document on Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration.” Report of the FOCUS Work Group on Degradation Kinetics, EC Document Reference SANCO/10058/2005 version 2.0, 434 pp.;
- FOCUS (2011): “Generic guidance for Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration”, version 1.0 (issued on 23 November 2011).

GLP: No, not applicable – this is a modelling study;

RMS comments: RMS verified the study for its compliance with the provisions of the Guidelines listed above. It was stated that the study generally complied with the two evoked Guidance Documents. The aim of the study was to identify the best-fit kinetic model for Flufenacet and one of its major degradation products – FOE 5043-Trifluoroethanesulfonic acid. The examined data came from two already summarised route-and-rate-of-degradation studies – [Hein; 2012] (Study 5 when summarised under the point B.8.1.1.1.1.) and [Hein; 2012a] (Study 6 when summarised under the point B.8.1.1.1.1.). Their partial kinetic analysis, aimed on the determination of the best kinetic fit for the parent compound – Flufenacet radiolabelled in Thiadiazole-C5 position, was performed and its results were presented above, as Study 4 and Study 5. Never the less for the purpose of this examination it was repeated and RMS decided to present its results as well. It was also noticed that although the study was aimed on the determination of the trigger endpoints for FOE 5043-Trifluoroethanesulfonic acid, the kinetic analysis was performed for the whole data sets. Finally, RMS stated that the soil names used in the study report were slightly altered in comparison to those used in the source study reports. In order to maintain the internal coherence of the Renewal Assessment Report, RMS used the soil names as they were provided in the source study reports.

Summary:

The aim of the study was to perform the kinetic analysis of the data obtained for Flufenacet and its degradation product FOE 5043-Trifluoroethanesulfonic acid in two laboratory studies examining degradation of [Thiadiazole-5-¹⁴C] Flufenacet in aerobic soils – by [Hein; 2012] and by [Hein; 2012a], both summarised under the point B.8.1.1.1.1. of this report as, respectively, Study 5 and Study 6. It was carried out in order to identify the best kinetic fit for both compounds in each test soil and derive half-lives for FOE 5043-Trifluoroethanesulfonic acid (and Flufenacet) suitable for trigger evaluation. The characteristic of the test soils used in each of these experiments was presented above in the summaries of the Study 4 and Study 5, therefore in order to not overburden the Assessment Report, RMS decided not to present it here. The experimental conditions used in each experiment are summarised below in the table B.8.1.1.2.1.1._CA-86.

Table B.8.1.1.2.1.1._CA-86: The experimental conditions used in each experiment.

Study	Test soil		Incubation temperature <i>T</i> [°C]	Experimental conditions		
	Name	Type (USDA classification)		In experiment	Soil moisture	
					Reference value	
<i>Hein; 2012</i>	Hoefchen Am Hohenseh 4a	Silt loam	19.7 ± 0.1	55% MWHC	61.1	29.8
<i>Hein; 2012a</i>	Laaherhof AXXa	Loamy sand	19.9 ± 0.2	55% MWHC	49.1	18.7
	Dollendorf II	Clay loam	19.9 ± 0.2	55% MWHC	79.8	46.0
	Laacherhof Wurmweise	Loam	19.9 ± 0.2	55% MWHC	59.9	23.3

The not processed input data used in the kinetic analysis are presented below in the table B.8.1.1.2.1.1._CA-87. Additionally, in the table B.8.1.1.2.1.1._CA-88 are presented the DAT-0 total recovery and LOD values, subsequently used in data processing.

Table B.8.1.1.2.1.1_CA-87: The not processed data obtained in the test soils used as input in kinetic analysis.

The data obtained in Hoefchen Am Hohenseh 4a silt loam soil (study by [Hein; 2012]):								
Time Point – DAT [days]	Concentration, expressed as [% AR], of:							
	<i>Flufenacet</i>		<i>FOE Thiadone</i>		<i>FOE 5043-Trifluoroethane-sulfonic acid</i>		<i>Trifluoroacetic acid (TFA)</i>	
	Replic. 1	Replic. 2	Replic. 1	Replic. 2	Replic. 1	Replic. 2	Replic. 1	Replic. 2
0	99.1	100.4	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
2	93.3	91.2	3.5	3.4	0.8	1.1	1.2	1.2
4	87.4	88.3	4.5	4.6	2.4	2.3	3.9	3.5
7	74.8	76.3	5.2	5.9	4.1	4.4	9.2	10.1
10	61.8	66.3	6.0	5.5	5.5	5.3	17.4	16.0
14	52.8	56.8	3.6	3.2	6.1	5.9	25.4	24.8
35	13.4	14.2	1.7	1.5	4.8	5.0	61.2	61.0
60	4.1	3.4	0.6	0.6	2.5	2.7	71.7	74.3
87	1.7	1.6	< LOD	< LOD	< LOD	0.6	76.6	78.8
120	0.9	0.9	< LOD	< LOD	< LOD	< LOD	77.7	77.5
The data obtained in Laacherhof AXXa loamy sand soil (study by [Hein; 2012a]):								
Time Point – DAT ¹⁾ [days]	Concentration, expressed as [% AR], of:							
	<i>Flufenacet</i>		<i>FOE Thiadone</i>		<i>FOE 5043-Trifluoroethane-sulfonic acid</i>		<i>Trifluoroacetic acid (TFA)</i>	
	Replic. 1	Replic. 2	Replic. 1	Replic. 2	Replic. 1	Replic. 2	Replic. 1	Replic. 2
0	98.9	98.5	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
1	97.9	96.2	1.8	1.8	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
2	92.3	91.3	1.7	2.0	n. d. ¹⁾	n. d. ¹⁾	1.4	1.7
4	89.7	90.0	2.9	2.1	1.4	1.9	2.3	3.0
7	80.6	82.2	2.6	3.0	3.2	3.2	7.2	7.2
10	70.7	70.5	2.4	2.6	4.1	4.8	13.1	14.6
14	60.2	59.6	2.9	2.5	2.9	3.5	21.9	22.3
35	29.0	22.4	1.6	1.6	2.4	3.0	44.9	51.5
63	5.1	10.0	0.8	1.1	1.1	1.2	69.4	62.3
91	3.0	3.3	0.6	n. d. ¹⁾	< LOD	< LOD	71.0	72.0
121	1.6	1.3	< LOD	< LOD	0.5	0.5	74.9	73.2
The data obtained in Dollendorf II clay loam soil (study by [Hein; 2012a]):								
Time Point – DAT ¹⁾ [days]	Concentration, expressed as [% AR], of:							
	<i>Flufenacet</i>		<i>FOE Thiadone</i>		<i>FOE 5043-Trifluoroethane-sulfonic acid</i>		<i>Trifluoroacetic acid (TFA)</i>	
	Replic. 1	Replic. 2	Replic. 1	Replic. 2	Replic. 1	Replic. 2	Replic. 1	Replic. 2
0	101.2	98.6	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
1	97.7	96.0	1.8	2.5	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
2	88.0	88.4	2.5	2.5	n. d. ¹⁾	n. d. ¹⁾	1.9	2.2
4	86.9	88.5	4.3	3.6	0.6	< LOD	5.6	5.8
7	75.1	78.9	5.1	2.9	2.3	2.0	10.1	9.3
10	62.7	67.5	6.2	5.0	3.8	3.1	20.6	17.3
14	57.6	54.3	4.5	5.2	1.7	1.8	27.6	28.7
35	15.9	14.8	3.5	3.0	1.6	1.6	67.0	66.6
63	2.4	2.6	0.6	0.9	0.5	0.6	78.8	78.3
91	0.9	1.5	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	79.4	83.6
121	1.0	0.9	n. d. ¹⁾	n. d. ¹⁾	< LOD	< LOD	81.0	81.0
The data obtained in Laacherhof Wurmwiiese loam soil (study by [Hein; 2012a]):								
Time Point – DAT ¹⁾ [days]	Concentration, expressed as [% AR], of:							
	<i>Flufenacet</i>		<i>FOE Thiadone</i>		<i>FOE 5043-Trifluoroethane-sulfonic acid</i>		<i>Trifluoroacetic acid (TFA)</i>	
	Replic. 1	Replic. 2	Replic. 1	Replic. 2	Replic. 1	Replic. 2	Replic. 1	Replic. 2
0	97.4	99.9	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
1	96.8	96.8	1.5	1.5	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
2	89.5	91.4	2.3	1.7	< LOD	< LOD	1.2	1.5
4	87.5	85.0	2.7	3.4	0.7	0.8	4.9	5.4
7	74.6	74.2	3.3	5.8	1.6	1.6	11.5	11.4
10	64.3	62.6	3.2	3.5	1.9	1.9	19.4	18.8
14	46.5	48.3	3.4	2.8	0.5	0.6	32.4	30.8
35	13.8	12.8	1.7	1.7	< LOD	< LOD	60.8	59.3
63	3.4	3.8	0.9	0.5	0.8	< LOD	69.7	70.3
91	1.3	1.4	n. d. ¹⁾	n. d. ¹⁾	< LOD	< LOD	75.4	74.1
121	1.2	0.8	n. d. ¹⁾	n. d. ¹⁾	< LOD	< LOD	73.1	74.4

Footnotes to the table:

1) n. d. = not detected.

Table B.8.1.1.2.1.1._CA-88: The DAT-0 recoveries and LOD determined for each experiment

Study	Test soil		Determined parameter		
	Soil name	Soil type (USDA classification)	DAT-0 recovery [% AR]		LOD [% AR]
			Rep. 1	Rep 2.	
Hein; 2012	Hoefchen am Hohenseh 4a	Silt loam	99.5	100.9	0.5
	Laacherhof AXXa	Loamy sand	99.3	98.9	0.4
Hein; 2012a	Dollendorf II	Clay loam	102.4	99.6	0.4
	Laacherhof Wurmwiese	Loam	98.1	100.6	0.4

The data presented above were subjected to a multistep evaluation procedure, used with some alterations in all kinetic analyses of the data performed for Flufenacet and its degradation products. RMS stated that it was performed in line with the recommendations of FOCUS Kinetics Guidelines [FOCUS; 2006]. It consisted of the following steps:

- **Step 1:** Processing of the raw input data;
- **Step 2:** Kinetic evaluation of the processed data using the following 1st – order kinetic models: SFO, FOMC and DFOP, and KinGUI 2 as a modelling tool. That step consisted of the two sub-steps:
 - **Sub-step 1:** kinetic evaluation of the data for parent compound (Flufenacet) only, in order to determine the appropriate kinetic model. It was declared that at that stage of analysis all three kinetic models listed above were tested, RMS noticed however, that the analysis was limited only to two – SFO and FOMC;
 - **Sub-step 2:** kinetic evaluation of the data for parent compound (Flufenacet) and its degradation products using for Flufenacet the kinetic model identified at previous stage as appropriate, and SFO model for degradation products;
- **Step 3:** Evaluation of the results of kinetic examination of the data;
- **Step 4:** Reporting of the obtained results, in particular kinetic parameters recommended for modelling.

The raw input data, presented in table B.8.1.1.2.1.1._CA-87, were processed following the recommendations given by FOCUS. In general terms it looked as follows:

- Measured and reported true replicates were taken into account singularly;
- The data sets were checked for their consistency and clear outliers. In case the outliers were found and removed, that was clearly indicated.

The particular measures taken in the processing of the data for the parent compound – Flufenacet, were following:

- The total AR recovery recorded in DAT-0 samples was used as concentration of Flufenacet at that time point, but the M_0 value was allowed to be estimated by the model; For that purpose the data presented in the table B.8.1.1.2.1.1._CA-88 – “DAT-0 recovery” values, were used;
- Values between LOD and LOQ were set to measured values;
- All single values <LOD or the non-detects (n. d.) were set to $\frac{1}{2}$ LOD. The same procedure was applied to the first appearances. However, when the values <LOD/n.d. appeared consecutively for second and next times, the kinetic curve was cut off until the appearance of the first value >LOQ. For that purpose the data presented in the table B.8.1.1.2.1.1._CA-88 – “LOD” values, were used.

The values for degradation products were processed in a following way:

- The initial, DAT-0, concentration was set to 0. That value, unlike the free-fitted M_0 for the parent compound, was a fixed value;
- The values for subsequent time points, if reported as <LOD or non-detects were also set to 0 until the last time point before the first detectable amount was recorded;
- The value reported as <LOD/n.d. appearing just before the first detectable amount was recorded was set to $\frac{1}{2}$ LOD. For that purpose the data presented in the table B.8.1.1.2.1.1._CA-88 – LOD values, were used.
- Values between LOD and LOQ were set to measured values;
- In the decline phase the first values <LOD/n.d. were also set $\frac{1}{2}$ LOD. For the consecutive second and next such appearances the kinetic curve was cut off until, eventually, the first value >LOQ appeared. For that purpose the data presented in the table B.8.1.1.2.1.1._CA-88 – “LOD” values, were used.

The processed values used as input data for the kinetic examination are presented below in the table B.8.1.1.2.1.1._CA-89.

Table B.8.1.1.2.1.1_CA-89: The processed data obtained in the test soils used as input in kinetic analysis.

The data obtained in Hoefchen am Hohenseh 4a silt loam soil (study by [Hein; 2012]):								
Time Point – DAT [days]	Concentration, expressed as [% AR], of:							
	<i>Flufenacet</i>		<i>FOE Thiadone</i>		<i>FOE 5043-Trifluoroethane-sulfonic acid</i>		<i>Trifluoroacetic acid (TFA)</i>	
	Replic. 1	Replic. 2	Replic. 1	Replic. 2	Replic. 1	Replic. 2	Replic. 1	Replic. 2
0	99.5	100.9	0.0	0.0	0.0	0.0	0.0	0.0
2	93.3	91.2	3.5	3.4	0.8	1.1	1.2	1.2
4	87.4	88.3	4.5	4.6	2.4	2.3	3.9	3.5
7	74.8	76.3	5.2	5.9	4.1	4.4	9.2	10.1
10	61.8	66.3	6.0	5.5	5.5	5.3	17.4	16.0
14	52.8	56.8	3.6	3.2	6.1	5.9	25.4	24.8
35	13.4	14.2	1.7	1.5	4.8	5.0	61.2	61.0
60	4.1	3.4	0.6	0.6	2.5	2.7	71.7	74.3
87	1.7	1.6	0.3 ¹⁾	0.3 ¹⁾	0.3 ¹⁾	0.6	76.6	78.8
120	0.9	0.9	NaN ²⁾	NaN ²⁾	NaN ²⁾	0.3 ¹⁾	77.7	77.5
The data obtained in Laacherhof AXXa loamy sand soil (study by [Hein; 2012a]):								
Time Point – DAT ¹⁾ [days]	Concentration, expressed as [% AR], of:							
	<i>Flufenacet</i>		<i>FOE Thiadone</i>		<i>FOE 5043-Trifluoroethane-sulfonic acid</i>		<i>Trifluoroacetic acid (TFA)</i>	
	Replic. 1	Replic. 2	Replic. 1	Replic. 2	Replic. 1	Replic. 2	Replic. 1	Replic. 2
0	99.3	98.9	0.0	0.0	0.0	0.0	n. d. ¹⁾	n. d. ¹⁾
1	97.9	96.2	1.8	1.8	NaN ²⁾	NaN ²⁾	n. d. ¹⁾	n. d. ¹⁾
2	92.3	91.3	1.7	2.0	0.2 ¹⁾	0.2 ¹⁾	1.4	1.7
4	89.7	90.0	2.9	2.1	1.4	1.9	2.3	3.0
7	80.6	82.2	2.6	3.0	3.2	3.2	7.2	7.2
10	70.7	70.5	2.4	2.6	4.1	4.8	13.1	14.6
14	60.2	59.6	2.9	2.5	2.9	3.5	21.9	22.3
35	29.0	22.4	1.6	1.6	2.4	3.0	44.9	51.5
63	5.1	10.0	0.8	1.1	1.1	1.2	69.4	62.3
91	3.0	3.3	0.6	0.2 ¹⁾	0.2 ¹⁾	0.2 ¹⁾	71.0	72.0
121	1.6	1.3	0.2 ¹⁾	NaN ²⁾	0.5	0.5	74.9	73.2
The data obtained in Dollendorf II clay loam soil (study by [Hein; 2012a]):								
Time Point – DAT ¹⁾ [days]	Concentration, expressed as [% AR], of:							
	<i>Flufenacet</i>		<i>FOE Thiadone</i>		<i>FOE 5043-Trifluoroethane-sulfonic acid</i>		<i>Trifluoroacetic acid (TFA)</i>	
	Replic. 1	Replic. 2	Replic. 1	Replic. 2	Replic. 1	Replic. 2	Replic. 1	Replic. 2
0	102.4	99.6	0.0	0.0	0.0	0.0	0.0	0.0
1	97.7	96.0	1.8	2.5	NaN ²⁾	NaN ²⁾	0.2 ¹⁾	0.2 ¹⁾
2	88.0	88.4	2.5	2.5	0.2 ¹⁾	NaN ²⁾	1.9	2.2
4	86.9	88.5	4.3	3.6	0.6	0.2 ¹⁾	5.6	5.8
7	75.1	78.9	5.1	2.9	2.3	2.0	10.1	9.3
10	62.7	67.5	6.2	5.0	3.8	3.1	20.6	17.3
14	57.6	54.3	4.5	5.2	1.7	1.8	27.6	28.7
35	15.9	14.8	3.5	3.0	1.6	1.6	67.0	66.6
63	2.4	2.6	0.6	0.9	0.5	0.6	78.8	78.3
91	0.9	1.5	0.2 ¹⁾	0.2 ¹⁾	0.2 ¹⁾	0.2 ¹⁾	79.4	83.6
121	1.0	0.9	NaN ²⁾	NaN ²⁾	NaN ²⁾	NaN ²⁾	81.0	81.0
The data obtained in Laacherhof Wurmwiiese loam soil (study by [Hein; 2012a]):								
Time Point – DAT ¹⁾ [days]	Concentration, expressed as [% AR], of:							
	<i>Flufenacet</i>		<i>FOE Thiadone</i>		<i>FOE 5043-Trifluoroethane-sulfonic acid</i>		<i>Trifluoroacetic acid (TFA)</i>	
	Replic. 1	Replic. 2	Replic. 1	Replic. 2	Replic. 1	Replic. 2	Replic. 1	Replic. 2
0	98.17.4	100.6	0.0	0.0	0.0	0.0	0.0	0.0
1	96.8	96.8	1.5	1.5	NaN ²⁾	NaN ²⁾	n. d. ¹⁾	n. d. ¹⁾
2	89.5	91.4	2.3	1.7	0.2 ¹⁾	0.2 ¹⁾	1.2	1.5
4	87.5	85.0	2.7	3.4	0.7	0.8	4.9	5.4
7	74.6	74.2	3.3	5.8	1.6	1.6	11.5	11.4
10	64.3	62.6	3.2	3.5	1.9	1.9	19.4	18.8
14	46.5	48.3	3.4	2.8	0.5	0.6	32.4	30.8
35	13.8	12.8	1.7	1.7	0.2 ¹⁾	0.2 ¹⁾	60.8	59.3
63	3.4	3.8	0.9	0.5	0.8	NaN ²⁾	69.7	70.3
91	1.3	1.4	0.2 ¹⁾	0.2 ¹⁾	0.2 ¹⁾	NaN ²⁾	75.4	74.1
121	1.2	0.8	NaN ²⁾	NaN ²⁾	NaN ²⁾	NaN ²⁾	73.1	74.4

Footnotes to the table:

- 1) Value set to ½ LOD;
 2) NaN = Not a Number;

The processed data were kinetically examined using KinGUI ver. 2 modelling tool, developed by Bayer. The optimisation was performed using IRLS (Iteratively Reweighed Nonlinear Least Squares) algorithm. The fitting procedure was a two-stage one. The first step, further called **Step 1**, consisted on the determination of the appropriate kinetic model for the parent compound – Flufenacet. At that stage two 1st-order kinetic models were tested: SFO and FOMC (alteration of the general multistep evaluation procedure characterised above). During the next stage, further called **Step 2**, the whole data set – data for the Flufenacet and its degradation products, was kinetically examined. In case of Flufenacet the tested kinetic model was that determined appropriate at **Step 1**, while for the degradation products the SFO model was used. The conceptual metabolic pathway built in the modelling tool is presented below on figure B.8.1.1.2.1.1._CA-29. The following abbreviations were used:

- FFA for Flufenacet (parent compound);
- THIA for FOE Thiadone;
- TFA for Trifluoroacetic acid (TFA);
- TFESA for FOE 5043-Trifluoroethanesulfonic acid;

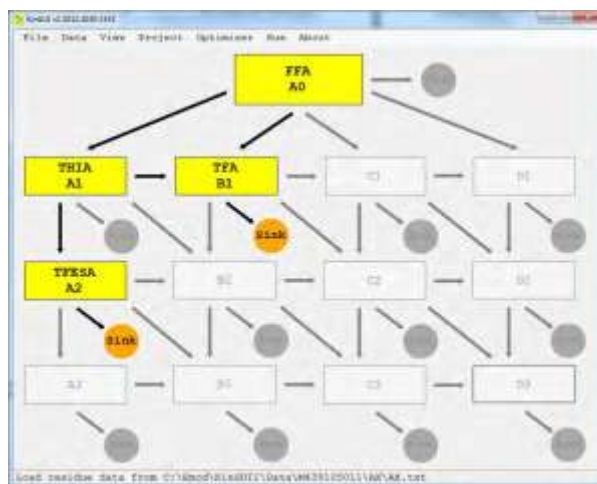


Figure B.8.1.1.2.1.1._CA-29: The conceptual transformation scheme assumed in the modelling tool (copied from the study report).

The obtained results of the kinetic analysis were evaluated by the Applicant. That was done by means of a detailed statistical analysis comprising the following components:

- visual assessment of the fit;
- χ^2 -error statistics;
- t-test significance;
- correlation analysis.

The detailed characteristic of that evaluation is provided in the summary of the **Study 2**, on pages 168 – 169.

The whole assessment was carried out as a multistep procedure, similar to that outlined in the presented above summary of the **Study 3**, on page 201. However, as it slightly differed from that scheme, RMS decided to present it in this summary. It consisted of the following steps:

- **Step 1:** the data for the parent compound were fitted using two kinetic models: SFO and FOMC and verified for passing the acceptance criteria (χ^2 -error and distribution of residuals); in case the SFO fit was found visually acceptable and statistically more appropriate than FOMC, it was selected as the best-fit model;
- **Step 2:** in case the SFO model was found not to be more appropriate than FOMC, it was refined in three-step procedure, by removing the outliers, fixing model parameters and data weighing, until the best-fit was achieved;
- **Step 3:** if the **Step-2** fitting for SFO model still failed the χ^2 -error test, and FOMC was demonstrated to be more appropriate, the DFOP model was tested in order to determine if bi-phasic model is acceptable and if so, which one should be selected as returning the best fit;
- **Step 4:** once the best-fit model was determined, the data for the degradation products were added to the data set and the kinetic analysis repeated using the identified best-fit model for Flufenacet (parent compound) and SFO for the metabolites in order to estimate trigger endpoints for them. In case SFO

model was found not acceptable, further analysis was performed using case-to-case approach in line with the recommendations of FOCUS Kinetics [FOCUS; 2006, 2011].

Analysing the proposed assessment procedure RMS stated that it complied with the procedure for determination of the trigger kinetic endpoints presented in FOCUS Kinetics Guidance Document [FOCUS; 2006].

The results of the kinetic examination of the data and their evaluation are provided below, individually for each test soil.

- The results of the kinetic analysis of the data obtained in **Hoefchen am Hohenseh 4a** Silt loam soil (study by [Hein; 2012]):

The analysis for this data-set was a two-step analysis. Its results are presented below, individually for each step.

- a) Results obtained at **Step 1** – fitting of the data for the parent compound (Flufenacet) alone:

The results of the kinetic analysis performed by the Applicant are presented below, in graphical form on figure B.8.1.1.2.1.1._CA-30 and in numerical form in the table B.8.1.1.2.1.1._CA-90.

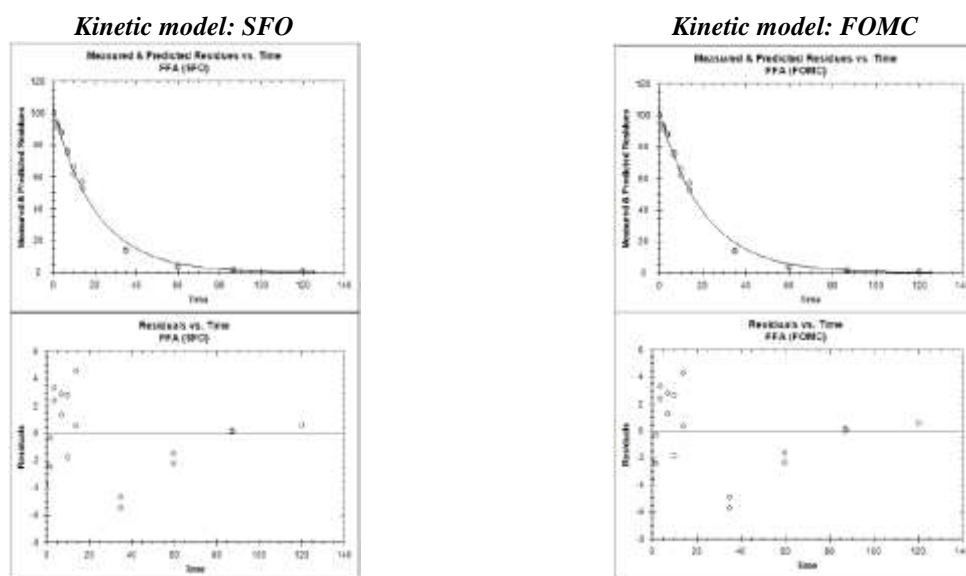


Figure B.8.1.1.2.1.1._CA-30: The graphical results of the kinetic analysis (copied from the study report).

Table B.8.1.1.2.1.1._CA-90: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment ¹⁾
				Lower	Upper			
SFO	M_0	103.30	1.333	100.60	105.868	< 2 E-16	3.960	1.0; Good fit
	k	0.04858	1.794 E-3	0.04507	0.052	2.44 E-16		
FOMC	M_0	103.099	0.985	101.169	105.00	< 2 E-16	4.179	1.0; Good fit
	α	624.316	659.079	-667.455	1916.10	0.178		
	β	12935.739	13657.756	-13832.971	39704.40	0.178		

Footnotes to the table:

1) Visual assessment of the kinetic curve as reported by the Applicant.

The Applicant stated that the fit returned by the SFO model was visually and statistically acceptable, therefore it was selected as appropriate and used at the next step to kinetically examine the data for Flufenacet and its

degradation products. The analysis using FOMC model did not result in any improvement of the fit and the kinetic parameters were not reliable (the CI values for both α and β passed through zero). As a result, the DFOP model was not tested and SFO was indicated as the best-fit model for Flufenacet in this trial. RMS accepted that choice.

The best-fit kinetic endpoints determined for Flufenacet in this kinetic assessment are following: $DT_{50} = 14.27$ days, $DT_{90} = 47.40$ days, kinetic model: SFO.

- b) Results obtained at **Step 2** – fitting of the data for the parent compound (Flufenacet) and its degradation products:

The results of the kinetic analysis performed by the Applicant are presented below, in graphical form on figure B.8.1.1.2.1.1_CA-31 and in numerical form in the table B.8.1.1.2.1.1_CA-91.

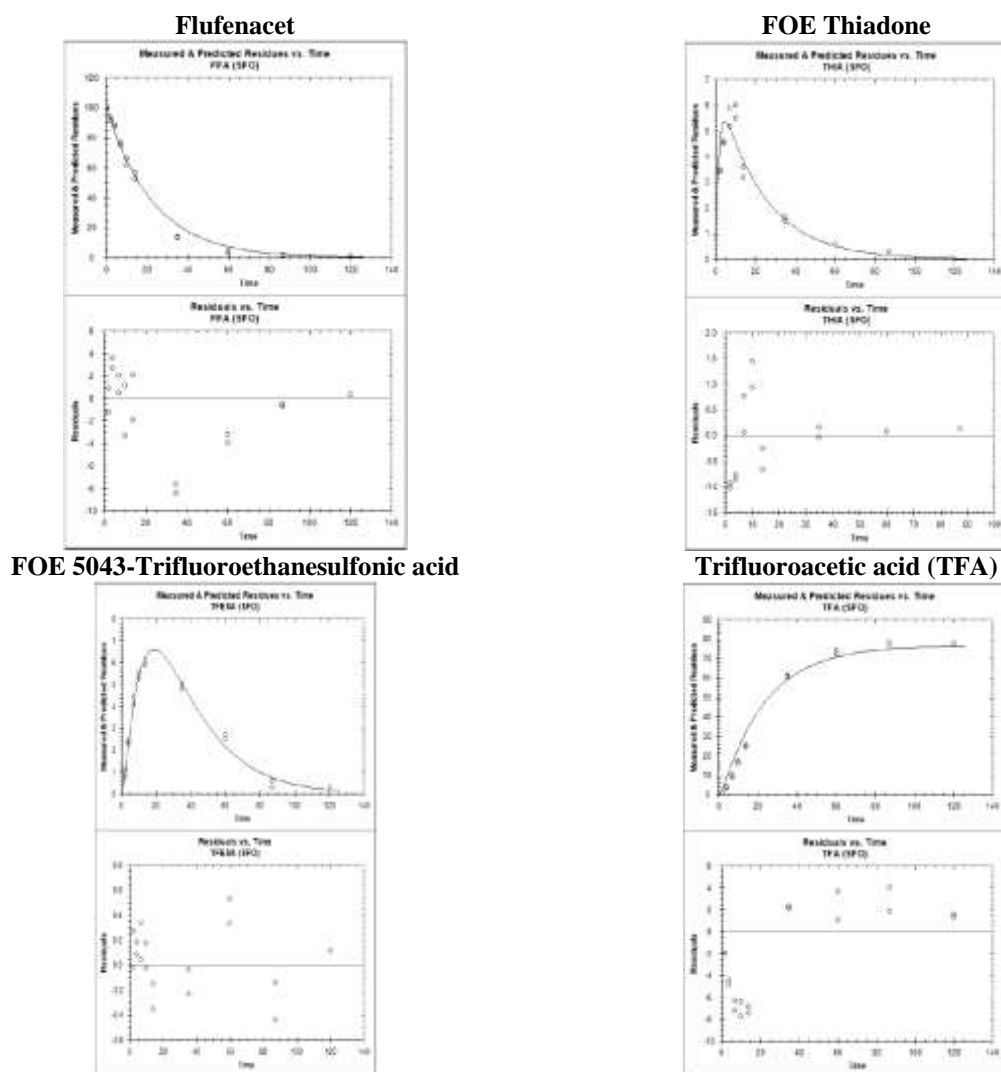


Figure B.8.1.1.2.1.1_CA-31: The graphical results of the kinetic examination of the data for Flufenacet, FOE Thiadone, FOE 5043-Trifluoroethanesulfonic acid and Trifluoroacetic acid obtained in Hoefchen am Hohenseh 4a soil (copied from the study report).

Table B.8.1.1.2.1.1._CA-91: The numerical results of the kinetic examination of the data for Flufenacet, FOE Thiadone, FOE 5043-Trifluoroethanesulfonic acid and Trifluoroacetic acid obtained in Hoefchen am Hohenseh 4a soil.

Compound	Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
			Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment ¹⁾
					Lower	Upper			
Flufenacet	SFO	M ₀	100.90	1.174	98.58	103.186	< 2 E-16	4.882	Good fit
		k	0.04377	1.20 E-3	0.04142	0.046	< 2 E-16		
FOE Thiadone	SFO	M ₀	0.0	----	----	----	----	16.421	Good fit
		k	0.6111	0.08961	0.4354	0.787	1.33 E-9		
		ff	0.913	0.126	----	----	----		
FOE 5043-Trifluoroethane-sulfonic acid	SFO	M ₀	0.0	----	----	----	----	5.845	0.99; Good fit
		k	0.07617	4.53 E-3	0.0673	0.085	< 2 E-16		
		ff	0.264	----	----	----	----		
Trifluoroacetic acid	SFO	M ₀	0.0	----	----	----	----	10.492	Good fit
		k	1.4 E-10	4.85 E-4	-9.51 E-4	0.001	0.500		
		ff ²⁾	0.087	0.044	----	----	----		
		ff ₂ ³⁾	0.736	----	----	----	----		

Footnotes to the table:

- 1) The Applicant provided the R² value and the assessment of the visual fit only for FOE 5043-Trifluoroethanesulfonic acid; for all remaining compounds R² is not reported while the visual assessment is that performed by RMS;
- 2) ff calculated for formation from the parent compound – Flufenacet;
- 3) ff calculated for the formation from FOE Thiadone;

The Applicant stated that in that kinetic analysis it was possible to obtain the reliable trigger kinetic endpoints for FOE 5043-Trifluoroethanesulfonic acid. The determined kinetic parameters reported by the Applicant were following: **DT₅₀ = 9.1 days, DT₉₀ = 30.2 days.**

RMS performed own analysis of the obtained results. It led to the following conclusions:

- It was possible to obtain reliable kinetic fits and kinetic parameters for the following compounds: Flufenacet, FOE Thiadone and FOE 5043-Trifluoroethanesulfonic acid;
- In case of Trifluoroacetic acid the fit is reliable, however of the determined kinetic parameters only the kinetic formation fractions – ff, may be considered reliable. The lack of reliability of the degradation rate constant and resulting from it DT₅₀ and DT₉₀ values is due to the fact that the kinetic curve was in its formation phase and even the would-be maximum was not reached.

The final set of the kinetic parameters considered acceptable by the RMS is presented below in the table B.8.1.1.2.1.1._CA-92.

Table B.8.1.1.2.1.1._CA-92: The reliable set of the kinetic parameters determined in the experiment

Determined parameter	Compound			
	Flufenacet	FOE Thiadone	FOE 5043-Trifluoroethane-sulfonic acid	Trifluoroacetic acid
DT ₅₀ [days]	15.84	1.34	9.10	1000
DT ₉₀ [days]	52.61	3.77	30.23	> 1000
Kinetic formation fraction ff	Not applicable	0.913 ± 0.013	0.264	0.087 ± 0.004
Precursor	Not applicable	Flufenacet	FOE Thiadone	Flufenacet
Kinetic model	SFO	SFO	SFO	SFO

As the decline phase was not reached for Trifluoroacetic acid, RMS proposed as estimated kinetic endpoints for that compound **DT₅₀ = 1000 days and DT₉₀ > 1000 days.**

- 2) The results of the kinetic analysis of the data obtained in **Laacherhof AXXa** Loamy sand soil (study by [Hein; 2012a]):

The analysis for this data-set was a two-step analysis. Its results are presented below, individually for each step.

- a) Results obtained at **Step 1** – fitting of the data for the parent compound (Flufenacet) alone:

The results of the kinetic analysis performed by the Applicant are presented below, in graphical form on figure B.8.1.1.2.1.1._CA-32 and in numerical form in the table B.8.1.1.2.1.1._CA-93.

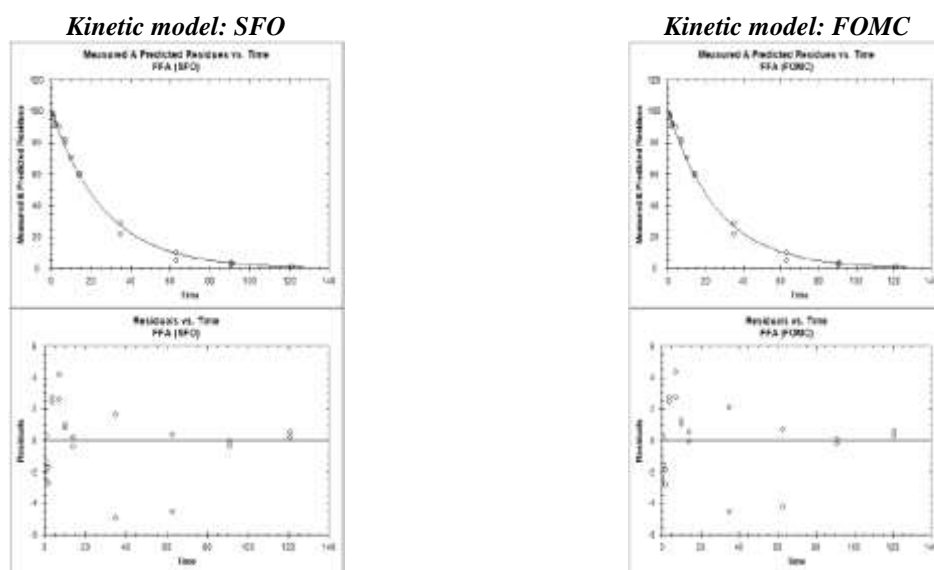


Figure B.8.1.1.2.1.1._CA-32: The graphical results of the kinetic analysis (copied from the study report).

Table B.8.1.1.2.1.1._CA-93: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment ¹⁾
				Lower	Upper			
SFO	M_0	101.30	0.906	99.54	103.09	< 2 E-16	2.578	1.0; Good fit
	k	0.03741	1.141 E-3	0.03517	0.040	< 2 E-16		
FOMC	M_0	101.60	0.899	99.80	103.30	< 2 E-16	2.724	1.0; Good fit
	α	883.4	809.0	-702.1	2469.0	0.144		
	β	23250	21310	-18520	65027.4	0.144		

Footnotes to the table:

- 1) Visual assessment of the kinetic curve as reported by the Applicant.

The Applicant stated that the fit returned by the SFO model was visually and statistically acceptable, therefore it was selected as appropriate and used at the next step to kinetically examine the data for Flufenacet and its degradation products. The analysis using FOMC model did not result in any improvement of the fit and the kinetic parameters were not reliable (the CI values for both α and β passed through zero). As a result the DFOP model was not tested and SFO was indicated as the best-fit model for Flufenacet in this trial. RMS accepted that choice.

The best-fit kinetic endpoints determined for Flufenacet in this kinetic assessment are following: **DT₅₀ = 18.53 days, DT₉₀ = 61.56 days, kinetic model: SFO.**

- b) Results obtained at **Step 2** – fitting of the data for the parent compound (Flufenacet) and its degradation products:

The results of the kinetic analysis performed by the Applicant are presented below, in graphical form on figure B.8.1.1.2.1.1._CA-33 and in numerical form in the table B.8.1.1.2.1.1._CA-94.

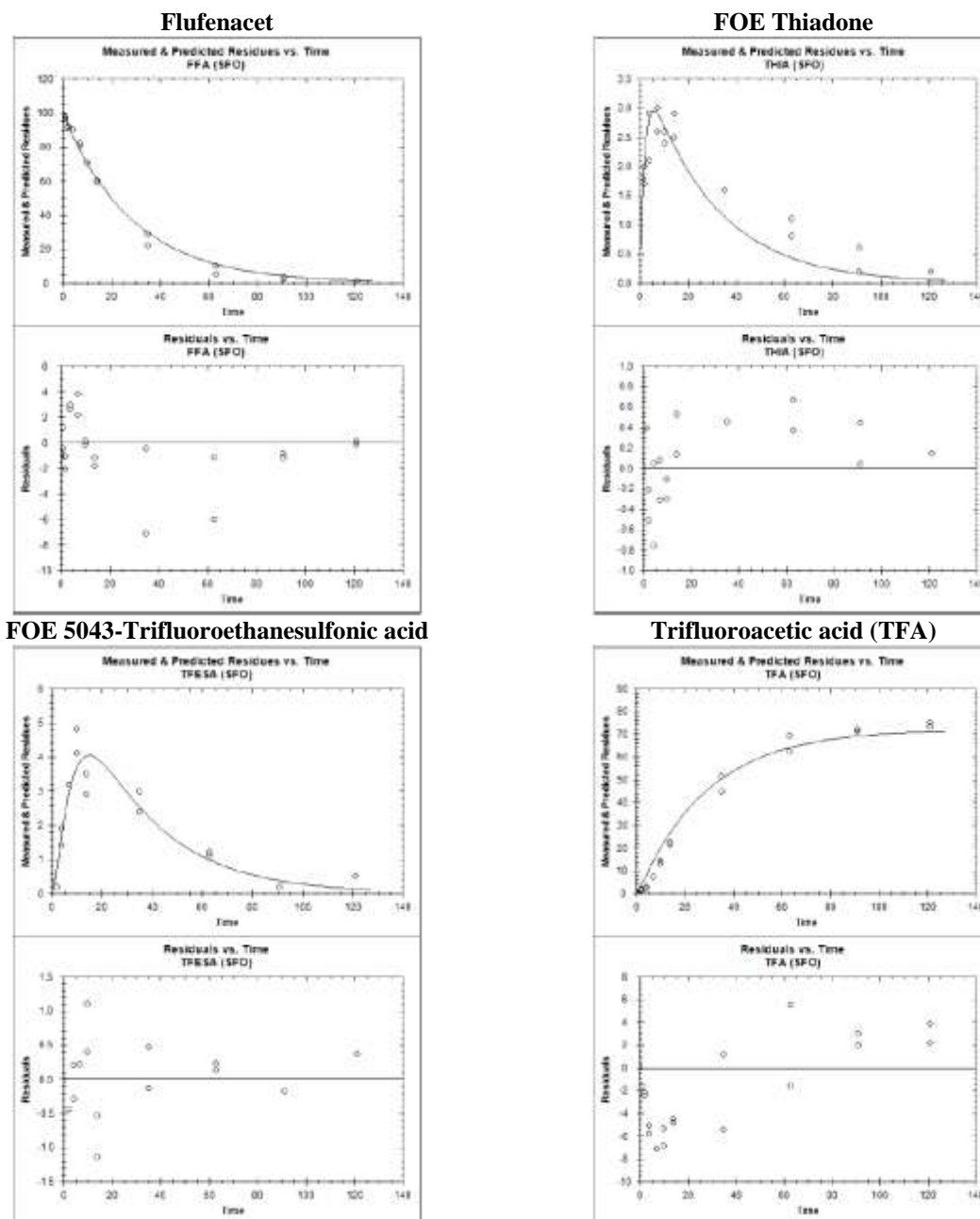


Figure B.8.1.1.2.1.1._CA-33: The graphical results of the kinetic examination of the data for Flufenacet, FOE Thiadone, FOE 5043-Trifluoroethanesulfonic acid and Trifluoroacetic acid obtained in Laacherhof AXXa soil (copied from the study report).

Table B.8.1.1.2.1.1._CA-94: The numerical results of the kinetic examination of the data for Flufenacet, FOE Thiadone, FOE 5043-Trifluoroethanesulfonic acid and Trifluoroacetic acid obtained in Laacherhof AXXa soil.

Compound	Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
			Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment ¹⁾
					Lower	Upper			
Flufenacet	SFO	M ₀	100.10	0.894	98.37	101.871	< 2 E-16	3.092	Good fit
		k	0.03492	9.57 E-4	0.03305	0.037	< 2 E-16		
FOE Thiadone	SFO	M ₀	0.0	----	----	----	----	15.644	Acceptable fit
		k	0.5087	0.0885	0.3354	0.682	8.26 E-8		
		ff	0.524	0.082	----	----	----		
FOE 5043-Trifluoroethane-sulfonic acid	SFO	M ₀	0.0	----	----	----	----	18.252	0.86; Acceptable fit
		k	0.1548	0.0236	0.1086	0.201	2.67 E-9		
		ff	0.534	----	----	----	----		
Trifluoroacetic acid	SFO	M ₀	0.0	----	----	----	----	10.339	Good fit
		k	1.29 E-9	6.58 E-4	-1.29 E-3	0.001	0.5		
		ff ²⁾	0.476	0.118	----	----	----		
		ff ₂ ³⁾	0.466	----	----	----	----		

Footnotes to the table:

- 1) The Applicant provided the R² value and the assessment of the visual fit only for FOE 5043-Trifluoroethanesulfonic acid; for all remaining compounds R² is not reported while the visual assessment is that performed by RMS;
- 2) ff calculated for formation from the parent compound – Flufenacet;
- 3) ff calculated for the formation from FOE Thiadone;

The Applicant stated that in that kinetic analysis it was possible to obtain the reliable trigger kinetic endpoints for FOE 5043-Trifluoroethanesulfonic acid. The determined kinetic parameters reported by the Applicant were following: **DT₅₀ = 4.5 days, DT₉₀ = 14.9 days.**

RMS performed own analysis of the obtained results. It led to the following conclusions:

- It was possible to obtain reliable kinetic fits and kinetic parameters for the following compounds: Flufenacet, FOE Thiadone and FOE 5043-Trifluoroethanesulfonic acid;
- In case of Trifluoroacetic acid the fit is reliable, however of the determined kinetic parameters only the kinetic formation fractions – ff, may be considered reliable. The lack of reliability of the degradation rate constant and resulting from it DT₅₀ and DT₉₀ values is due to the fact that the kinetic curve was in its formation phase and even the would-be maximum was not reached.

The final set of the kinetic parameters considered acceptable by the RMS is presented below in the table B.8.1.1.2.1.1._CA-95.

Table B.8.1.1.2.1.1._CA-95: The reliable set of the kinetic parameters determined in the experiment

Determined parameter	Compound			
	Flufenacet	FOE Thiadone	FOE 5043-Trifluoroethane-sulfonic acid	Trifluoroacetic acid
DT ₅₀ [days]	19.85	1.36	4.48	1000
DT ₉₀ [days]	65.93	4.53	14.87	> 1000
Kinetic formation fraction ff	Not applicable	0.524 ± 0.082	0.534	0.476 ± 0.117
Precursor	Not applicable	Flufenacet	FOE Thiadone	Flufenacet
Kinetic model	SFO	SFO	SFO	SFO

As the decline phase was not reached for Trifluoroacetic acid, RMS proposed as estimated kinetic endpoints for that compound **DT₅₀ = 1000 days and DT₉₀ > 1000 days.**

- 3) The results of the kinetic analysis of the data obtained in **Dollendorf II** Clay loam soil (study by [Hein; 2012a]):

The analysis for this data-set was a three-step analysis. The additional step added was the kinetic examination of the data for FOE 5043-Trifluoroethanesulfonic acid fitted alone using the top-down approach. Its results are presented below, individually for each step.

- a) Results obtained at **Step 1** – fitting of the data for the parent compound (Flufenacet) alone:

The results of the kinetic analysis performed by the Applicant are presented below, in graphical form on figure B.8.1.1.2.1.1_CA-34 and in numerical form in the table B.8.1.1.2.1.1_CA-96.

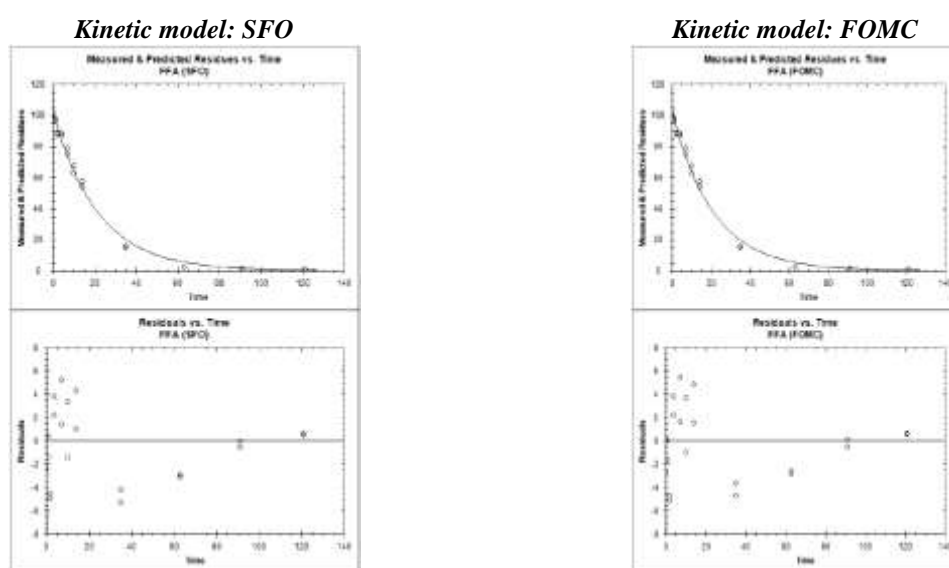


Figure B.8.1.1.2.1.1_CA-34: The graphical results of the kinetic analysis (copied from the study report).

Table B.8.1.1.2.1.1_CA-96: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment ¹⁾
SFO	M_0	102.00	1.277	99.47	104.48	< 2 E-16	4.133	1.0; Good fit
	k	0.04638	1.876 E-3	0.04270	0.050	< 2 E-16		
FOMC	M_0	102.352	1.291	99.822	104.90	< 2 E-16	4.365	1.0; Good fit
	α	481.666	717.865	-925.324	1888.70	0.255		
	β	10165.15	15181.65	-19590.34	39920.60	0.256		

Footnotes to the table:

- 1) Visual assessment of the kinetic curve as reported by the Applicant.

The Applicant stated that the fit returned by the SFO model was visually and statistically acceptable, therefore it was selected as appropriate and used at the next step to kinetically examine the data for Flufenacet and its degradation products. The analysis using FOMC model did not result in any improvement of the fit and the kinetic parameters were not reliable (the CI values for both α and β passed through zero). As a result the DFOP model was not tested and SFO was indicated as the best-fit model for Flufenacet in this trial. RMS accepted that choice.

The best-fit kinetic endpoints determined for Flufenacet in this kinetic assessment are following: **DT₅₀ = 14.95 days, DT₉₀ = 49.65 days, kinetic model: SFO.**

- b) Results obtained at **Step 2** – fitting of the data for the parent compound (Flufenacet) and its degradation products:

The results of the kinetic analysis performed by the Applicant are presented below, in graphical form on figure B.8.1.1.2.1.1._CA-35 and in numerical form in the table B.8.1.1.2.1.1._CA-97.

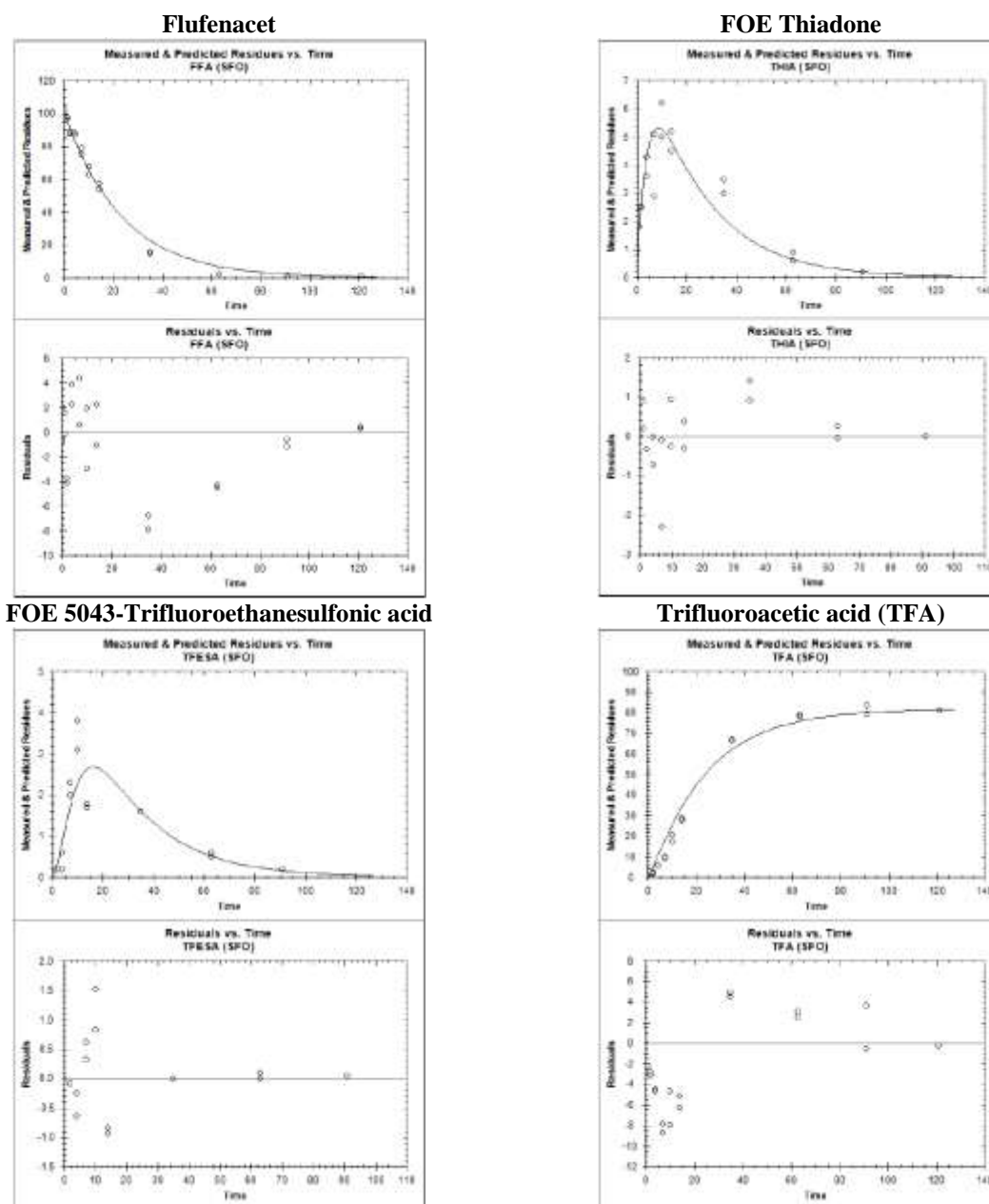


Figure B.8.1.1.2.1.1._CA-35: The graphical results of the kinetic examination of the data for Flufenacet, FOE Thiadone, FOE 5043-Trifluoroethanesulfonic acid and Trifluoroacetic acid obtained in Dollendorf II soil (copied from the study report).

Table B.8.1.1.2.1.1._CA-97: The numerical results of the kinetic examination of the data for Flufenacet, FOE Thiadone, FOE 5043-Trifluoroethanesulfonic acid and Trifluoroacetic acid obtained in Dollendorf II soil.

Compound	Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
			Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment ¹⁾
					Lower	Upper			
Flufenacet	SFO	M ₀	100.30	1.188	97.98	102.643	< 2 E-16	4.665	Good fit
		k	0.0425	1.44 E-3	0.0368	0.045	< 2 E-16		
FOE Thiadone	SFO	M ₀	0.0	----	----	----	----	16.356	Good fit
		k	0.2438	0.04665	0.1523	0.335	7.74 E-7		
		ff	0.438	0.066	----	----	----		
FOE 5043-Trifluoroethanesulfonic acid	SFO	M ₀	0.0	----	----	----	----	35.241	0.74; Poor fit
		k	0.1727	0.0441	0.08624	0.259	9.97 E-5		
		ff	0.422	----	----	----	----		
Trifluoroacetic acid	SFO	M ₀	0.0	----	----	----	----	9.451	Good fit
		k	1.85 E-9	5.95 E-4	-1.17 E-3	0.001	0.4999		
		ff ²⁾	0.562	0.113	----	----	----		
		ff ³⁾	0.578	----	----	----	----		

Footnotes to the table:

- 1) The Applicant provided the R² value and the assessment of the visual fit only for FOE 5043-Trifluoroethanesulfonic acid; for all remaining compounds R² is not reported while the visual assessment is that performed by RMS;
- 2) ff calculated for formation from the parent compound – Flufenacet;
- 3) ff calculated for the formation from FOE Thiadone;

The Applicant stated that using the data from that experiment it was not possible to obtain the reliable trigger kinetic endpoints for FOE 5043-Trifluoroethanesulfonic acid. That was due to the fact that the visual fitting was poor and the χ^2 error high, making the whole fit unreliable. RMS confirms the correctness of that conclusion. As a result the Applicant performed an additional fitting for FOE 5043-Trifluoroethanesulfonic acid alone, using the top-down approach. The results of that analysis are presented below under the letter-point c).

RMS performed own analysis of the obtained results. It led to the following conclusions:

- It was possible to obtain reliable kinetic fits and kinetic parameters for the following compounds: Flufenacet and FOE Thiadone;
- In case of Trifluoroacetic acid the fit is reliable, however of the determined kinetic parameters only the kinetic formation fractions – ff, may be considered reliable. The lack of reliability of the degradation rate constant and resulting from it DT₅₀ and DT₉₀ values is due to the fact that the kinetic curve was in its formation phase and even the would-be maximum was not reached;
- In case of FOE 5043-Trifluoroethanesulfonic acid it was not possible to obtain the reliable kinetic fit. Although the visual inspection showed that fit is acceptable – the Applicant classified it as poor, but RMS is of the opinion that the conformity of the determined kinetic curve and experimental data was not bad, what was also conformed by the value of R², but high level of χ^2 error makes it statistically not reliable. As a result, also calculated kinetic endpoints – DT₅₀ and DT₉₀ values cannot be considered reliable in spite of the fact that the calculated rate constant k is reliable according to the results of the t-test (the prob. > t is well below the level of 0.05). RMS noticed that problems with obtaining the reliable kinetic curve were most probably due to the low concentrations of the compound in this experiment. However, the distribution of the data points implied that the acceptable fit may be obtained when these are fitted alone using the top-down approach.

The set of the kinetic parameters considered acceptable by the RMS is presented below in the table B.8.1.1.2.1.1._CA-98. It shall be noted that in case of FOE 5043-Trifluoroethanesulfonic acid the conclusion is provided only for this fitting exercise and not definitive, as it was superseded by the results of the next fitting step.

Table B.8.1.1.2.1.1._CA-98: The reliable set of the kinetic parameters determined in the experiment

Determined parameter	Compound			
	<i>Flufenacet</i>	<i>FOE Thiadone</i>	<i>FOE 5043-Trifluoroethanesulfonic acid</i>	<i>Trifluoroacetic acid</i>
DT ₅₀ [days]	16.30	2.84	Not determined	1000
DT ₉₀ [days]	54.18	9.45	Not determined	> 1000
Kinetic formation fraction <i>ff</i>	Not applicable	0.438 ± 0.066	0.422	0.562 ± 0.113
Precursor	Not applicable	Flufenacet	FOE Thiadone	Flufenacet
Kinetic model	SFO	SFO	SFO	SFO

As the decline phase was not reached for Trifluoroacetic acid, RMS proposed as estimated kinetic endpoints for that compound **DT₅₀ = 1000 days** and **DT₉₀ > 1000 days**.

- c) Results obtained at **Step 3** for FOE 5043-Trifluoroethanesulfonic acid fitted alone using the top-down approach:

As the last step of the analysis of the data obtained in the experiment on Dollendorf II soil, the data for FOE 5043-Trifluoroethanesulfonic acid were fitted alone using the top-down approach. To do that the Applicant identified the time point at which the maximum concentration of the compound of concern was recorded. That point was used as a starting point in the analysis. The resulting data set used in the fitting exercise is presented below in the table B.8.1.1.2.1.1._CA-99.

Table B.8.1.1.2.1.1._CA-99: The input data for FOE 5043-Trifluoroethanesulfonic acid fitted alone using the top-down approach.

Time Point – DAT [days]	Concentration of FOE 5043-Trifluoroethanesulfonic acid expressed as [%AR]	
	Replicate 1	Replicate 2
10	3.8	3.1
14	1.7	1.8
35	1.6	1.6
63	0.5	0.6
91	0.2	0.2
121	NaN	NaN

The fitting was performed using two kinetic models – SFO and FOMC and followed the procedure outlined above. RMS, having examined the data set used in the fitting stated that the number of data points for which measurable values were available – five (DAT 121 was not taken into account), was sufficient for performing the fitting with a bi-phasic model – FOMC (in such cases the current Guidelines recommend that the minimal number of data points should be five).

The results of the kinetic analysis performed by the Applicant are presented below, in graphical form on figure B.8.1.1.2.1.1._CA-36 and in numerical form in the table B.8.1.1.2.1.1._CA-100.

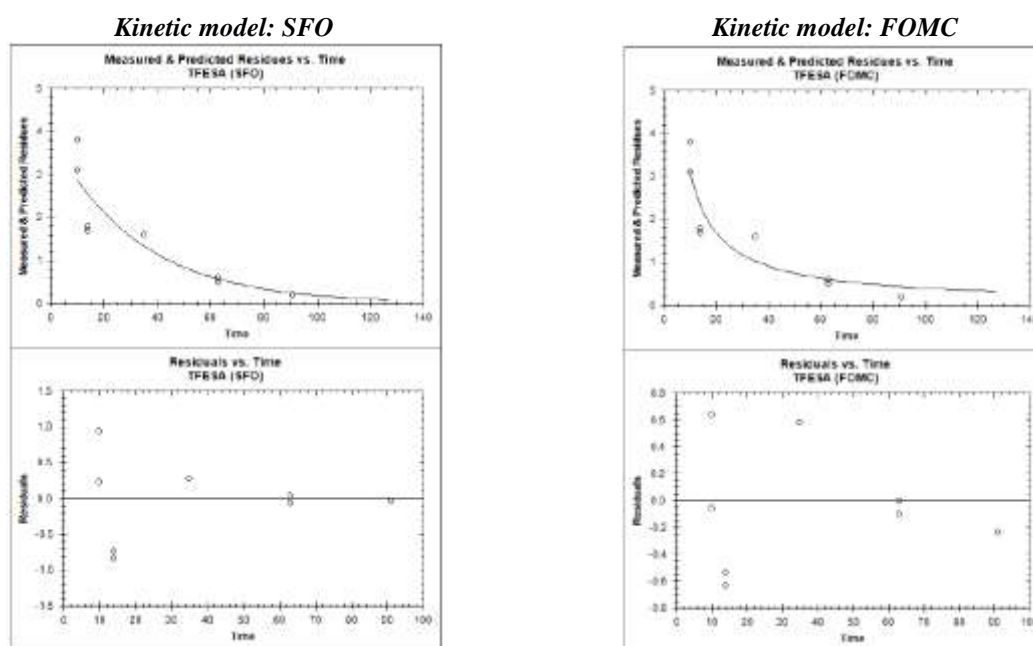


Figure B.8.1.1.2.1.1_CA-36: The graphical results of the kinetic analysis (copied from the study report).

Table B.8.1.1.2.1.1_CA-100: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment ¹⁾
				Lower	Upper			
SFO	M_0	3.911	0.633	2.669	5.152	1.33 E-4	24.06	0.82; Good fit
	k	0.03084	0.00876	0.01368	0.048	0.00391		
FOMC	M_0	542.10	2043.0	-3462.0	4546.13	0.3992	24.44	0.86; Acceptable fit
	α	0.9024	0.1560	0.5966	1.208	3.37 E-4		
	β	0.03352	0.1386	-0.2382	0.305	0.4079		

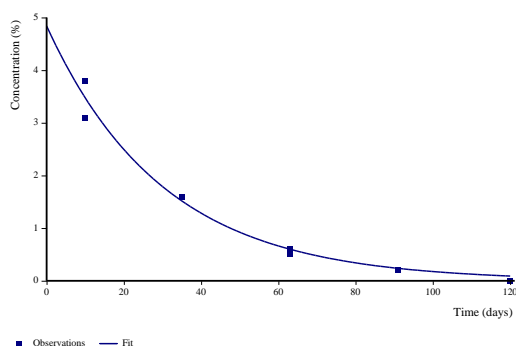
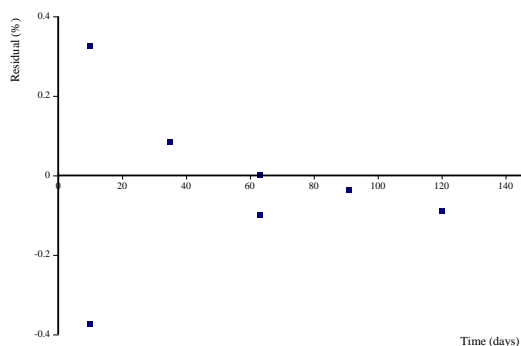
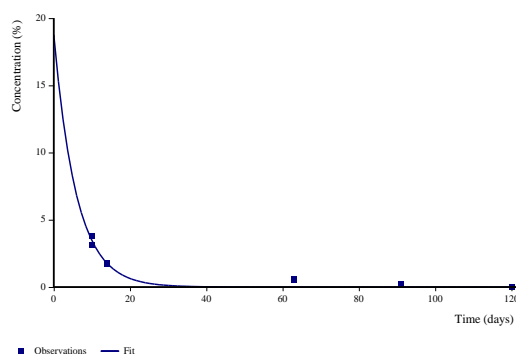
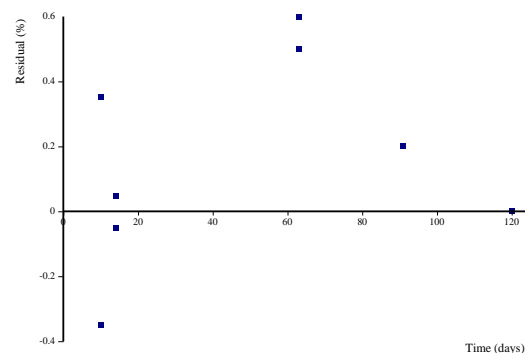
Footnotes to the table:

1) Visual assessment of the kinetic curve as reported by the Applicant.

The Applicant stated that the fit returned by the SFO model was visually and statistically acceptable, therefore it was selected as appropriate to derive the trigger kinetic endpoints for FOE 5043-Trifluoroethanesulfonic acid. The analysis using FOMC model did not result in any improvement of the fit and the kinetic parameters were not reliable (the CI values for β passed through zero and the calculated M_0 bore very high level of uncertainty). As a result the DFOP model was not tested and SFO was indicated as the best-fit model for FOE 5043-Trifluoroethanesulfonic acid in this experiment for the fitted-alone data set. RMS accepted that choice noticing however that although the fit was visually acceptable and the determined rate constant was reliable, statistically it bore significant level of uncertainty.

Examining the determined kinetic curve RMS noticed that one of the data point – either DAT-14 or DAT-35 might an outlier, the removal of which could improve the fit visually and statistically. To verify that hypothesis the additional modelling was performed. The modelling tool used in that exercise was CAKE 3.1, developed by Tessella. The optimisation was performed using IRLS (Iteratively Reweighed Nonlinear Least Squares) algorithm.

The results of the kinetic analysis performed by the RMS are presented below, in graphical form on figure B.8.1.1.2.1.1_CA-37 and in numerical form in the table B.8.1.1.2.1.1_CA-101.

Kinetic model: SFO, DAT-14 time point omitted**Graphical Summary:****Observations and Fitted Model:****Residuals:****Kinetic model: SFO, DAT-35 time point omitted****Graphical Summary:****Observations and Fitted Model:****Residuals:****Figure B.8.1.2.1.1._CA-37:** The graphical results of the kinetic analysis.**Table B.8.1.2.1.1._CA-101:** The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment
				Lower	Upper			
SFO, DAT-14 removed	M_0	4.838	0.265	4.228	5.449	----	4.31	0.983; Good fit
	k	0.03315	0.00271	0.0296	0.039	9.28 E-7		
SFO, DAT-35 removed	M_0	18.76	7.959	0.408	37.12	----	17.6	0.965; Good fit
	k	0.1694	0.0388	0.0799	0.259	0.001194		

The calculated kinetic endpoints were following:

- for the fit with DAT-14 time point omitted: $DT_{50} = 20.9$ days, $DT_{90} = 69.5$ days;
- for the fit with DAT-35 time point omitted: $DT_{50} = 4.09$ days, $DT_{90} = 13.6$.

The obtained results of the fitting indicate that the DAT-14 time point may be considered an outlier and as such removed from data set. The results obtained for that variant were much better, in both visual inspection of the fit and statistical term, than those with DAT-35 time point removed from the data set. It was also noted that both estimated parameters, and M_0 in particular, were much more reliable for the data set with DAT-14 data point removed.

Additionally the RMS performed the fitting with the initial time point – DAT-10, omitted. However, that did not result in any significant improvement, on the contrary the obtained fit was worst of the three. RMS decided not to present these results.

On the basis of the evaluation presented above it may be stated that for FOE 5043-Trifluoroethanesulfonic acid it was possible to obtain the reliable kinetic fit using the data set presented in the table

B.8.1.1.2.1.1._CA-99, modified by the removal of the results for the DAT-14 time point identified as an outlier. It is possible that similar results would be obtained for the same compound fitted in the whole data set once that time point had been removed, but that hypothesis was not verified by the RMS.

The resulting set of the trigger endpoints for FOE 5043-trifluoroethanesulfonic acid is therefore following: **DT₅₀ = 20.9 days, DT₉₀ = 69.5 days**, kinetic model: **SFO**.

Final conclusion:

The final set of the trigger kinetic endpoints resulting from that experiment is presented below in the table B.8.1.1.2.1.1._CA-102.

Table B.8.1.1.2.1.1._CA-102: The reliable set of the kinetic parameters determined in the experiment

Determined parameter	Compound				
	<i>Flufenacet</i>	<i>FOE Thiadone</i>	<i>FOE 5043-Trifluoroethane-sulfonic acid</i>	<i>Trifluoroacetic acid</i>	
DT ₅₀ [days]	16.30	2.84	20.9	1000	
DT ₉₀ [days]	54.18	9.45	69.5	> 1000	
Kinetic formation fraction <i>ff</i>	Not applicable	0.438 ± 0.066	0.422	0.562 ± 0.113	0.578
Precursor	Not applicable	Flufenacet	FOE Thiadone	Flufenacet	FOE Thiadone
Kinetic model	SFO	SFO	SFO	SFO	

As the decline phase was not reached for Trifluoroacetic acid, RMS proposed as estimated kinetic endpoints for that compound **DT₅₀ 1000 days** and **DT₉₀ > 1000 days**.

- 4) The results of the kinetic analysis of the data obtained in **Laacherhof Wurmwiese** Loam soil (study by [Hein; 2012a]):

The analysis for this data-set was a three-step analysis. The additional step added was the kinetic examination of the data for FOE 5043-Trifluoroethanesulfonic acid fitted alone using the top-down approach. Its results are presented below, individually for each step.

- a) Results obtained at **Step 1** – fitting of the data for the parent compound (Flufenacet) alone:

The results of the kinetic analysis performed by the Applicant are presented below, in graphical form on figure B.8.1.1.2.1.1._CA-38 and in numerical form in the table B.8.1.1.2.1.1._CA-103.

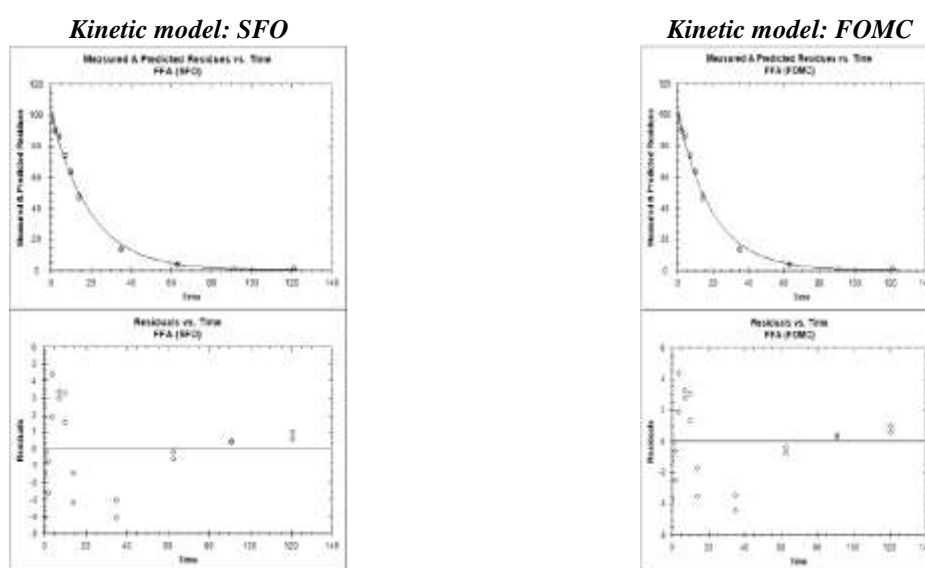


Figure B.8.1.1.2.1.1._CA-38: The graphical results of the kinetic analysis (copied from the study report).

Table B.8.1.1.2.1.1._CA-103: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment ¹⁾
				Lower	Upper			
SFO	M_0	102.10	1.032	100.10	104.137	< 2 E-16	3.436	1.0; Good fit
	k	0.05144	1.64 E-3	0.0482	0.055	< 2 E-16		
FOMC	M_0	101.886	0.995	99.936	103.8	< 2 E-16	3.612	1.0; Good fit
	α	729.806	893.260	-1020.951	2480.6	0.212		
	β	14354.096	17570.073	-20082.62	48790.80	0.144		

Footnotes to the table:

- 1) Visual assessment of the kinetic curve as reported by the Applicant.

The Applicant stated that the fit returned by the SFO model was visually and statistically acceptable, therefore it was selected as appropriate and used at the next step to kinetically examine the data for Flufenacet and its degradation products. The analysis using FOMC model did not result in any improvement of the fit and the kinetic parameters were not reliable (the CI values for both α and β passed through zero). As a result the DFOP model was not tested and SFO was indicated as the best-fit model for Flufenacet in this trial. RMS accepted that choice.

The best-fit kinetic endpoints determined for Flufenacet in this kinetic assessment are following: **DT₅₀ = 13.47 days, DT₉₀ = 44.76 days, kinetic model: SFO.**

- b) Results obtained at **Step 2** – fitting of the data for the parent compound (Flufenacet) and its degradation products:

The results of the kinetic analysis performed by the Applicant are presented below, in graphical form on figure B.8.1.1.2.1.1._CA-39 and in numerical form in the table B.8.1.1.2.1.1._CA-104.

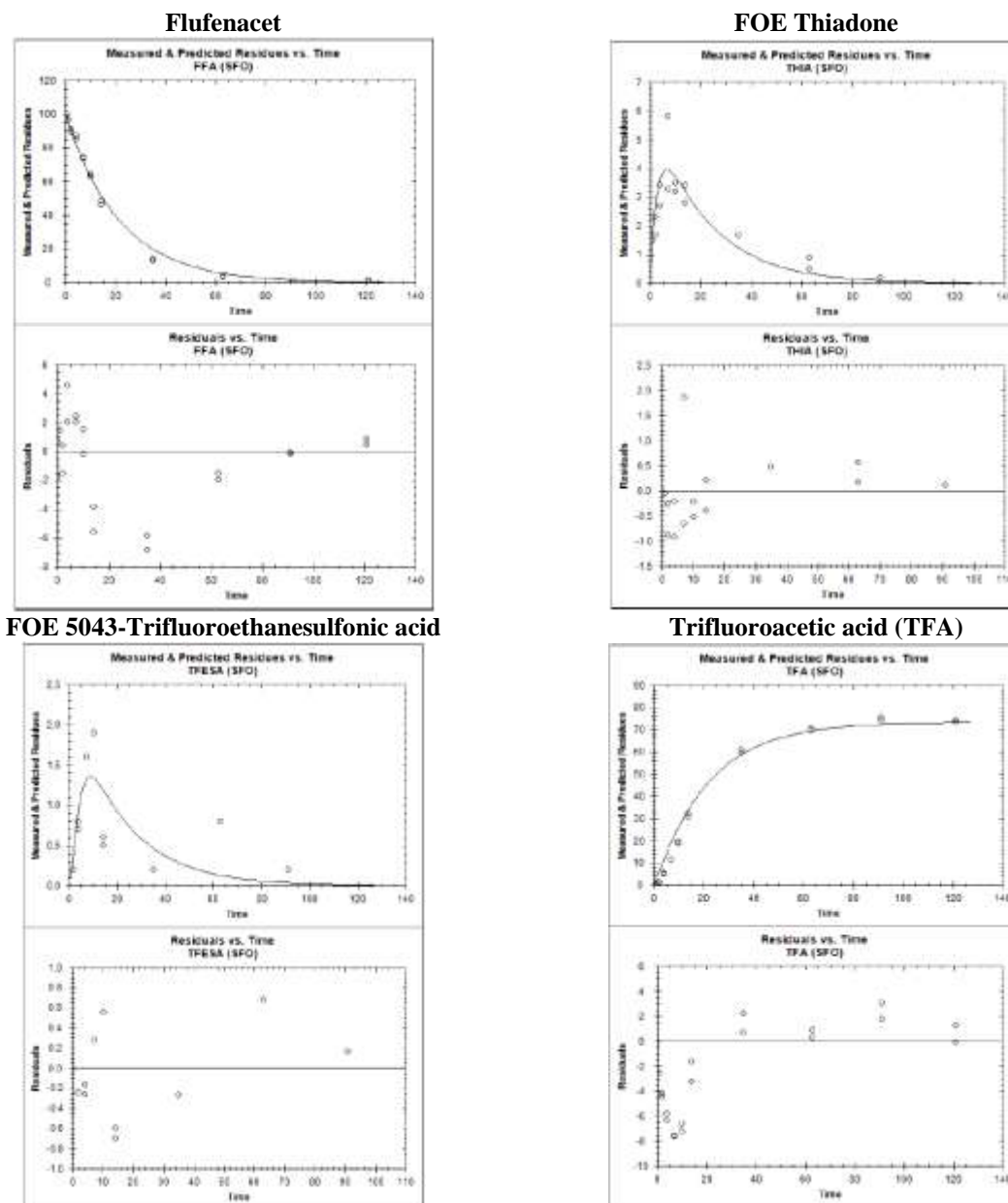


Figure B.8.1.1.2.1.1._CA-39: The graphical results of the kinetic examination of the data for Flufenacet, FOE Thiadone, FOE 5043-Trifluoroethanesulfonic acid and Trifluoroacetic acid obtained in Laacherhof Wurmwiese soil (copied from the study report).

Table B.8.1.1.2.1.1._CA-104: The numerical results of the kinetic examination of the data for Flufenacet, FOE Thiadone, FOE 5043-Trifluoroethanesulfonic acid and Trifluoroacetic acid obtained in Laacherhof Wurmwise soil.

Compound	Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
			Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment ¹⁾
					Lower	Upper			
Flufenacet	SFO	M ₀	99.88	1.180	97.57	102.194	< 2 E-16	4.269	Good fit
		k	0.04648	1.67 E-3	0.04321	0.050	< 2 E-16		
FOE Thiadone	SFO	M ₀	0.0	----	----	----	----	14.731	Acceptable fit
		k	0.3490	0.0569	0.2376	0.460	1.96 E-8		
		ff	0.405	0.056	----	----	----		
FOE 5043-Trifluoroethane-sulfonic acid	SFO	M ₀	0.0	----	----	----	----	43.983	0.86; Acceptable fit
		k	0.6478	0.1406	0.3722	0.923	8.48 E-6		
		ff	0.655	----	----	----	----		
Trifluoroacetic acid	SFO	M ₀	0.0	----	----	----	----	9.436	Good fit
		k	4.73 E-9	7.12 E-4	-1.40 E-3	0.001	0.5		
		ff ²⁾	0.596	0.149	----	----	----		
		ff ₂ ³⁾	0.345	----	----	----	----		

Footnotes to the table:

- 1) The Applicant provided the R² value and the assessment of the visual fit only for FOE 5043-Trifluoroethanesulfonic acid; for all remaining compounds R² is not reported while the visual assessment is that performed by RMS;
- 2) ff calculated for formation from the parent compound – Flufenacet;
- 3) ff calculated for the formation from FOE Thiadone;

The Applicant stated that using the data from that experiment it was not possible to obtain the reliable trigger kinetic endpoints for FOE 5043-Trifluoroethanesulfonic acid. That was due to the fact that the visual fitting was poor and the χ^2 error high, making the whole fit unreliable. RMS confirms the correctness of that conclusion. As a result the Applicant performed an additional fitting, for FOE 5043-Trifluoroethanesulfonic acid fitted alone using the top-down approach. The results of that analysis are presented below under the letter-point c).

RMS performed own analysis of the obtained results. It led to the following conclusions:

- It was possible to obtain reliable kinetic fits and kinetic parameters for the following compounds: Flufenacet and FOE Thiadone;
- In case of Trifluoroacetic acid the fit is reliable, however of the determined kinetic parameters only the kinetic formation fractions – ff, may be considered reliable. The lack of reliability of the degradation rate constant and resulting from it DT₅₀ and DT₉₀ values is due to the fact that the kinetic curve was in its formation phase and even the would-be maximum was not reached;
- In case of FOE 5043-Trifluoroethanesulfonic acid it was not possible to obtain the reliable kinetic fit. RMS confirms the Applicant's statement in that area noticing that not only the fit was statistically not acceptable due to the high level of χ^2 error, but also visually – the plotted kinetic curve poorly reproduced the distribution of the experimental points. RMS noticed also that within the decline phase a second local maximum occurred on DAT 63. It is possible that that time point was an outlier. It shall be also noted that the measured value was obtained only for one replicate, while the second was a value < LOD. Therefore that value should probably be removed as an outlier and the last measurable values (½ LOD) should be set for the preceding time point – DAT 35, cutting the subsequent time points off.

RMS did additional kinetic fitting using the modified data set for FOE 5043-Trifluoroethanesulfonic acid to verify the hypothesis presented above. However, even with that modified data set it was not possible to obtain the reliable kinetic fit for that compound, most probably because of the very low concentrations of the compound of concern. RMS decided not to present the results of that fitting in order not to overburden the Report.

The set of the kinetic parameters considered acceptable by the RMS is presented below in the table B.8.1.1.2.1.1._CA-105. It shall be noted that in case of FOE 5043-Trifluoroethanesulfonic acid the conclusion is provided only for this fitting exercise and not definitive, as it was superseded by the results of the next fitting step.

Table B.8.1.1.2.1.1._CA-105: The reliable set of the kinetic parameters determined in the experiment

Determined parameter	Compound			
	<i>Flufenacet</i>	<i>FOE Thiadone</i>	<i>FOE 5043-Trifluoroethanesulfonic acid</i>	<i>Trifluoroacetic acid</i>
DT ₅₀ [days]	14.91	1.99	Not determined	1000
DT ₉₀ [days]	49.54	6.60	Not determined	> 1000
Kinetic formation fraction <i>ff</i>	Not applicable	0.404 ± 0.056	0.655	0.596 ± 0.149 0.345
Precursor	Not applicable	Flufenacet	FOE Thiadone	Flufenacet FOE Thiadone
Kinetic model	SFO	SFO	SFO	SFO

As the decline phase was not reached for Trifluoroacetic acid, RMS proposed as estimated kinetic endpoints for that compound **DT₅₀ = 1000 days** and **DT₉₀ > 1000 days**.

- c) Results obtained at **Step 3** for FOE 5043 Trifluoroethanesulfonic acid fitted alone using the top-down approach:

As the last step of the analysis of the data obtained in the experiment on Laacherhof Wurmwielse soil, the data for FOE 5043-Trifluoroethanesulfonic acid were fitted alone using the top-down approach. To do that the Applicant identified the time point at which the maximum concentration of the compound of concern was recorded. That point was used as a starting point in the analysis. The resulting data set used in the fitting exercise is presented below in the table B.8.1.1.2.1.1._CA-106.

Table B.8.1.1.2.1.1._CA-106: The input data for FOE 5043-Trifluoroethanesulfonic acid fitted alone using the top-down approach.

Time Point – DAT [days]	Concentration of FOE 5043-Trifluoroethanesulfonic acid expressed as [%AR]	
	Replicate 1	Replicate 2
10	1.9	1.9
14	0.5	0.6
35	0.2	0.2
63	0.8	NaN
91	0.2	NaN
121	NaN	NaN

The fitting was performed using two kinetic models – SFO and FOMC and followed the procedure outlined above. RMS, having examined the data set used in the fitting stated that the number of data points for which measurable values were available – five (DAT 121 was not taken into account), was sufficient for performing the fitting with a bi-phasic model – FOMC (in such cases the current Guidelines recommend that the minimal number of data points should be five).

The results of the kinetic analysis performed by the Applicant are presented below, in graphical form on figure B.8.1.1.2.1.1._CA-40 and in numerical form in the table B.8.1.1.2.1.1._CA-109.

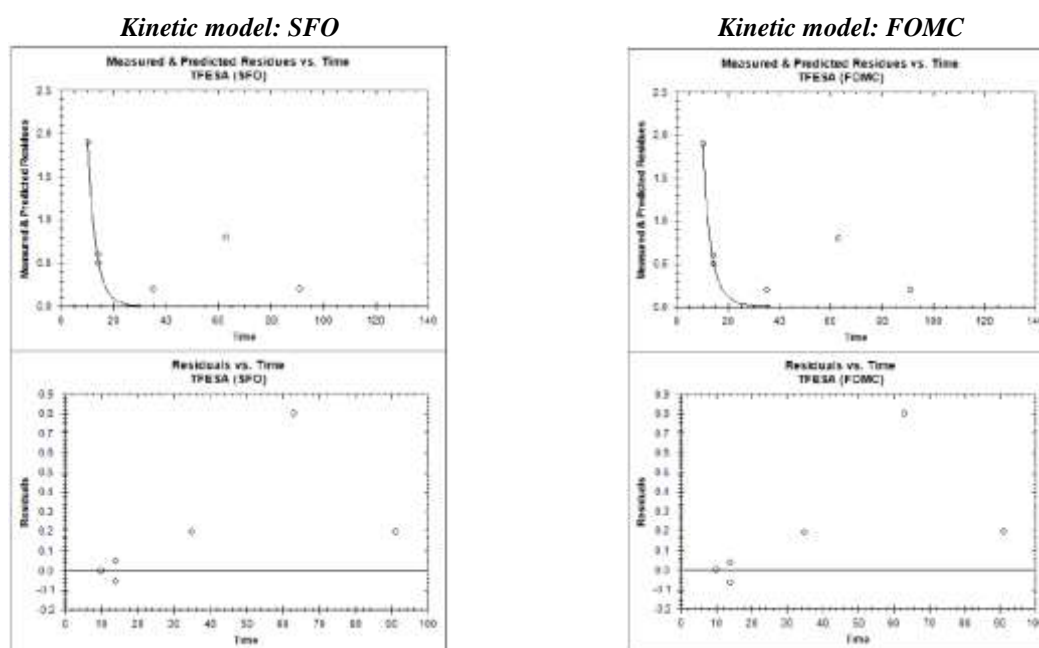


Figure B.8.1.1.2.1.1_CA-40: The graphical results of the kinetic analysis (copied from the study report).

Table B.8.1.1.2.1.1_CA-107: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment ¹⁾
				Lower	Upper			
SFO	M_0	41.726	49.146	-54.598	138.050	0.2142	41.57	0.90; Poor fit
	k	0.30895	0.1140	0.08545	0.532	0.0176		
FOMC	M_0	95.473	99.078	-98.717	289.66	0.190	47.42	0.90; Poor fit
	α	9.912	10.381	-10.434	30.26	0.192		
	β	20.624	19.913	-18.405	59.65	0.174		

Footnotes to the table:

1) Visual assessment of the kinetic curve as reported by the Applicant.

The Applicant stated that neither SFO nor FOMC returned visually and statistically acceptable. As a result it was stated that it was not possible to obtain reliable kinetic endpoints for FOE 5043-Trifluoroethanesulfonic acid fitted alone using the top-down approach.

RMS however, analysing the data set for FOE 5043-Trifluoroethanesulfonic acid noticed that the problem was possibly related to the occurrence of the second maximum observed on DAT 63. The measurable concentration was determined at that time point only for one replicate, what may indicate that in fact that value is an outlier. Therefore RMS decided to repeat the fitting removing that value and all subsequent data points. In order to have the minimal required amount of data points – four, RMS decided to use the DAT 63 as the last time point with the concentrations of the compound of concern set to zero. The resulting modified data set used in that fitting is presented below in the table B.8.1.1.2.1.1_CA-108.

Table B.8.1.1.2.1.1_CA-108: The modified input data for FOE 5043-Trifluoroethanesulfonic acid used in the repeated kinetic analysis performed by the RMS using the top-down approach.

Time Point – DAT [days]	Concentration of FOE 5043-Trifluoroethanesulfonic acid expressed as [%AR]	
	Replicate 1	Replicate 2
10	1.9	1.9
14	0.5	0.6
35	0.2	0.2
63	0.0	0.0

The kinetic analysis was performed using CAKE 3.1, developed by Tessella, as a modelling tool. The optimisation was performed using IRLS (Iteratively Reweighed Nonlinear Least Squares) algorithm. Because of the limited number of the data points – only four were available, solely the SFO model was tested.

The results of the kinetic analysis performed by the RMS are presented below, in graphical form on figure B.8.1.1.2.1.1._CA-41 and in numerical form in the table B.8.1.1.2.1.1._CA-109.

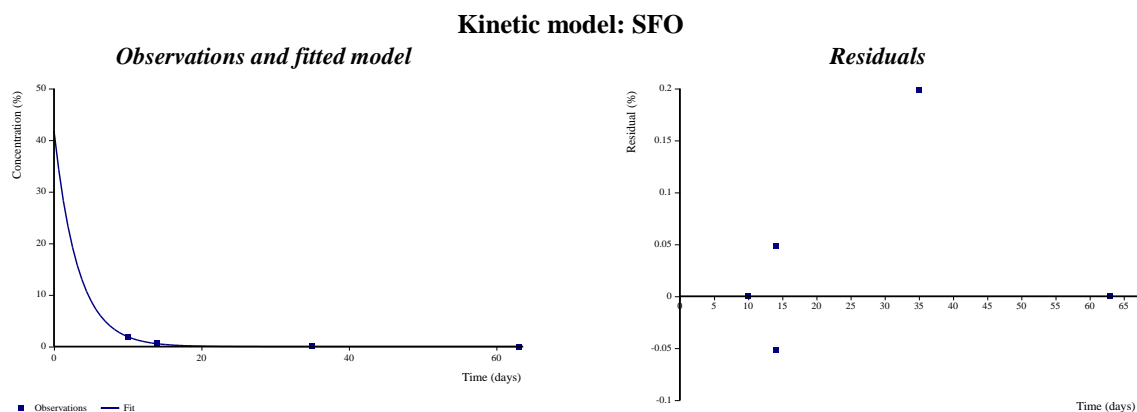


Figure B.8.1.1.2.1.1._CA-41: The graphical results of the kinetic analysis.

Table B.8.1.1.2.1.1._CA-109: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment
				Lower	Upper			
SFO	M_0	41.75	17.11	-0.1286	83.62	----	12.3	0.988; Good fit
	k	0.309	0.03954	0.2122	0.406	1.16 E-4		

The calculated kinetic endpoints were following: **DT₅₀ = 2.24 days, DT₉₀ = 7.45 days;**

The obtained results of the fitting indicate that with the elimination of the measurable value for DAT-63 time point it was possible to obtain visually good and statistically reliable fit using the SFO kinetic model. It shall be noted that the kinetic curve bears a considerable level of uncertainty with regard to the estimated M_0 value, but on the other hand that value is close to the determined kinetic formation fraction ff . That taken into account, it may be stated that the kinetic curve may be considered as a good estimation of the kinetic behaviour of FOE 5043-Trifluoroethanesulfonic acid in the test soil, therefore the fit and derived from it kinetic endpoints may be considered reliable.

The resulting set of the trigger endpoints for FOE 5043-Trifluoroethanesulfonic acid is therefore following: **DT₅₀ = 2.24 days, DT₉₀ = 7.45 days, kinetic model: SFO.**

Final conclusion:

The final set of the trigger kinetic endpoints resulting from that experiment is presented below in the table B.8.1.1.2.1.1._CA-110.

Table B.8.1.1.2.1.1._CA-110: The reliable set of the kinetic parameters determined in the experiment

Determined parameter	Compound				
	Flufenacet	FOE Thiadone	FOE 5043-Trifluoroethane-sulfonic acid	Trifluoroacetic acid	
DT ₅₀ [days]	14.91	1.99	2.24	1000	
DT ₉₀ [days]	49.54	6.60	7.45	> 1000	
Kinetic formation fraction <i>ff</i>	Not applicable	0.404 ± 0.056	0.655	0.596 ± 0.149	0.345
Precursor	Not applicable	Flufenacet	FOE Thiadone	Flufenacet	FOE Thiadone
Kinetic model	SFO	SFO	SFO	SFO	

As the decline phase was not reached for Trifluoroacetic acid, RMS proposed as estimated kinetic endpoints for that compound **DT₅₀ 1000 days** and **DT₉₀ > 1000 days**.

Final conclusion of the study:

On the basis of the results of the kinetic evaluation presented above it was possible to derive the definitive sets of the trigger kinetic endpoints for each evaluated compounds. These are presented below in the table B.8.1.1.2.1.1._CA-111.

Table B.8.1.1.2.1.1._CA-111: The final set of reliable kinetic endpoints determined in the study.

Study	Test soil	Compound	Determined parameter				
			Kinetic model	Rate constant <i>k</i>	DT ₅₀ [days]	DT ₉₀ [days]	Kinetic formation fraction <i>ff</i>
Hein; 2012	Hoefchen am Hohenseh 4a	Flufenacet	SFO	0.04377	15.84	52.61	Not applicable
		FOE Thiadone	SFO	0.6111	1.34	3.77	0.913
		FOE 5043-Trifluoroethane-sulfonic acid	SFO	0.07617	9.10	30.23	0.264
		Trifluoroacetic acid	SFO	<i>n. d.</i> ¹⁾	1000	> 1000	0.087 ²⁾ 0.736 ³⁾
Hein 2012a	Laacherhof AXXa	Flufenacet	SFO	0.03492	19.85	65.93	Not applicable
		FOE Thiadone	SFO	0.5087	1.36	4.53	0.524
		FOE 5043-Trifluoroethane-sulfonic acid	SFO	0.1548	4.48	14.87	0.534
		Trifluoroacetic acid	SFO	<i>n. d.</i> ¹⁾	1000	> 1000	0.476 ²⁾ 0.466 ³⁾
	Dollendorf II	Flufenacet	SFO	0.0425	16.30	54.18	Not applicable
		FOE Thiadone	SFO	0.2438	2.84	9.45	0.438
		FOE 5043-Trifluoroethane-sulfonic acid	SFO – top-down approach	0.03315	20.9	69.5	0.422
		Trifluoroacetic acid	SFO	<i>n. d.</i> ¹⁾	1000	> 1000	0.562 ²⁾ 0.578 ³⁾
	Laacherhof Wurmweise	Flufenacet	SFO	0.04648	14.91	49.54	Not applicable
		FOE Thiadone	SFO	0.3490	1.99	6.60	0.404
		FOE 5043-Trifluoroethane-sulfonic acid	SFO – top-down approach	0.309	2.24	7.45	0.655
		Trifluoroacetic acid	SFO	<i>n. d.</i> ¹⁾	1000	> 1000	0.596 ²⁾ 0.345 ³⁾

Footnotes to the table:

- 1) The reliable value was not determined – the estimate provided by the model cannot be considered such;
- 2) For formation from parent compound – Flufenacet;
- 3) For formation from FOE Thiadone.

Study 7:

Report: Reinken G., Partsch S., (2014): “Kinetic Evaluation of [thiadiazole-5-¹⁴C] flufenacet and its Degradation Products under Aerobic Conditions in Laboratory According to FOCUS Kinetics Using the KinGUI 2 Tool. Flufenacet (FOE 5043), FOE-thiadone, FOE 5043-trifluoroethane sulfonic acid, Trifluoroacetic acid.”; Bayer Crop Science AG, Environmental Safety, Alfred-Nobel-Strasse 50, 40789 Monheim, Germany; unpublished Study Report No. En-Sa-12-0577; 2014. 02; study reference number: M-477835-01-1;.

Guidelines: The study was declared to be performed to comply with the following guidelines:

- FOCUS (2006): “Guidance Document on Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration.” Report of the FOCUS Work Group on Degradation Kinetics, EC Document Reference SANCO/10058/2005 version 2.0, 434 pp.;
- FOCUS (2011): “Generic guidance for Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration”, version 1.0 (issued on 23 November 2011).

GLP: No, not applicable – this is a modelling study;

RMS comments: RMS verified the study for its compliance with the provisions of the Guidelines listed above. It was stated that the study generally complied with the two evoked Guidance Documents. It was also noted that it was aimed on the derivation of the kinetic endpoints to be used in modelling. Therefore the best-fit model for Flufenacet was not identified, also because that was done in the **Study 6** summarised above. Instead the SFO model was generally indicated as returning acceptable fit for parent compound – Flufenacet. Also the first step of the evaluation – verification of the acceptability of SFO fit for Flufenacet fitted alone, was not performed, as that has been done in three previous studies. As a result, when the data for parent and metabolites were kinetically examined only the combination SFO-SFO was tested, unless the top-down approach was used for any of the degradation products. RMS summarising the study used the soil names as they were provided in the source study reports (in the study report they were slightly altered) to maintain the internal coherence of the document.

Summary:

The aim of the study was to kinetically examine the data obtained in the experiments in which [Thiadiazole-5-¹⁴C] Flufenacet was used. That was done in order to derive the kinetic parameters suitable for modelling and environmental risk assessment.

The data were taken from the following studies: [Hein; 2012] – a route- and rate-of-degradation study, summarised under the point B.8.1.1.1.1.as **Study 5** and under this point as **Study 4**, and [Hein; 2012a] – a route- and rate-of-degradation study, summarised under the point B.8.1.1.1.1.as **Study 6** and under this point as **Study 5**. The characteristic of the test soils used in each of these experiments was presented above in the summaries of the **Study 4** and **Study 5**, therefore to not overburden unnecessarily the Assessment Report, RMS decided not to present these data. The experimental conditions used in each experiment are summarised below in the table B.8.1.1.2.1.1._CA-112.

Table B.8.1.1.2.1.1._CA-112: The experimental conditions used in each experiment.

Study	Test soil		Incubation temperature <i>T</i> [°C]	Experimental conditions		
	Name	Type (USDA classification)		Soil moisture		
				In experiment	Reference value	
					MWHC [%]	FC at pF 2.0 [%]
<i>Hein; 2012</i>	Hoefchen Am Hohenseh 4a	Silt loam	19.7 ± 0.1	55% MWHC	61.1	29.8
<i>Hein; 2012a</i>	Laaherhof AXXa	Loamy sand	19.9 ± 0.2	55% MWHC	49.1	18.7
	Dollendorf II	Clay loam	19.9 ± 0.2	55% MWHC	79.8	46.0
	Laacherhof Wurmweise	Loam	19.9 ± 0.2	55% MWHC	59.9	23.3

The not processed input data used in the kinetic analysis are presented below in the table B.8.1.1.2.1.1._CA-113. Additionally, in the table B.8.1.1.2.1.1._CA-114 are presented the DAT-0 total recovery and LOD values, subsequently used in data processing.

Table B.8.1.1.2.1.1_CA-113: The non-processed data obtained in the test soils used as input in kinetic analysis.

The data obtained in Hoefchen Am Hohenseh 4a Silt loam soil (study by [Hein; 2012]):								
Time Point – DAT [days]	Concentration, expressed as [% AR], of:							
	<i>Flufenacet</i>		<i>FOE Thiadone</i>		<i>FOE 5043-Trifluoroethane-sulfonic acid</i>		<i>Trifluoroacetic acid (TFA)</i>	
	Replic. 1	Replic. 2	Replic. 1	Replic. 2	Replic. 1	Replic. 2	Replic. 1	Replic. 2
0	99.1	100.4	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
2	93.3	91.2	3.5	3.4	0.8	1.1	1.2	1.2
4	87.4	88.3	4.5	4.6	2.4	2.3	3.9	3.5
7	74.8	76.3	5.2	5.9	4.1	4.4	9.2	10.1
10	61.8	66.3	6.0	5.5	5.5	5.3	17.4	16.0
14	52.8	56.8	3.6	3.2	6.1	5.9	25.4	24.8
35	13.4	14.2	1.7	1.5	4.8	5.0	61.2	61.0
60	4.1	3.4	0.6	0.6	2.5	2.7	71.7	74.3
87	1.7	1.6	< LOD	< LOD	< LOD	0.6	76.6	78.8
120	0.9	0.9	< LOD	< LOD	< LOD	< LOD	77.7	77.5
The data obtained in Laacherhof AXXa Loamy sand soil (study by [Hein; 2012a]):								
Time Point – DAT ¹⁾ [days]	Concentration, expressed as [% AR], of:							
	<i>Flufenacet</i>		<i>FOE Thiadone</i>		<i>FOE 5043-Trifluoroethane-sulfonic acid</i>		<i>Trifluoroacetic acid (TFA)</i>	
	Replic. 1	Replic. 2	Replic. 1	Replic. 2	Replic. 1	Replic. 2	Replic. 1	Replic. 2
0	98.9	98.5	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
1	97.9	96.2	1.8	1.8	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
2	92.3	91.3	1.7	2.0	n. d. ¹⁾	n. d. ¹⁾	1.4	1.7
4	89.7	90.0	2.9	2.1	1.4	1.9	2.3	3.0
7	80.6	82.2	2.6	3.0	3.2	3.2	7.2	7.2
10	70.7	70.5	2.4	2.6	4.1	4.8	13.1	14.6
14	60.2	59.6	2.9	2.5	2.9	3.5	21.9	22.3
35	29.0	22.4	1.6	1.6	2.4	3.0	44.9	51.5
63	5.1	10.0	0.8	1.1	1.1	1.2	69.4	62.3
91	3.0	3.3	0.6	n. d. ¹⁾	< LOD	< LOD	71.0	72.0
121	1.6	1.3	< LOD	< LOD	0.5	0.5	74.9	73.2
The data obtained in Dollendorf II Clay loam soil (study by [Hein; 2012a]):								
Time Point – DAT ¹⁾ [days]	Concentration, expressed as [% AR], of:							
	<i>Flufenacet</i>		<i>FOE Thiadone</i>		<i>FOE 5043-Trifluoroethane-sulfonic acid</i>		<i>Trifluoroacetic acid (TFA)</i>	
	Replic. 1	Replic. 2	Replic. 1	Replic. 2	Replic. 1	Replic. 2	Replic. 1	Replic. 2
0	101.2	98.6	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
1	97.7	96.0	1.8	2.5	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
2	88.0	88.4	2.5	2.5	n. d. ¹⁾	n. d. ¹⁾	1.9	2.2
4	86.9	88.5	4.3	3.6	0.6	< LOD	5.6	5.8
7	75.1	78.9	5.1	2.9	2.3	2.0	10.1	9.3
10	62.7	67.5	6.2	5.0	3.8	3.1	20.6	17.3
14	57.6	54.3	4.5	5.2	1.7	1.8	27.6	28.7
35	15.9	14.8	3.5	3.0	1.6	1.6	67.0	66.6
63	2.4	2.6	0.6	0.9	0.5	0.6	78.8	78.3
91	0.9	1.5	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	79.4	83.6
121	1.0	0.9	n. d. ¹⁾	n. d. ¹⁾	< LOD	< LOD	81.0	81.0
The data obtained in Laacherhof Wurmwiase Loam soil (study by [Hein; 2012a]):								
Time Point – DAT ¹⁾ [days]	Concentration, expressed as [% AR], of:							
	<i>Flufenacet</i>		<i>FOE Thiadone</i>		<i>FOE 5043-Trifluoroethane-sulfonic acid</i>		<i>Trifluoroacetic acid (TFA)</i>	
	Replic. 1	Replic. 2	Replic. 1	Replic. 2	Replic. 1	Replic. 2	Replic. 1	Replic. 2
0	97.4	99.9	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
1	96.8	96.8	1.5	1.5	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
2	89.5	91.4	2.3	1.7	< LOD	< LOD	1.2	1.5
4	87.5	85.0	2.7	3.4	0.7	0.8	4.9	5.4
7	74.6	74.2	3.3	5.8	1.6	1.6	11.5	11.4
10	64.3	62.6	3.2	3.5	1.9	1.9	19.4	18.8
14	46.5	48.3	3.4	2.8	0.5	0.6	32.4	30.8
35	13.8	12.8	1.7	1.7	< LOD	< LOD	60.8	59.3
63	3.4	3.8	0.9	0.5	0.8	< LOD	69.7	70.3
91	1.3	1.4	n. d. ¹⁾	n. d. ¹⁾	< LOD	< LOD	75.4	74.1
121	1.2	0.8	n. d. ¹⁾	n. d. ¹⁾	< LOD	< LOD	73.1	74.4

Footnotes to the table:

1) n. d. = not detected.

Table B.8.1.1.2.1.1._CA-114: The DAT-0 recoveries and LOD determined for each experiment

Study	Test soil		Determined parameter		
	Soil name	Soil type (USDA classification)	DAT-0 recovery [% AR]		LOD [% AR]
			Rep. 1	Rep 2.	
Hein; 2012	Hoefchen Am Hohenseh 4a	Silt loam	99.5	100.9	0.5
	Laacherhof AXXa	Loamy sand	99.3	98.9	0.4
Hein; 2012a	Dollendorf II	Clay loam	102.4	99.6	0.4
	Laacherhof Wurmwiese	Loam	98.1	100.6	0.4

The data presented above were subjected to a multistep evaluation procedure performed in line with the recommendations of FOCUS Kinetics Guidelines [FOCUS; 2006]. It consisted of the following steps:

- **Step 1:** Processing of the raw input data;
- **Step 2:** Kinetic evaluation of the processed data using the following 1st – order kinetic models: SFO, FOMC and DFOP, and KinGUI 2 as a modelling tool. That step consisted of the two sub-steps:
 - **Sub-step 1:** kinetic evaluation of the data for parent compound (Flufenacet) only, in order to determine the appropriate kinetic model. At that stage of analysis all three kinetic models listed above were tested;
 - **Sub-step 2:** kinetic evaluation of the data for parent compound (Flufenacet) and its degradation products using for Flufenacet the kinetic model identified as appropriate at previous stage, and SFO model for degradation products;
- **Step 3:** Evaluation of the results of kinetic examination of the data;
- **Step 4:** Reporting of the obtained results, in particular kinetic parameters recommended for modelling.

The raw input data, presented in table B.8.1.1.2.1.1._CA-113, were processed following the recommendations given by FOCUS. In general terms that looked as follows:

- Measured and reported true replicates were taken into account singularly;
- The data sets were checked for their consistency and clear outliers. In case the outliers were found and removed, that was clearly indicated.

The particular measures taken in the processing of the data for the parent compound – Flufenacet, were following:

- The total AR recovery recorded in DAT-0 samples was used as concentration of Flufenacet at that time point, but the M_0 value was allowed to be estimated by the model; For that purpose the data presented in the table B.8.1.1.2.1.1._CA-114 – DAT-0 recovery values, were used;
- Values between LOD and LOQ were set to measured values;
- All single values <LOD or the non-detects (n. d.) were set to $\frac{1}{2}$ LOD. The same procedure was applied to the first appearances. However, when the values <LOD/n.d. appeared consecutively for second and next times, the kinetic curve was cut off until the appearance of the first value >LOQ. For that purpose the data presented in the table B.8.1.1.2.1.1._CA-114 – “LOD” values, were used.

The values for degradation products were processed in a following way:

- The initial, DAT-0, concentration was set to 0. That value, unlike the free-fitted M_0 concentration for the parent compound, was a fixed value;
- The values for subsequent time points, if reported as <LOD or non-detects were also set to 0 until the last time point before the first detectable amount was recorded;
- The value reported as <LOD/n.d. appearing just before the first detectable amount was recorded was set to $\frac{1}{2}$ LOD. For that purpose the data presented in the table B.8.1.1.2.1.1._CA-88 – “LOD” values, were used.
- Values between LOD and LOQ were set to measured values;
- In the decline phase the first values <LOD/n.d. were also set $\frac{1}{2}$ LOD. For the consecutive second and next such appearances the kinetic curve was cut off until, eventually, the first value >LOQ appeared. For that purpose the data presented in the table B.8.1.1.2.1.1._CA-114 – “LOD” values, were used.

The processed values used as input data for the kinetic examination are presented below in the table B.8.1.1.2.1.1._CA-115.

Table B.8.1.1.2.1.1_CA-115: The processed data obtained in the test soils used as input in kinetic analysis.

The data obtained in Hoefchen Am Hohenseh 4a silt loam soil (study by [Hein; 2012]):								
Time Point – DAT [days]	Concentration, expressed as [% AR], of:							
	<i>Flufenacet</i>		<i>FOE Thiadone</i>		<i>FOE 5043-Trifluoroethane-sulfonic acid</i>		<i>Trifluoroacetic acid (TFA)</i>	
	Replic. 1	Replic. 2	Replic. 1	Replic. 2	Replic. 1	Replic. 2	Replic. 1	Replic. 2
0	99.5	100.9	0.0	0.0	0.0	0.0	0.0	0.0
2	93.3	91.2	3.5	3.4	0.8	1.1	1.2	1.2
4	87.4	88.3	4.5	4.6	2.4	2.3	3.9	3.5
7	74.8	76.3	5.2	5.9	4.1	4.4	9.2	10.1
10	61.8	66.3	6.0	5.5	5.5	5.3	17.4	16.0
14	52.8	56.8	3.6	3.2	6.1	5.9	25.4	24.8
35	13.4	14.2	1.7	1.5	4.8	5.0	61.2	61.0
60	4.1	3.4	0.6	0.6	2.5	2.7	71.7	74.3
87	1.7	1.6	0.3 ¹⁾	0.3 ¹⁾	0.3 ¹⁾	0.6	76.6	78.8
120	0.9	0.9	NaN ²⁾	NaN ²⁾	NaN ²⁾	0.3 ¹⁾	77.7	77.5
The data obtained in Laacherhof AXXa loamy sand soil (study by [Hein; 2012a]):								
Time Point – DAT¹⁾ [days]	Concentration, expressed as [% AR], of:							
	<i>Flufenacet</i>		<i>FOE Thiadone</i>		<i>FOE 5043-Trifluoroethane-sulfonic acid</i>		<i>Trifluoroacetic acid (TFA)</i>	
	Replic. 1	Replic. 2	Replic. 1	Replic. 2	Replic. 1	Replic. 2	Replic. 1	Replic. 2
0	99.3	98.9	0.0	0.0	0.0	0.0	n. d. ¹⁾	n. d. ¹⁾
1	97.9	96.2	1.8	1.8	NaN ²⁾	NaN ²⁾	n. d. ¹⁾	n. d. ¹⁾
2	92.3	91.3	1.7	2.0	0.2 ¹⁾	0.2 ¹⁾	1.4	1.7
4	89.7	90.0	2.9	2.1	1.4	1.9	2.3	3.0
7	80.6	82.2	2.6	3.0	3.2	3.2	7.2	7.2
10	70.7	70.5	2.4	2.6	4.1	4.8	13.1	14.6
14	60.2	59.6	2.9	2.5	2.9	3.5	21.9	22.3
35	29.0	22.4	1.6	1.6	2.4	3.0	44.9	51.5
63	5.1	10.0	0.8	1.1	1.1	1.2	69.4	62.3
91	3.0	3.3	0.6	0.2 ¹⁾	0.2 ¹⁾	0.2 ¹⁾	71.0	72.0
121	1.6	1.3	0.2 ¹⁾	NaN ²⁾	0.5	0.5	74.9	73.2
The data obtained in Dollendorf II clay loam soil (study by [Hein; 2012a]):								
Time Point – DAT¹⁾ [days]	Concentration, expressed as [% AR], of:							
	<i>Flufenacet</i>		<i>FOE Thiadone</i>		<i>FOE 5043-Trifluoroethane-sulfonic acid</i>		<i>Trifluoroacetic acid (TFA)</i>	
	Replic. 1	Replic. 2	Replic. 1	Replic. 2	Replic. 1	Replic. 2	Replic. 1	Replic. 2
0	102.4	99.6	0.0	0.0	0.0	0.0	0.0	0.0
1	97.7	96.0	1.8	2.5	NaN ²⁾	NaN ²⁾	0.2 ¹⁾	0.2 ¹⁾
2	88.0	88.4	2.5	2.5	0.2 ¹⁾	NaN ²⁾	1.9	2.2
4	86.9	88.5	4.3	3.6	0.6	0.2 ¹⁾	5.6	5.8
7	75.1	78.9	5.1	2.9	2.3	2.0	10.1	9.3
10	62.7	67.5	6.2	5.0	3.8	3.1	20.6	17.3
14	57.6	54.3	4.5	5.2	1.7	1.8	27.6	28.7
35	15.9	14.8	3.5	3.0	1.6	1.6	67.0	66.6
63	2.4	2.6	0.6	0.9	0.5	0.6	78.8	78.3
91	0.9	1.5	0.2 ¹⁾	0.2 ¹⁾	0.2 ¹⁾	0.2 ¹⁾	79.4	83.6
121	1.0	0.9	NaN ²⁾	NaN ²⁾	NaN ²⁾	NaN ²⁾	81.0	81.0
The data obtained in Laacherhof Wurmwiiese loam soil (study by [Hein; 2012a]):								
Time Point – DAT¹⁾ [days]	Concentration, expressed as [% AR], of:							
	<i>Flufenacet</i>		<i>FOE Thiadone</i>		<i>FOE 5043-Trifluoroethane-sulfonic acid</i>		<i>Trifluoroacetic acid (TFA)</i>	
	Replic. 1	Replic. 2	Replic. 1	Replic. 2	Replic. 1	Replic. 2	Replic. 1	Replic. 2
0	98.17.4	100.6	0.0	0.0	0.0	0.0	0.0	0.0
1	96.8	96.8	1.5	1.5	NaN ²⁾	NaN ²⁾	n. d. ¹⁾	n. d. ¹⁾
2	89.5	91.4	2.3	1.7	0.2 ¹⁾	0.2 ¹⁾	1.2	1.5
4	87.5	85.0	2.7	3.4	0.7	0.8	4.9	5.4
7	74.6	74.2	3.3	5.8	1.6	1.6	11.5	11.4
10	64.3	62.6	3.2	3.5	1.9	1.9	19.4	18.8
14	46.5	48.3	3.4	2.8	0.5	0.6	32.4	30.8
35	13.8	12.8	1.7	1.7	0.2 ¹⁾	0.2 ¹⁾	60.8	59.3
63	3.4	3.8	0.9	0.5	0.8	NaN ²⁾	69.7	70.3
91	1.3	1.4	0.2 ¹⁾	0.2 ¹⁾	0.2 ¹⁾	NaN ²⁾	75.4	74.1
121	1.2	0.8	NaN ²⁾	NaN ²⁾	NaN ²⁾	NaN ²⁾	73.1	74.4

Footnotes to the table:

- 1) Value set to ½ LOD;
 2) NaN = Not a Number;

The processed data were kinetically examined using KinGUI ver. 2 modelling tool, developed by Bayer. The optimisation was performed using IRLS (Iteratively Reweighed Nonlinear Least Squares) algorithm. The fitting procedure was a two-stage one. The first step, further called **Step 1**, consisted on the determination of the appropriate kinetic model for the parent compound – Flufenacet. At that stage three 1st-order kinetic models were tested: SFO, FOMC and DFOP. During the next stage, further called **Step 2**, the whole data set – data for the Flufenacet and its degradation products, was kinetically examined. In case of Flufenacet the tested kinetic model was that determined as appropriate at **Step 1**, while for the degradation products the SFO model was used. The conceptual metabolic pathway built in the modelling tool is presented below on figure B.8.1.1.2.1.1_CA-42. The following abbreviations were used:

- FFA for Flufenacet (parent compound);
- THIA for FOE Thiadone;
- TFA for Trifluoroacetic acid (TFA);
- TFESA for FOE 5043-Trifluoroethanesulfonic acid;

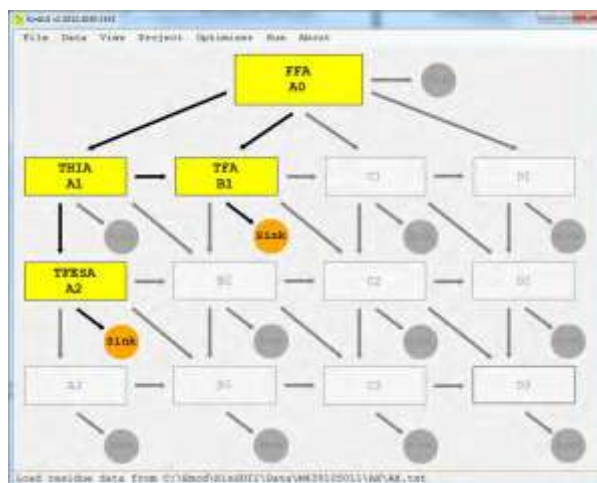


Figure B.8.1.1.2.1.1_CA-42: The conceptual transformation scheme assumed in the modelling tool (copied from the study report).

The obtained results of the kinetic analysis of the data were evaluated by the Applicant. That was done by means of a detailed statistical analysis comprising the following components:

- visual assessment of the fit;
- χ^2 -error statistics;
- t-test significance;
- correlation analysis.

The detailed characteristic of that evaluation is provided in the presented above summary of the **Study 2**, on pages 168 – 169.

On that basis the following multistep assessment procedure was developed. It was presented in the summary of the **Study 2** above, on page 169. RMS decided, for clarity, to repeat it below. It consisted of the following steps:

- **Step 1:** bearing in mind the aim of the kinetic evaluation of the data – determination of the kinetic parameters used in modelling, the SFO kinetic model was tested as first option and if passed the acceptance criteria (visually acceptable, χ^2 -error not exceeding or not significantly exceeding 15%, *prob.* > *t* value in t-test less than 0.05 for parent and 0.10 for the degradation products), it was considered acceptable;
- **Step 2:** in case the χ^2 -error was significantly greater than 15%, model parameters were fixed and fitting repeated using SFO model;
- **Step 3:** if the **Step-2** fitting failed the χ^2 -error test, bi-phasic models were included. These were FOMC, DFOP and, possibly HS. The model with smaller error was indicated as the most appropriate;
- **Step 4:** if none of the bi-phasic model returned significantly improved fit, SFO model was selected if visually acceptable; that was done in order to avoid of an over-parameterised model based on a marginally better fit.

Analysing the proposed assessment procedure RMS stated that it complied with the procedure for determination of the kinetic endpoints for modelling, presented in FOCUS Kinetics Guidance Document [FOCUS; 2006].

The results of the kinetic examination of the data and their evaluation are provided below, individually for each test soil.

- 1) The results of the kinetic analysis of the data obtained in **Hoefchen am Hohenseh 4a** Silt loam soil (study by [Hein; 2012]):

The analysis for this data-set was a single-step analysis in which the data for the parent compound and metabolites were kinetically examined together. The results of the kinetic analysis performed by the Applicant are presented below, in graphical form on figure B.8.1.1.2.1.1_CA-43 and in numerical form in the table B.8.1.1.2.1.1_CA-115.

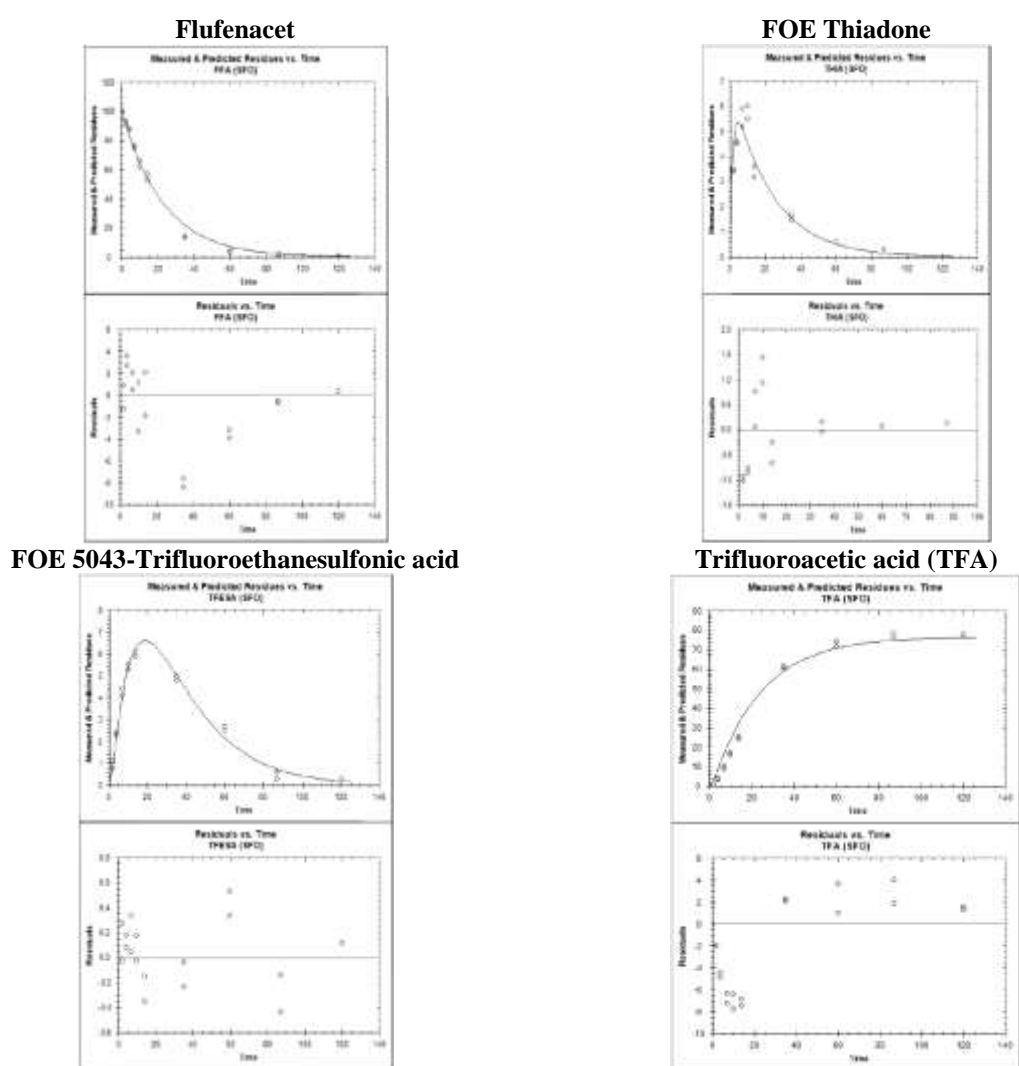


Figure B.8.1.1.2.1.1_CA-43: The graphical results of the kinetic examination of the data for Flufenacet, FOE Thiadone, FOE 5043-Trifluoroethanesulfonic acid and Trifluoroacetic acid obtained in Hoefchen am Hohenseh 4a soil (copied from the study report).

Table B.8.1.1.2.1.1._CA-115: The numerical results of the kinetic examination of the data for Flufenacet, FOE Thiadone, FOE 5043-Trifluoroethanesulfonic acid and Trifluoroacetic acid obtained in Hoefchen am Hohenseh 4a soil.

Compound	Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
			Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment ¹⁾
					Lower	Upper			
Flufenacet	SFO	M ₀	100.90	1.174	98.58	103.186	< 2 E-16	4.882	0.995; Good fit
		k	0.04377	1.20 E-3	0.04142	0.046	< 2 E-16		
FOE Thiadone	SFO	M ₀	0.0	----	----	----	----	16.421	0.913; Good fit
		k	0.6110	0.08962	0.4354	0.787	1.34 E-9		
		ff	0.913	0.126	----	----	----		
FOE 5043-Trifluoroethane-sulfonic acid	SFO	M ₀	0.0	----	----	----	----	5.845	0.988; Good fit
		k	0.07617	4.53 E-3	0.0673	0.085	< 2 E-16		
		ff	0.264	----	----	----	----		
Trifluoroacetic acid	SFO	M ₀	0.0	----	----	----	----	10.492	0.991; Good fit
		k	7.1 E-10	4.85 E-4	-9.51 E-4	0.001	0.500		
		ff ²⁾	0.087	0.044	----	----	----		
		ff ₂ ³⁾	0.736	----	----	----	----		

Footnotes to the table:

- 1) Visual assessment of the kinetic curve as proposed by the Applicant;
- 2) ff calculated for formation from the parent compound – Flufenacet;
- 3) ff calculated for the formation from FOE Thiadone;

RMS performed own analysis of the obtained results. It led to the following conclusions:

- It was possible to obtain reliable kinetic fits and kinetic parameters for the following compounds: Flufenacet, FOE Thiadone and FOE 5043-Trifluoroethanesulfonic acid;
- In case of Trifluoroacetic acid the fit is reliable, however of the determined kinetic parameters only the kinetic formation fractions – ff, may be considered reliable. The lack of reliability of the degradation rate constant and resulting from it DT₅₀ and DT₉₀ values is due to the fact that the kinetic curve was in its formation phase and even the would-be maximum was not reached.

The final set of the kinetic parameters considered acceptable by the RMS is presented below in the table B.8.1.1.2.1.1._CA-116.

Table B.8.1.1.2.1.1._CA-116: The reliable set of the kinetic parameters determined in the experiment

Determined parameter	Compound			
	Flufenacet	FOE Thiadone	FOE 5043-Trifluoroethane-sulfonic acid	Trifluoroacetic acid
DT ₅₀ [days]	15.84	1.13	9.10	1000
DT ₉₀ [days]	52.61	3.77	30.23	> 1000
Kinetic formation fraction ff	Not applicable	0.913 ± 0.013	0.264	0.087 ± 0.004 0.736
Precursor	Not applicable	Flufenacet	FOE Thiadone	Flufenacet FOE Thiadone
Kinetic model	SFO	SFO	SFO	SFO

As the decline phase was not reached for Trifluoroacetic acid, RMS proposed as estimated kinetic endpoints for that compound DT₅₀ = 1000 days and DT₉₀ > 1000 days.

- 2) The results of the kinetic analysis of the data obtained in **Laacherhof AXXa** Loamy sand soil (study by [Hein; 2012a]):

The analysis for this data-set was a single-step analysis in which the data for the parent compound and metabolites were kinetically examined together. The results of the kinetic analysis performed by the Applicant are presented below, in graphical form on figure B.8.1.1.2.1.1._CA-44 and in numerical form in the table B.8.1.1.2.1.1._CA-117.

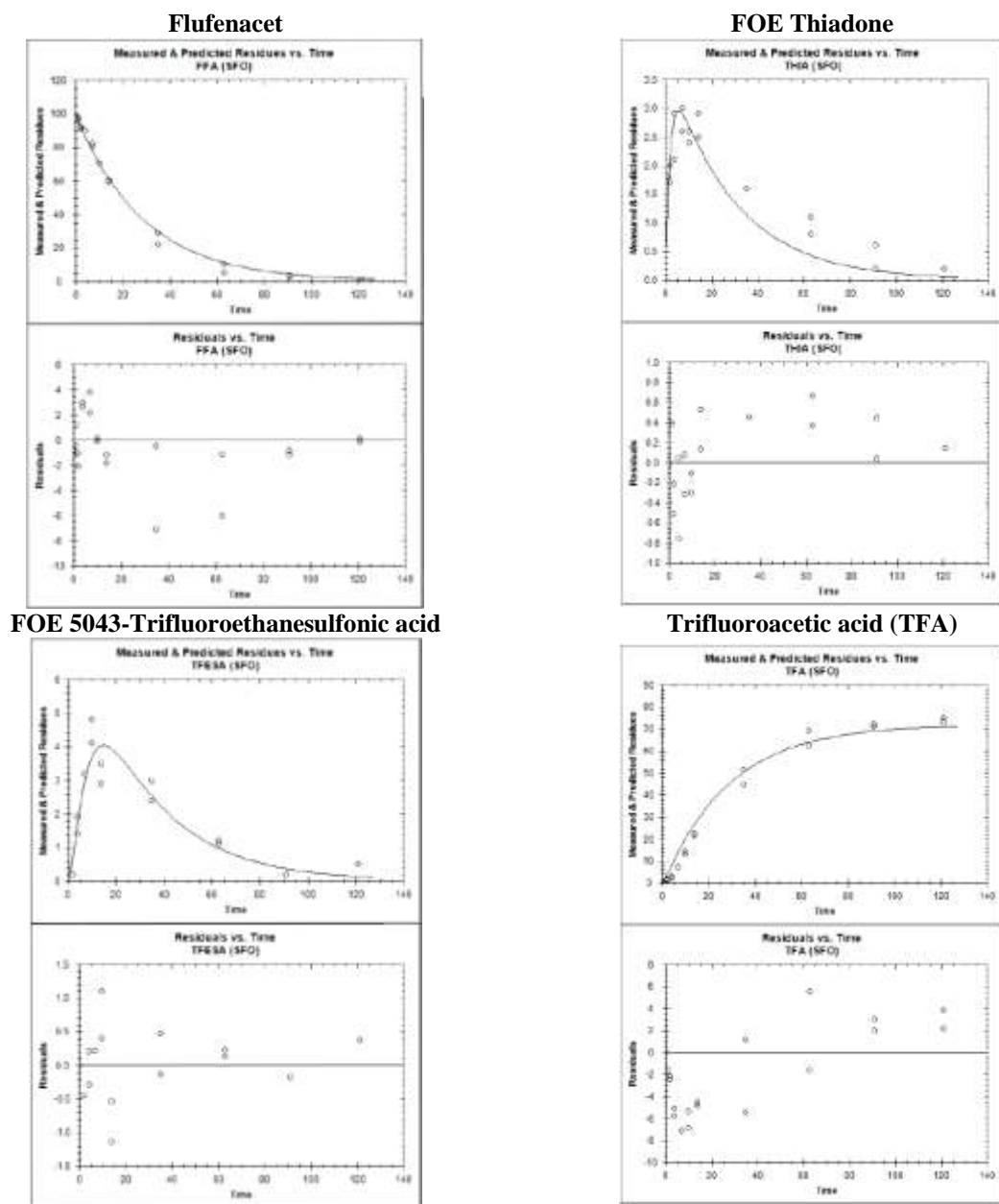


Figure B.8.1.1.2.1.1._CA-44: The graphical results of the kinetic examination of the data for Flufenacet, FOE Thiadone, FOE 5043-Trifluoroethanesulfonic acid and Trifluoroacetic acid obtained in Laacherhof AXXa soil (copied from the study report).

Table B.8.1.1.2.1.1._CA-117: The numerical results of the kinetic examination of the data for Flufenacet, FOE Thiadone, FOE 5043-Trifluoroethanesulfonic acid and Trifluoroacetic acid obtained in Laacherhof AXXa soil.

Compound	Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
			Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment ¹⁾
					Lower	Upper			
Flufenacet	SFO	M ₀	100.10	0.894	98.37	101.871	< 2 E-16	3.029	0.997; Good fit
		k	0.03492	9.57 E-4	0.03305	0.037	< 2 E-16		
FOE Thiadone	SFO	M ₀	0.0	----	----	----	----	15.645	0.898; Good fit
		k	0.5087	0.0885	0.3354	0.682	8.30 E-8		
		ff	0.524	0.082	----	----	----		
FOE 5043-Trifluoroethane-sulfonic acid	SFO	M ₀	0.0	----	----	----	----	18.252	0.908; Good fit
		k	0.1548	0.0236	0.1086	0.201	2.67 E-9		
		ff	0.534	----	----	----	----		
Trifluoroacetic acid	SFO	M ₀	0.0	----	----	----	----	10.340	0.990; Good fit
		k	6.41 E-9	6.58 E-4	-1.29 E-3	0.001	0.5		
		ff ²⁾	0.476	0.118	----	----	----		
		ff ₂ ³⁾	0.466	----	----	----	----		

Footnotes to the table:

- 1) Visual assessment of the kinetic curve as proposed by the Applicant;
- 2) ff calculated for formation from the parent compound – Flufenacet;
- 3) ff calculated for the formation from FOE Thiadone;

RMS performed own analysis of the obtained results. It led to the following conclusions:

- It was possible to obtain reliable kinetic fits and kinetic parameters for the following compounds: Flufenacet, FOE Thiadone and FOE 5043-Trifluoroethanesulfonic acid;
- In case of Trifluoroacetic acid the fit is reliable, however of the determined kinetic parameters only the kinetic formation fractions – ff, may be considered reliable. The lack of reliability of the degradation rate constant and resulting from it DT₅₀ and DT₉₀ values is due to the fact that the kinetic curve was in its formation phase and even the would-be maximum was not reached.

The final set of the kinetic parameters considered acceptable by the RMS is presented below in the table B.8.1.1.2.1.1._CA-118.

Table B.8.1.1.2.1.1._CA-118: The reliable set of the kinetic parameters determined in the experiment

Determined parameter	Compound			
	Flufenacet	FOE Thiadone	FOE 5043-Trifluoroethane-sulfonic acid	Trifluoroacetic acid
DT ₅₀ [days]	19.85	1.36	4.48	1000
DT ₉₀ [days]	65.93	4.53	14.87	> 1000
Kinetic formation fraction ff	Not applicable	0.524 ± 0.082	0.534	0.476 ± 0.117
Precursor	Not applicable	Flufenacet	FOE Thiadone	Flufenacet
Kinetic model	SFO	SFO	SFO	SFO

As the decline phase was not reached for Trifluoroacetic acid, RMS proposed as estimated kinetic endpoints for that compound DT₅₀ = 1000 days and DT₉₀ > 1000 days.

- 3) The results of the kinetic analysis of the data obtained in **Dollendorf II** Clay loam soil (study by [Hein; 2012a]):

The analysis for this data-set was a single-step analysis in which the data for the parent compound and metabolites were kinetically examined together. The results of the kinetic analysis performed by the Applicant are presented below, in graphical form on figure B.8.1.2.1.1._CA-45 and in numerical form in the table B.8.1.2.1.1._CA-119.

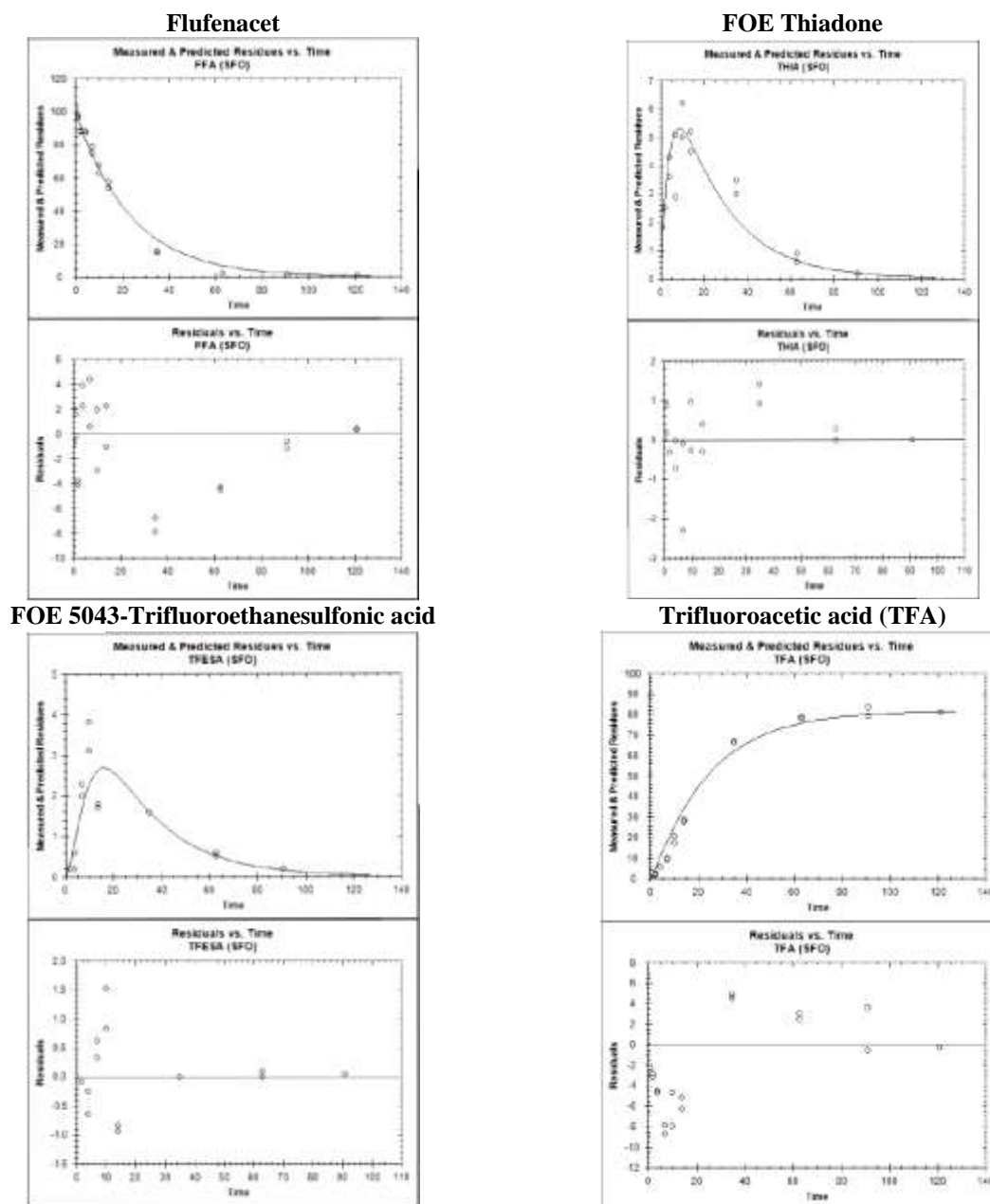


Figure B.8.1.2.1.1._CA-45: The graphical results of the kinetic examination of the data for Flufenacet, FOE Thiadone, FOE 5043-Trifluoroethanesulfonic acid and Trifluoroacetic acid obtained in Dollendorf II soil (copied from the study report).

Table B.8.1.1.2.1.1_CA-119: The numerical results of the kinetic examination of the data for Flufenacet, FOE Thiadone, FOE 5043-Trifluoroethanesulfonic acid and Trifluoroacetic acid obtained in Dollendorf II soil.

Compound	Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
			Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment ¹⁾
					Lower	Upper			
Flufenacet	SFO	M ₀	100.30	1.188	97.98	102.643	< 2 E-16	4.665	0.994; Good fit
		k	0.0425	1.44 E-3	0.0397	0.045	< 2 E-16		
FOE Thiadone	SFO	M ₀	0.0	----	----	----	----	16.356	0.862; Good fit
		k	0.2438	0.04665	0.1523	0.335	7.73 E-7		
		ff	0.438	0.066	----	----	----		
FOE 5043-Trifluoroethane-sulfonic acid	SFO	M ₀	0.0	----	----	----	----	35.241	0.741; Good fit
		k	0.1727	0.0441	0.08624	0.259	9.97 E-5		
		ff	0.422	----	----	----	----		
Trifluoroacetic acid	SFO	M ₀	0.0	----	----	----	----	9.451	0.991; Good fit
		k	2.33 E-9	5.95 E-4	-1.17 E-3	0.001	0.4999		
		ff ²⁾	0.562	0.113	----	----	----		
		ff ₂ ³⁾	0.578	----	----	----	----		

Footnotes to the table:

- 1) Visual assessment of the kinetic curve as proposed by the Applicant;
- 2) ff calculated for formation from the parent compound – Flufenacet;
- 3) ff calculated for the formation from FOE Thiadone;

The Applicant stated that for FOE 5043-Trifluoroethanesulfonic acid the kinetic fit was not fully reliable due to the high χ^2 error. For that reason the Applicant performed an additional fitting, for FOE 5043-Trifluoroethanesulfonic acid fitted alone using the top-down approach. The results of that analysis are presented further down this point.

RMS performed own analysis of the obtained results. It led to the following conclusions:

- It was possible to obtain reliable kinetic fits and kinetic parameters for the following compounds: Flufenacet and FOE Thiadone;
- In case of Trifluoroacetic acid the fit is reliable, however of the determined kinetic parameters only the kinetic formation fractions – ff, may be considered reliable. The lack of reliability of the degradation rate constant and resulting from it DT₅₀ and DT₉₀ values is due to the fact that the kinetic curve was in its formation phase and even the would-be maximum was not reached;
- In case of FOE 5043-Trifluoroethanesulfonic acid it was not possible to obtain the reliable kinetic fit. Although the visual inspection showed that fit is acceptable high level of χ^2 error makes it statistically not reliable. As a result, also calculated kinetic endpoints – DT₅₀ and DT₉₀ values, cannot be considered reliable in spite of the fact that the calculated rate constant k is reliable according to the results of the t-test (the prob. > t is well below the level of 0.05). RMS noticed that problems with obtaining the reliable kinetic curve were most probably due to the low concentrations of the compound in this experiment. However, the distribution of the data points implied that the acceptable fit may be obtained when these are fitted alone using the top-down approach.

As the final step of the analysis of the data obtained in the experiment on Dollendorf II soil, the data for FOE 5043-Trifluoroethanesulfonic acid were fitted alone using the top-down approach. To do that the Applicant identified the time point at which the maximum concentration of the compound of concern was recorded. That point was used as a starting point in the analysis. The resulting data set used in the fitting exercise is presented below in the table B.8.1.1.2.1.1_CA-120.

Table B.8.1.1.2.1.1._CA-120: The input data for FOE 5043-Trifluoroethanesulfonic acid fitted alone using the top-down approach.

Time Point – DAT [days]	Concentration of FOE 5043-Trifluoroethanesulfonic acid expressed as [%AR]	
	Replicate 1	Replicate 2
10	3.8	3.1
14	1.7	1.8
35	1.6	1.6
63	0.5	0.6
91	0.2	0.2
121	NaN	NaN

The fitting was performed using SFO model and followed the procedure outlined above. The results of that kinetic analysis are presented below, in graphical form on figure B.8.1.1.2.1.1._CA-46 and in numerical form in the table B.8.1.1.2.1.1._CA-121.

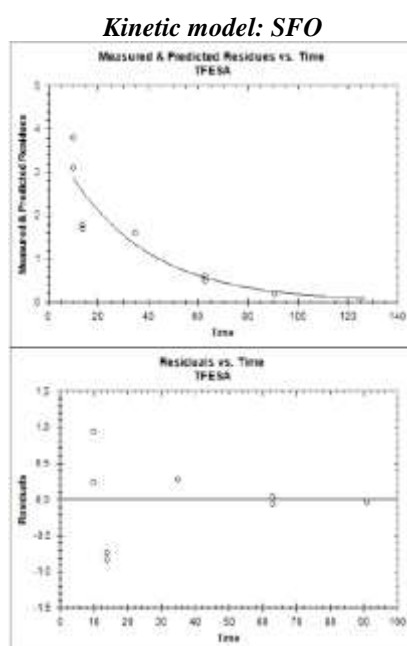


Figure B.8.1.1.2.1.1._CA-46: The graphical results of the kinetic analysis (copied from the study report).

Table B.8.1.1.2.1.1._CA-121: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment ¹⁾
				Lower	Upper			
SFO	M_0	3.911	0.609	2.716	5.105	1.33 E-4	24.06	0.824; Good fit
	k	0.03084	0.00858	0.01403	0.048	0.00351		

Footnotes to the table:

1) Visual assessment of the kinetic curve as reported by the Applicant.

The Applicant stated that the fit returned by the SFO model was visually and statistically acceptable.

Examining the determined kinetic curve RMS noticed that one of the data points – DAT-14 was an outlier, the removal of which may improve the fit visually and statistically. That hypothesis was verified and the results of that verification are presented in the summary of the **Study 6** above, on pages 245 – 247.

Therefore RMS repeated the kinetic analysis of the data set modified by the elimination of the values for DAT-14 time point. The modelling was performed using CAKE 3.1 modelling tool, developed by Tessella, and IRLS (Iteratively Reweighted Nonlinear Least Squares) algorithm as optimisation method.

The results of the kinetic analysis performed by the RMS are presented below, in graphical form on figure B.8.1.1.2.1.1._CA-47 and in numerical form in the table B.8.1.1.2.1.1._CA-122.

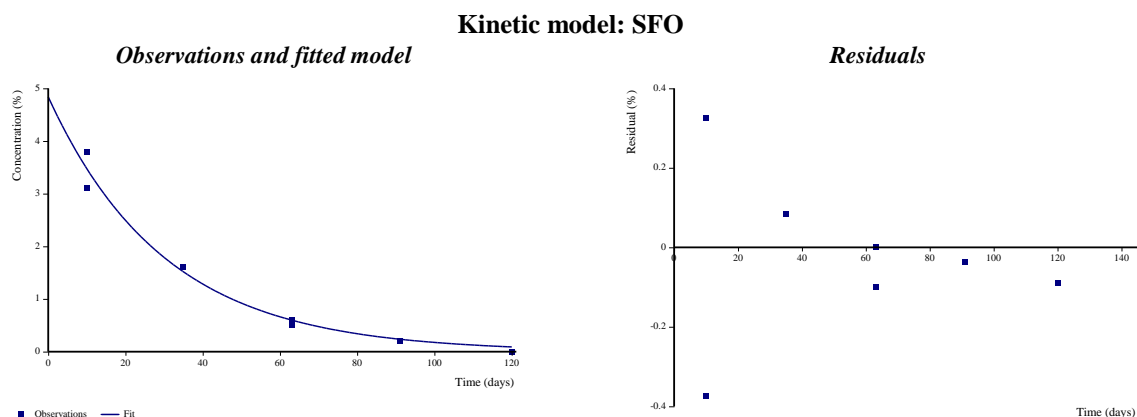


Figure B.8.1.1.2.1.1._CA-47: The graphical results of the kinetic analysis.

Table B.8.1.1.2.1.1._CA-122: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment
				Lower	Upper			
SFO, DAT-14 removed	M_0	4.838	0.265	4.228	5.449	----	4.31	0.983; Good fit
	k	0.03315	0.00271	0.0296	0.039	9.28 E-7		

The calculated kinetic endpoints were following: **DT₅₀ = 20.9 days, DT₉₀ = 69.5 days;**

On the basis of the evaluation presented above it may be stated that for FOE 5043-Trifluoroethanesulfonic acid it was possible to obtain the reliable kinetic fit using the data set presented in the table B.8.1.1.2.1.1._CA-120, modified by the removal of the results for the DAT-14 time point identified as an outlier.

Additionally RMS checked the possibility that similar results could be obtained for the same compound fitted in the whole data set once that time point had been removed. The kinetic analysis was performed using CAKE 3.1 modelling tool, developed by Tessella, and IRLS (Iteratively Reweighed Nonlinear Least Squares) algorithm as optimisation method. No significant improvement was achieved, so RMS decided not to present the results of that kinetic analysis in order not to overburden the Renewal Assessment Report.

The final set of the trigger kinetic endpoints resulting from that experiment is presented below in the table B.8.1.1.2.1.1._CA-123.

Table B.8.1.1.2.1.1._CA-123: The reliable set of the kinetic parameters determined in the experiment

Determined parameter	Compound			
	Flufenacet	FOE Thiadone	FOE 5043-Trifluoroethanesulfonic acid	Trifluoroacetic acid
DT ₅₀ [days]	16.30	2.84	20.9	1000
DT ₉₀ [days]	54.18	9.45	69.5	> 1000
Kinetic formation fraction <i>ff</i>	Not applicable	0.438 ± 0.066	0.422	0.562 ± 0.113
Precursor	Not applicable	Flufenacet	FOE Thiadone	Flufenacet
Kinetic model	SFO	SFO	SFO	SFO

As the decline phase was not reached for Trifluoroacetic acid, RMS proposed as estimated kinetic endpoints for that compound **DT₅₀ = 1000 days and DT₉₀ > 1000 days.**

- 4) The results of the kinetic analysis of the data obtained in **Laacherhof Wurmwiese** Loam soil (study by [Hein; 2012a]):

The analysis for this data-set was a single-step analysis in which the data for the parent compound and metabolites were kinetically examined together. The results of the kinetic analysis performed by the Applicant are presented below, in graphical form on figure B.8.1.1.2.1.1._CA-48 and in numerical form in the table B.8.1.1.2.1.1._CA-124.

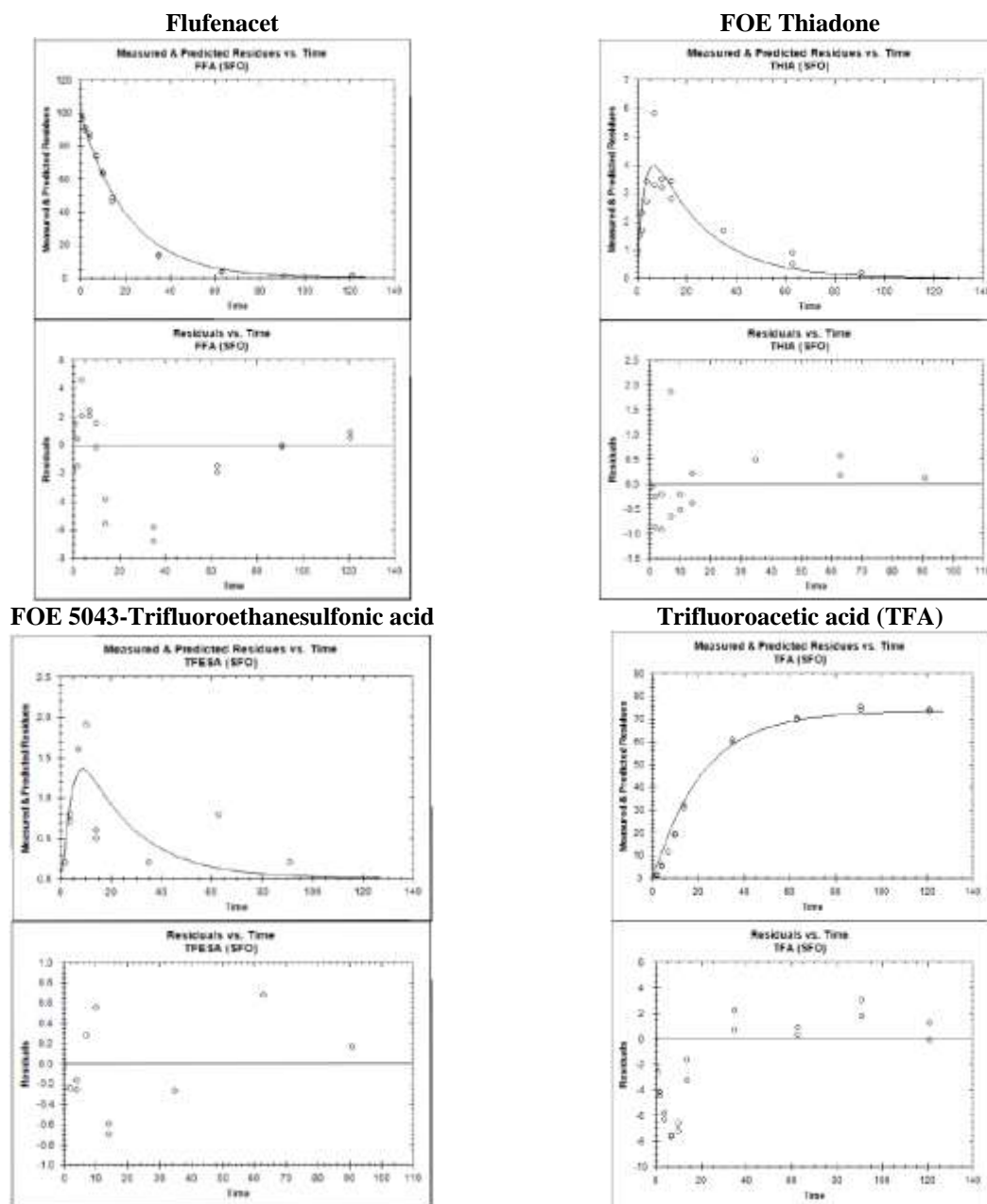


Figure B.8.1.1.2.1.1._CA-48: The graphical results of the kinetic examination of the data for Flufenacet, FOE Thiadone, FOE 5043-Trifluoroethanesulfonic acid and Trifluoroacetic acid obtained in Laacherhof Wurmwiese soil (copied from the study report).

Table B.8.1.1.2.1.1._CA-124: The numerical results of the kinetic examination of the data for Flufenacet, FOE Thiadone, FOE 5043-Trifluoroethanesulfonic acid and Trifluoroacetic acid obtained in Laacherhof Wurmwise soil.

Compound	Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
			Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment ¹⁾
					Lower	Upper			
Flufenacet	SFO	M ₀	99.88	1.180	97.57	102.194	< 2 E-16	4.270	0.995; Good fit
		k	0.04648	1.67 E-3	0.04321	0.050	< 2 E-16		
FOE Thiadone	SFO	M ₀	0.0	----	----	----	----	14.730	0.850; Good fit
		k	0.3490	0.0569	0.2376	0.460	1.97 E-8		
		ff	0.405	0.056	----	----	----		
FOE 5043-Trifluoroethane-sulfonic acid	SFO	M ₀	0.0	----	----	----	----	43.983	0.640; Acceptable fit
		k	0.6478	0.1406	0.3722	0.923	8.50 E-6		
		ff	0.655	----	----	----	----		
Trifluoroacetic acid	SFO	M ₀	0.0	----	----	----	----	9.435	0.993; Good fit
		k	2.2 E-10	7.12 E-4	-1.40 E-3	0.001	0.5		
		ff ²⁾	0.596	0.149	----	----	----		
		ff ₂ ³⁾	0.345	----	----	----	----		

Footnotes to the table:

- 1) Visual assessment of the kinetic curve as reported by the Applicant;
- 2) ff calculated for formation from the parent compound – Flufenacet;
- 3) ff calculated for the formation from FOE Thiadone;

The Applicant stated, that using the data from that experiment it was not possible to obtain the reliable kinetic endpoints for FOE 5043-Trifluoroethanesulfonic acid. That was due to the fact that the visual fitting was poor and the χ^2 error high, making the whole fit unreliable. RMS conforms the correctness of that conclusion. As a result the Applicant performed an additional fitting for FOE 5043-Trifluoroethanesulfonic acid fitted alone, using the top-down approach.

RMS performed own analysis of the obtained results. It led to the following conclusions:

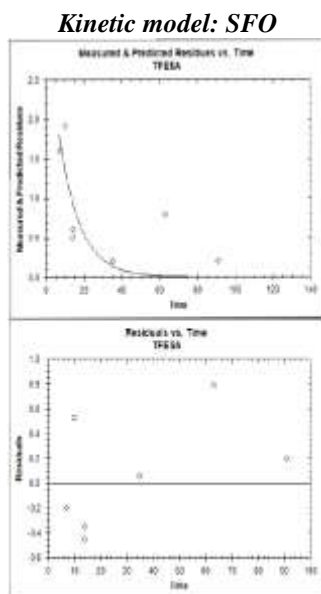
- It was possible to obtain reliable kinetic fits and kinetic parameters for the following compounds: Flufenacet and FOE Thiadone;
- In case of Trifluoroacetic acid the fit is reliable, however of the determined kinetic parameters only the kinetic formation fractions – ff, may be considered reliable. The lack of reliability of the degradation rate constant and resulting from it DT₅₀ and DT₉₀ values is due to the fact that the kinetic curve was in its formation phase and even the would-be maximum was not reached;
- In case of FOE 5043-Trifluoroethanesulfonic acid it was not possible to obtain the reliable kinetic fit. RMS conforms the Applicant's statement in that area noticing that not only the fit was statistically not acceptable due to the high level of χ^2 error, but also visually – the plotted kinetic curve poorly reproduced the distribution of the experimental points. RMS noticed also that within the decline phase a second local maximum occurred on DAT 63. It is possible that that time point was an outlier.

RMS did additional kinetic fitting using the modified data set for FOE 5043-Trifluoroethanesulfonic acid to verify the hypothesis presented above. However, even with that modified data set it was not possible to obtain the reliable kinetic fit for that compound, most probably because of the very low concentrations of the compound of concern. RMS decided not to present the results of that fitting in order not to overburden the Report.

The results of the kinetic examination of the data for FOE 5043-Trifluoroethanesulfonic acid fitted alone using the top-down approach, performed by the Applicant, are presented below in graphical form on figure B.8.1.1.2.1.1._CA-49 and in numerical form in the table B.8.1.1.2.1.1._CA-126. They are preceded by the table B.8.1.1.2.1.1._CA-125, containing the data set used in the fitting exercise. The fitting was performed using one kinetic model – SFO, and followed the procedure outlined above.

Table B.8.1.1.2.1.1._CA-125: The input data for FOE 5043-Trifluoroethanesulfonic acid fitted alone using the top-down approach.

Time Point – DAT [days]	Concentration of FOE 5043-Trifluoroethanesulfonic acid expressed as [%AR]	
	Replicate 1	Replicate 2
10	1.9	1.9
14	0.5	0.6
35	0.2	0.2
63	0.8	NaN
91	0.2	NaN
121	NaN	NaN

**Figure B.8.1.1.2.1.1._CA-49:** The graphical results of the kinetic analysis (copied from the study report).**Table B.8.1.1.2.1.1._CA-126:** The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter				Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error
				Lower	Upper		
SFO	M ₀	3.407	1.439	0.588	6.227	0.0227	39.76
	k	0.09120	0.0460	9.46 E-3	0.181	0.0415	
							R ² and visual assessment ¹⁾
							0.701; Acceptable fit

Footnotes to the table:

1) Visual assessment of the kinetic curve as reported by the Applicant.

The Applicant stated that the fit was of a sufficient quality to determine the reliable kinetic endpoints to be used as input to derive the modelling endpoints. That statement however stands in clear contrast to the conclusion made in the previous study – for the experiment on that soil it was not possible to determine the reliable kinetic endpoints for FOE 5043-Trifluoroethanesulfonic acid. RMS is also of the opinion that the quality of the fit is not sufficient to derive reliable kinetic endpoints that could be subsequently used to calculate the average values used in modelling.

However, analysing the data set for FOE 5043-Trifluoroethanesulfonic acid RMS stated that the problem was related to the occurrence of the second maximum observed on DAT 63. There are several indicators for that time point being an outlier:

- measurable concentration was determined at that time point only for one replicate,
- for both preceding and following time point in both replicates the compound was not detected and the proposed measurable values are resulting from the processing of the data set according to the principles set by FOCUS,
- for the last time point with measurable concentrations of FOE 5043-Trifluoroethanesulfonic acid – DAT 14, these were lower than the measured DAT-63 concentration.

RMS thinks that all that indicate that the DAT-63 concentration of FOE 5043-Trifluoroethanesulfonic acid of 0.8% is in fact an analytical artefact that should be removed from the data set during the data-processing. Therefore RMS decided to repeat the fitting, removing that value and all subsequent data points. In order to have the minimal required amount of data points – four, RMS decided to use the DAT-63 time point as the last time point with the concentrations of the compound of concern set to zero. The resulting modified data set used in that fitting is presented below in the table B.8.1.1.2.1.1._CA-127.

Table B.8.1.1.2.1.1._CA-127: The modified input data for FOE 5043-Trifluoroethanesulfonic acid used in the repeated kinetic analysis performed by the RMS using the top-down approach.

Time Point – DAT [days]	Concentration of FOE 5043-Trifluoroethanesulfonic acid expressed as [%AR]	
	Replicate 1	Replicate 2
10	1.9	1.9
14	0.5	0.6
35	0.2	0.2
63	0.0	0.0

The kinetic analysis was performed using CAKE 3.1, developed by Tessella, as a modelling tool. The optimisation was performed using IRLS (Iteratively Reweighed Nonlinear Least Squares) algorithm. Because of the limited number of the data points – only four were available, solely the SFO model was tested.

The results of the kinetic analysis performed by the RMS are presented below, in graphical form on figure B.8.1.1.2.1.1._CA-50 and in numerical form in the table B.8.1.1.2.1.1._CA-128.

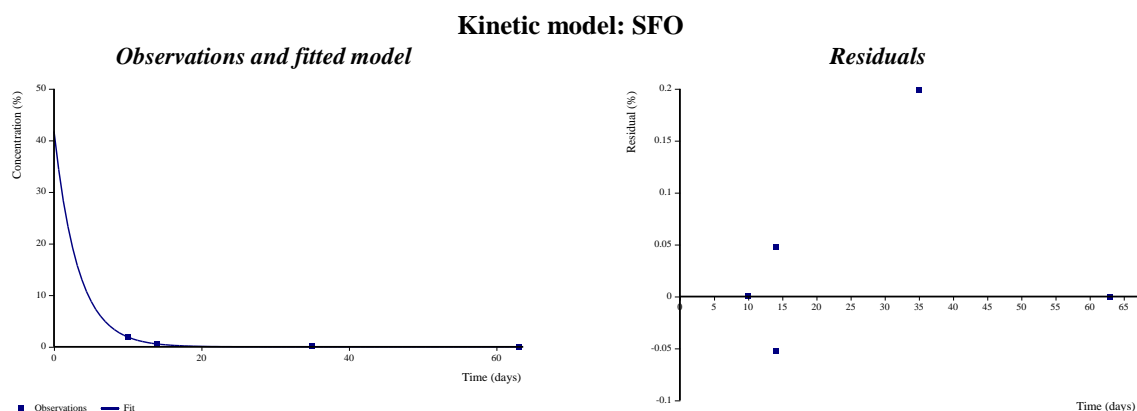


Figure B.8.1.1.2.1.1._CA-50: The graphical results of the kinetic analysis.

Table B.8.1.1.2.1.1._CA-128: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment
				Lower	Upper			
SFO	M_0	41.75	17.11	-0.1286	83.62	----	12.3	0.988; Good fit
	k	0.309	0.03954	0.2122	0.406	1.16 E-4		

The calculated kinetic endpoints were following: $DT_{50} = 2.24$ days, $DT_{90} = 7.45$ days;

The obtained results of the fitting indicate that with the elimination of the measurable value for DAT-63 time point it was possible to obtain visually good and statistically reliable fit using the SFO kinetic model. It shall be noted that the kinetic curve bears a considerable level of uncertainty with regard to the estimated M_0 value, but on the other hand that value is close to the determined kinetic formation fraction ff . That taken into account, it may be stated that the kinetic curve may be considered as a good estimation of the kinetic behaviour of FOE 5043-Trifluoroethanesulfonic acid in the test soil, therefore the fit and derived from it kinetic parameters may be considered reliable.

The final set of the kinetic parameters resulting from that experiment and considered acceptable by the RMS is presented below in the table B.8.1.1.2.1.1._CA-129.

Table B.8.1.1.2.1.1._CA-129: The reliable set of the kinetic parameters determined in the experiment

Determined parameter	Compound			
	Flufenacet	FOE Thiadone	FOE 5043-Trifluoroethane-sulfonic acid	Trifluoroacetic acid
DT ₅₀ [days]	14.91	1.99	2.24	1000
DT ₉₀ [days]	49.54	6.60	7.45	> 1000
Kinetic formation fraction <i>ff</i>	Not applicable	0.404 ± 0.056	0.655	0.596 ± 0.149
Precursor	Not applicable	Flufenacet	FOE Thiadone	Flufenacet
Kinetic model	SFO	SFO	SFO	SFO

As the decline phase was not reached for Trifluoroacetic acid, RMS proposed as estimated kinetic endpoints for that compound DT₅₀ = 1000 days and DT₉₀ > 1000 days.

Final conclusion of the study:

On the basis of the results of the kinetic evaluation presented above it was possible to derive the definitive sets of the kinetic endpoints for each evaluated compounds. These are presented below in the table B.8.1.1.2.1.1._CA-130. It shall be noted that they are identical to the results obtained in previously summarised **Study 8**. It shall be also indicated that these values are not-normalised values, requiring normalisation before being used to calculate the averaged kinetic endpoint to be used in GW and SW modelling. That will be done separately further down the Report.

Table B.8.1.1.2.1.1._CA-130: The final set of reliable kinetic endpoints determined in the study.

Study	Test soil	Compound	Determined parameter				
			Kinetic model	Rate constant <i>k</i>	DT ₅₀ [days]	DT ₉₀ [days]	Kinetic formation fraction <i>ff</i>
Hein; 2012	<i>Hoefchen am Hohenseh 4a</i>	Flufenacet	SFO	0.04377	15.84	52.61	Not applicable
		FOE Thiadone	SFO	0.6111	1.13	3.77	0.913
		FOE 5043-Trifluoroethane-sulfonic acid	SFO	0.07617	9.10	30.23	0.264
		Trifluoroacetic acid	SFO	n. d. ¹⁾	1000	> 1000	0.087 ²⁾ 0.736 ³⁾
Hein 2012a	<i>Laacherhof AXXa</i>	Flufenacet	SFO	0.03492	19.85	65.93	Not applicable
		FOE Thiadone	SFO	0.5087	1.36	4.53	0.524
		FOE 5043-Trifluoroethane-sulfonic acid	SFO	0.1548	4.48	14.87	0.534
		Trifluoroacetic acid	SFO	n. d. ¹⁾	1000	> 1000	0.476 ²⁾ 0.466 ³⁾
	<i>Dollendorf II</i>	Flufenacet	SFO	0.0425	16.30	54.18	Not applicable
		FOE Thiadone	SFO	0.2438	2.84	9.45	0.438
		FOE 5043-Trifluoroethane-sulfonic acid	SFO – top-down approach	0.03315	20.9	69.5	0.422
		Trifluoroacetic acid	SFO	n. d. ¹⁾	1000	> 1000	0.562 ²⁾ 0.578 ³⁾
	<i>Laacherhof Wurmwiase</i>	Flufenacet	SFO	0.04648	14.91	49.54	Not applicable
		FOE Thiadone	SFO	0.3490	1.99	6.60	0.404
		FOE 5043-Trifluoroethane-sulfonic acid	SFO – top-down approach	0.309	2.24	7.45	0.655
		Trifluoroacetic acid	SFO	n. d. ¹⁾	1000	> 1000	0.596 ²⁾ 0.345 ³⁾

Footnotes to the table:

- 1) The reliable value was not determined – the estimate provided by the model cannot be considered such;
- 2) For formation from parent compound – Flufenacet;
- 3) For formation from FOE Thiadone.

Study 8:

Report: Reinken G., Partsch S., (2014): „Kinetic Evaluation of the Degradation of [thiadiazole-2-¹⁴C] flufenacet and its Degradation Product under Aerobic Soil Conditions in Laboratory According to FOCUS Kinetics using the KinGUI 2 Tool. Flufenacet (FOE 5043); FOE-thiadone.”; Bayer CropScience AG, Environmental Safety, Alfred-Nobel-Strasse 50, 40789 Monheim, Germany; unpublished Study Report No. EnSa-12-0576; 2014. 02.17; study reference number: M-477885-01-1;

Guidelines: The study was declared to be performed to comply with the following guidelines:

- FOCUS (2006): “Guidance Document on Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration.” Report of the FOCUS Work Group on Degradation Kinetics, EC Document Reference SANCO/10058/2005 version 2.0, 434 pp.;
- FOCUS (2011): “Generic guidance for Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration”, version 1.0 (issued on 23 November 2011).

GLP: No, not applicable – this is a modelling study;

RMS comments: RMS verified the study for its compliance with the provisions of the Guidelines listed above.

It was stated that the study generally compiled with the two evoked Guidance Documents. It was also noted that it was aimed on the derivation of the kinetic endpoints to be used in modelling. For that reason the best fit was not identified and SFO model was generally indicated as returning acceptable fit for parent compound – Flufenacet. For that reason when the data for parent and metabolites were kinetically examined only the combination SFO-SFO was tested.

Summary:

The aim of the study was to kinetically examine the data obtained in the experiments in which [Thiadiazole-2-¹⁴C] Flufenacet was used. That was done in order to derive the kinetic parameters suitable for modelling and environmental risk assessment.

The data were taken from the study by [Pangilinan and Smith; 1994a] – a route-of-degradation study, summarised as **Study 4** under the point B.8.1.1.1.1. The characteristic of the test soil used in the experiment with [Thiadiazole-2-¹⁴C] Flufenacet is provided below in the table B.8.1.1.2.1.1._CA-131. To maintain the consistency of reporting, only physicochemical properties are reported. The data on soil microbial activity were not given here. To check them please refer to adequate summaries of the source studies.

Table B.8.1.1.21.1._CA-131: The characteristic of soil used in the study.

Parameter		Soil:			
		395			
Soil origin		Howe, Indiana, USA			
Batch analysed		A ¹⁾	B ²⁾	C ³⁾	Average
Soil type (USDA)		Sandy loam	Sandy loam	Sandy loam	Sandy loam
Particle size distribution	Sand [%]	72.5	77.5	70.4	73.5
	Silt [%]	20.0	17.2	20.0	19.1
	Clay [%]	7.5	5.3	9.6	7.5
pH value (in water, 1:1)		6.1	6.4	6.2	6.2
pH value in CaCl ₂ ⁴⁾		5.5	5.9	5.6	5.6 ⁵⁾
Organic matter content (OM) [%]		0.2	0.4	1.2	0.6
Organic carbon content (C _{org}) [%] ⁵⁾		0.12	0.23	0.70	0.35
Cation Exchange Capacity – CEC [mEq/100g]		6.9	7.4	5.1	6.5
Bulk density (disturbed) [g/cm ³]		1.31	1.33	1.47	1.37
Moisture holding capacity at ½ bar [%]		14.8	13.1	11.3	13.1

Footnotes to the table:

- 1) Analysis performed by Agvise Inc. on 13 August 1991;
- 2) Analysis performed by Agvise Inc. on 4 February 1992;
- 3) Analysis performed by A&L Great Lakes Laboratories Inc. on 29 March 1993;
- 4) Value recalculated by the RMS using the following equation: $pH_{H_2O} = 0.982 pH_{CaCl_2} + 0.648$;
- 5) Value calculated from the corresponding pH in water;
- 6) Value calculated by RMS using the following relationship: OC = OM/1.724.

The experimental conditions in the experiment are presented below summarised below in the table B.8.1.1.2.1.1._CA-132.

Table B.8.1.1.2.1.1._CA-132: The experimental conditions in the experiment.

Study	Test soil		Incubation temperature <i>T</i> [°C]	Experimental conditions	
	Name	Type (USDA classification)		Soil moisture	
				In experiment	Reference value at ½bar
<i>Pangilinan and Smith; 1994a</i>	Howe, Indiana	Sandy loam	21 ± 1	75% of ½ bar	13.1%

The not processed input data used in the kinetic analysis are presented below in the table B.8.1.1.2.1.1._CA-133. Only the averages of two replicates are given as only such were provided in the source study report.

Table B.8.1.1.2.1.1._CA-133: The not processed data obtained in **Howe, Indiana**, Sandy loam soil (study by [Pangilinan and Smith; 1994a]) used as input in kinetic analysis.

Time Point – DAT ¹⁾ [days]	Concentration, expressed as [% AR], of:	
	<i>Flufenacet</i>	<i>FOE Thiadone</i>
0	100.6	1.2
7	87.7	3.9
14	81.6	2.6
32	69.7	1.4
90	66.7	1.0
181	54.5	1.0
270	48.0	1.4
368	43.7	0.9

Footnotes to the table:

1) DAT stands for “Days After Treatment”;

The data presented above were subjected to a multistep evaluation procedure performed in line with the recommendations of FOCUS Kinetics Guideline [FOCUS; 2006]. It consisted of the following steps:

- **Step 1:** Processing of the raw input data;
- **Step 2:** Kinetic evaluation of the processed data using the following 1st – order kinetic models: SFO, FOMC and DFOP, and KinGUI 2 as a modelling tool. That step consisted of the two sub-steps:
 - **Sub-step 1:** kinetic evaluation of the data for parent compound (Flufenacet) only, in order to determine the appropriate kinetic model. At that stage of analysis all three kinetic models listed above were tested;
 - **Sub-step 2:** kinetic evaluation of the data for parent compound (Flufenacet) and its degradation products using for Flufenacet the kinetic model identified at previous stage as appropriate, and SFO model for degradation products;
- **Step 3:** Evaluation of the results of kinetic examination of the data;
- **Step 4:** Reporting of the obtained results, in particular kinetic parameters recommended for modelling.

The raw input data, presented in the table B.8.1.1.2.1.1._CA-133, were processed following the recommendations given by FOCUS. In general terms that looked as follows:

- Measured and reported true replicates were taken into account singularly;
- The data sets were checked for their consistency and clear outliers. In case the outliers were found and removed, that was clearly indicated.
- All data after the time point DAT 32 were removed. That was due to the fact that the collapse of soil microbial activity was observed after that time point. RMS stated that the measure taken by the Applicant was in line with the provisions of FOCUS Kinetics Guidance Document, [FOCUS; 2006].

The particular measures taken in the processing of the data for the parent compound – Flufenacet, were following:

- The total AR recovery recorded in DAT-0 sample – 102.7% AR, was used as concentration of Flufenacet at that time point, but the M_0 value was allowed to be estimated by the model;
- Values between LOD and LOQ were set to measured values;

- All single values <LOD or the non-detects (n. d.) were set to $\frac{1}{2}$ LOD. The same procedure was applied to the first appearances. However, when the values <LOD/n.d. appeared consecutively for second and next times, the kinetic curve was cut off until the appearance of the first value >LOQ.

The values for degradation product – FOE Thiadone, were processed in a following way:

- The initial, DAT-0, concentration was set to 0. That value, unlike the free-fitted M_0 concentration for the parent compound, was a fixed value;
- The values for subsequent time points, if reported as <LOD or non-detects, were also set to 0 until the last time point before the first detectable amount was recorded;
- The value reported as <LOD/n.d. appearing just before the first detectable amount was recorded was set to $\frac{1}{2}$ LOD.
- Values between LOD and LOQ were set to measured values;
- In the decline phase the first values <LOD/n.d. were also set $\frac{1}{2}$ LOD. For the consecutive second and next such appearances the kinetic curve was cut off until, eventually, the first value >LOQ appeared.

RMS noted that the presented above procedure of data-processing is a general procedure used by the Applicant for all experiments that underwent kinetic examination of the data.

In this particular case however, as there were no values below LOQ or LOD, as well as the “non-detects” were not reported, these elements were not performed as a part of data-processing.

The processed values used as input data for the kinetic examination are presented below in the table B.8.1.1.2.1.1._CA-134.

Table B.8.1.1.2.1.1._CA-134: The processed residue data for **Howe, Indiana**, Sandy loam soil (study [Pangilinan and Smith; 1994]).

Time Point – DAT ¹⁾ [days]	Concentration, expressed as [% AR], of:	
	<i>Flufenacet</i>	<i>FOE Thiadone</i>
0	102.7	0.0
7	87.7	3.9
14	81.6	2.6
32	69.7	1.4

Footnotes to the table:

1) DAT stands for “Days After Treatment”;

The processed data were kinetically examined using KinGUI ver. 2 modelling tool, developed by Bayer. The optimisation was performed using IRLS (Iteratively Reweighed Nonlinear Least Squares) algorithm. The fitting procedure was two-stage one. The first step, further called **Step 1**, consisted on the determination of the appropriate kinetic model for the parent compound – Flufenacet. At that stage three 1st-order kinetic models were tested: SFO, FOMC and DFOP. During the next stage, further called **Step 2**, the whole data set – data for the Flufenacet and its degradation products, was kinetically examined. In case of Flufenacet the tested kinetic model was that determined as appropriate at **Step 1**, while for the degradation products the SFO model was used.

The conceptual metabolic pathway built in the modelling tool was based on the transformation pathway which, in form of simplified scheme, is presented below on figure B.8.1.1.2.1.1._CA-51.

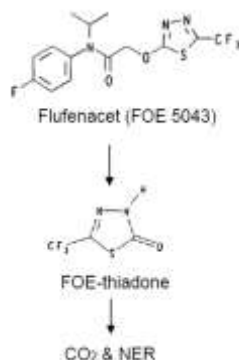


Figure B.8.1.1.2.1.1._CA-51: The simplified transformation pathway used to create conceptual transformation scheme assumed in the modelling tool (copied from the study report).

The obtained results of the kinetic analysis of the data were evaluated by the Applicant. That was done by means of a detailed statistical analysis comprising the following components:

- visual assessment of the fit;
- χ^2 -error statistics;
- t-test significance;
- correlation analysis.

The detailed characteristic of the evaluation procedure was presented in the summary of the **Study 2** on pages 168 – 169. RMS decided not to repeat it here in order to not overburden the Renewal Assessment Report.

On that basis the following multistep assessment procedure was followed:

- **Step 1:** bearing in mind the aim of the kinetic evaluation of the data – determination of the kinetic parameters used in modelling, the SFO kinetic model was tested as first option and if passed the acceptance criteria (visually acceptable, χ^2 -error not exceeding or not significantly exceeding 15%, *prob.* > *t* value in t-test less than 0.05 for parent and 0.10 for the degradation products), it was considered acceptable;
- **Step 2:** in case the χ^2 -error was significantly greater than 15%, model parameters were fixed and fitting repeated using SFO model;
- **Step 3:** if the **Step-2** fitting failed the χ^2 -error test, bi-phasic models were included. These were FOMC, DFOP and, possibly, HS. The model with smaller error was indicated as the most appropriate;
- **Step 4:** if none of the bi-phasic model returned significantly improved fit, SFO model was selected if visually acceptable; that was done in order to avoid of an over-parameterised model based on a marginally better fit.

Analysing the proposed assessment procedure RMS stated that it complied with the procedure for determination of the kinetic endpoints for modelling, presented in FOCUS Kinetics Guidance Document [FOCUS; 2006]. RMS also noticed that the data set used in kinetic analysis consisted of four experimental points only. Therefore, although the Applicant performed the kinetic analysis using two bi-phasic fits – FOMC and DFOP, but in RMS's opinion the data set consisting of only four data points may be too small to obtain reliable kinetic parameters for bi-phasic kinetic models, even if the results of the fitting (visual fit and its statistical evaluation as well as statistically determined reliability of the estimated parameters) are good.

The analysis for the data-set was a two-step analysis. At **Step 1** the appropriate kinetic model for the parent – Flufenacet, was identified. At **Step 2** the data for the degradation product – FOE Thiadone were added and the kinetic analysis repeated using the identified appropriate kinetic model for Flufenacet and SFO model for the degradation product. Its results are presented below, individually for each step.

a) Results obtained at **Step 1** – fitting of the data for the parent compound (Flufenacet) alone:

The results of the kinetic analysis performed by the Applicant are presented below, in graphical form on figure B.8.1.1.2.1.1._CA-52 and in numerical form in the table B.8.1.1.2.1.1._CA-135. Additionally the table B.8.1.1.2.1.1._CA-136 provides the kinetic endpoints obtained with each of the kinetic models tested.

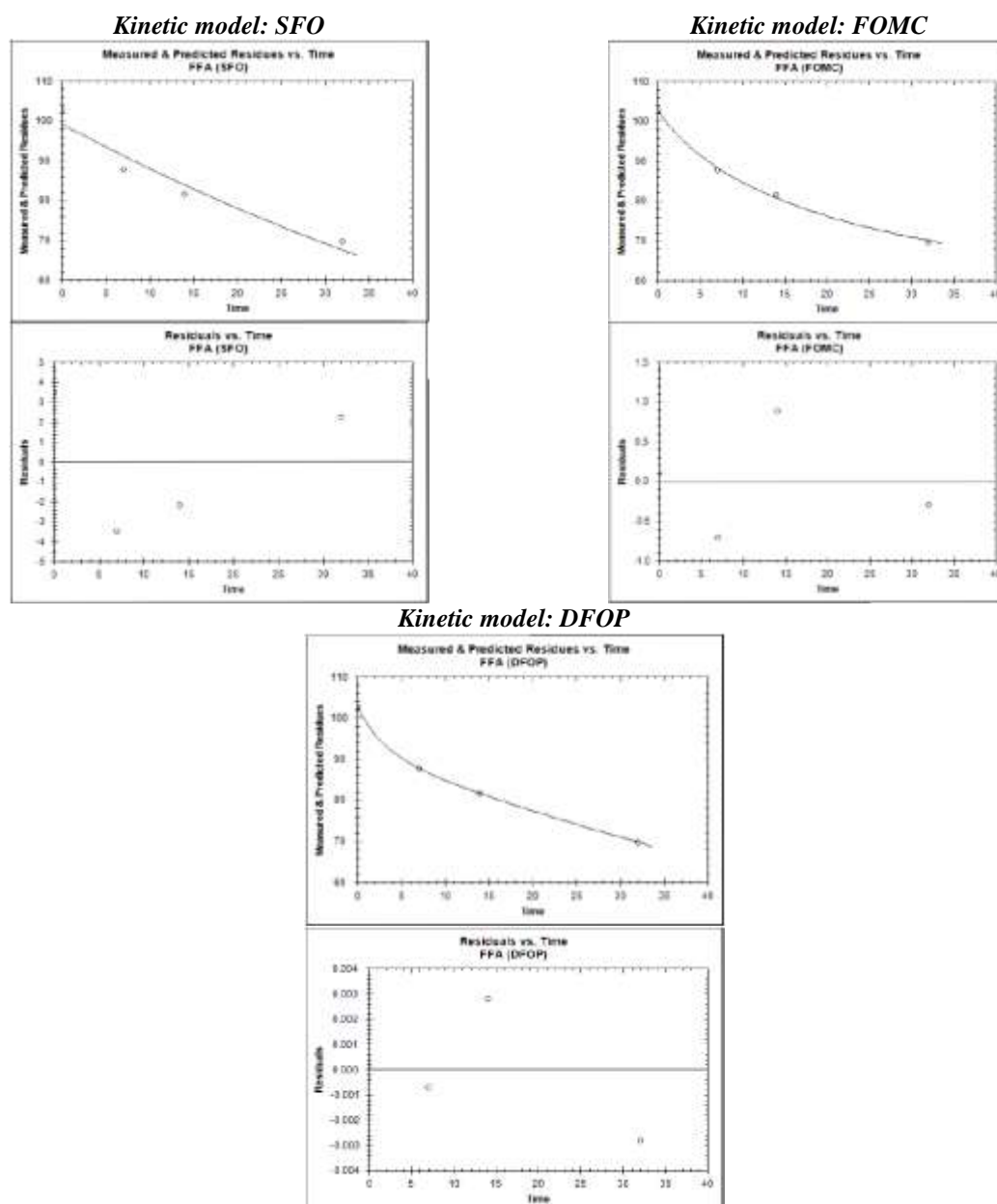


Figure B.8.1.1.2.1.1_CA-52: The graphical results of the kinetic analysis (copied from the study report).

Table B.8.1.1.2.1.1_CA-135: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment ¹⁾
				Lower	Upper			
SFO	M_0	99.169	3.316	92.669	105.668	5.58 E-4	2.796	0.94; Acceptable fit
	k	0.0120	0.00229	0.00755	0.0170	0.0171		
FOMC	M_0	102.590	1.151	100.333	104.846	0.00357	0.703	1.00; Good fit
	α	0.2391	0.05425	0.1328	0.345	0.0710		
	β	8.1089	3.3796	1.4850	14.733	0.1257		
DFOP	M_0	102.70	∞	$-\infty$	$+\infty$	Not determined	∞	1.00; Good fit
	k_1	0.3223	∞	$-\infty$	$+\infty$	Not determined		
	k_2	0.008673	∞	$-\infty$	$+\infty$	Not determined		
	g	0.1042	∞	$-\infty$	$+\infty$	Not determined		

Footnotes to the table:

1) Visual assessment of the kinetic curve as proposed by the Applicant.

Table B.8.1.1.2.1.1_CA-136: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested		
		<i>SFO</i>	<i>FOMC</i>	<i>DFOP</i>
<i>Flufenacet</i>	DT ₅₀ [days]	57.63	139.05	67.231
	DT ₉₀ [days]	191.42	123215	252.79

The Applicant stated that the fit returned by the SFO model was visually and statistically acceptable, therefore it was selected as appropriate and used at the next step to kinetically examine the data for Flufenacet and its degradation products. RMS accepted that choice. It shall be noted that although FOMC returned the fit visually and statistically superior to that obtained with SFO and for which estimated parameters were reliable, it cannot be taken into account as the concentration recorded at the last time point was significantly higher than 10%. Also DFOP returned the fit that was visually better than that obtained with SFO. It was however statistically not reliable.

- b) Results obtained at **Step 2** – fitting of the data for the parent compound (Flufenacet) and its degradation products:

The results of the kinetic analysis performed by the Applicant are presented below, in graphical form on figure B.8.1.1.2.1.1_CA-53 and in numerical form in the table B.8.1.1.2.1.1_CA-137.

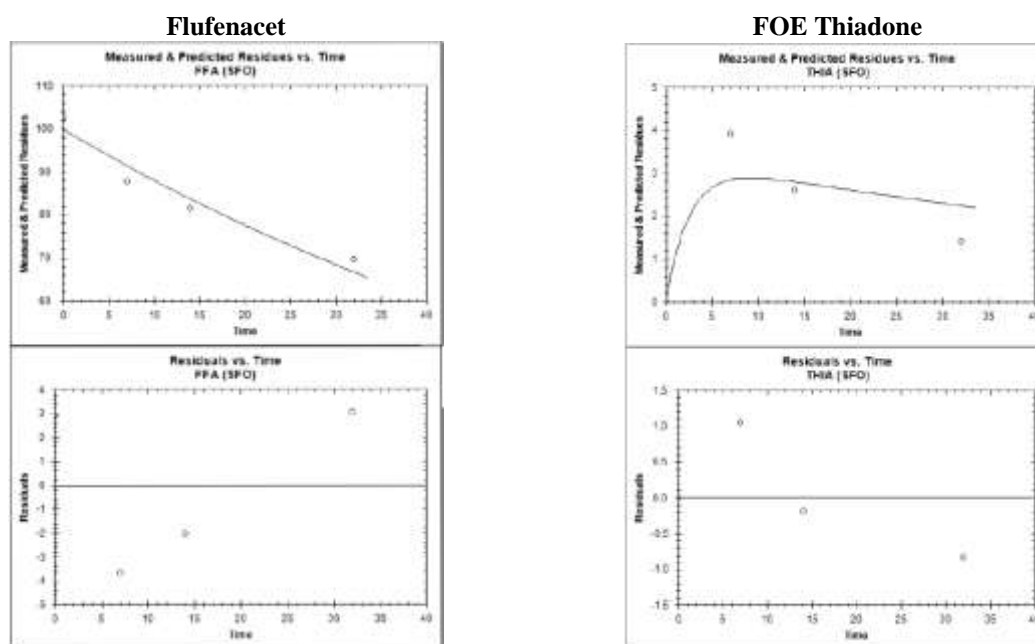


Figure B.8.1.1.2.1.1_CA-53: The graphical results of the kinetic examination of the data for Flufenacet and FOE Thiadone (copied from the study report).

Table B.8.1.1.2.1.1._CA-137: The numerical results of the kinetic examination of the data for Flufenacet and FOE Thiadone.

Compound	Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
			Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment ¹⁾
					Lower	Upper			
Flufenacet	SFO	M ₀	99.789	3.327	93.269	106.309	3.68 E-5	2.841	0.94; fit acceptable
		k	0.0126	0.00229	0.00813	0.0170	0.00264		
FOE Thiadone	SFO	M ₀	0.0	----	----	----	----	26.352	0.78; poor fit
		k	0.3885	0.2769	-0.1542	0.931	0.1166		
		ff	1.00	----	----	----	----		

Footnotes to the table:

1) Visual assessment of the kinetic curve as proposed by the Applicant.

Applicant stated that reliable kinetic endpoints from that kinetic fitting could be derived only for the parent compound – Flufenacet. The fit for FOE Thiadone was visually poor and statistically unreliable, therefore it was not possible to derive kinetic endpoints or even the kinetic formation fraction *ff*.

The reliable kinetic endpoints determined for Flufenacet were following: **DT₅₀ = 54.96 days** and **DT₉₀ = 182.56 days**.

RMS noticed however that the distribution of the data points for FOE Thiadone at would-be decline phase suggested that it was possible to obtain the acceptable fitting results in that experiment for that compound fitted alone using the top-down approach.

Such analysis was performed by the RMS using CAKE 3.1 modelling tool. IRLS (Iteratively Reweighed Nonlinear Least Squares) was used as optimisation algorithm. Due to very limited amount of the experimental points – only three were available, SFO model was solely tested. The data set used in that fitting is presented below in the table B.8.1.1.2.1.1._CA-138.

Table B.8.1.1.2.1.1._CA-138: The input data for FOE Thiadone used in the repeated kinetic analysis performed by the RMS.

Time Point – DAT [days]	Concentration of FOE Thiadone, expressed as [%AR]
7	3.9
14	2.6
32	1.4

The results are presented below, in graphical form on figure B.8.1.1.2.1.1._CA-54 and in numerical form in the table B.8.1.1.2.1.1._CA-139.

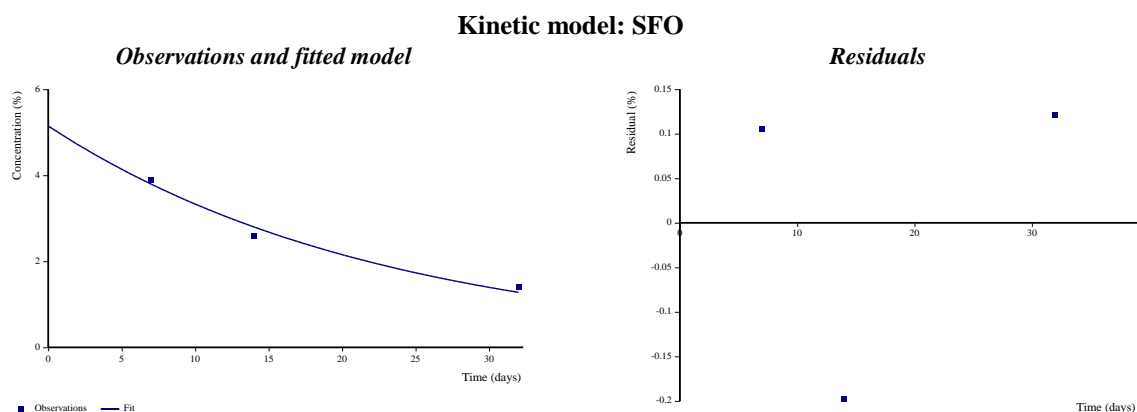
**Figure B.8.1.1.2.1.1._CA-54:** The graphical results of the kinetic analysis.

Table B.8.1.1.2.1.1._CA-139: The numerical results of the kinetic examination of the data for FOE Thiadone using the top-down approach.

Compound	Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
			Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment
					Lower	Upper			
FOE Thiadone	SFO	M ₀	5.146	0.526	-1.540	11.830	----	4.95	0.980; good fit
		k	0.04352	0.00798	-0.05794	0.1450	0.05776		

The kinetic re-examination of the data showed that it was possible to obtain the reliable fit for FOE Thiadone fitted alone using the top-down approach.

The calculated rate constant did not pass the t-test – the *prob. > t* was slightly above the threshold value of 0.05, but that may be related to the limited data base. Therefore the obtained kinetic endpoints presented below should be considered with care.

The model returned following kinetic endpoints: **DT₅₀ = 15.9 days** and **DT₉₀ = 52.9 days**. RMS noticed that these values were much higher than those determined for the same compound in **Study 7**. They were also higher than the kinetic endpoints obtained for FOE Thiadone in another study, summarised below as **Study 18**, in which FOE Thiadone was applied as a parent compound.

The final set of the kinetic parameters considered acceptable by the RMS is presented below in the table B.8.1.1.2.1.1._CA-140. It shall be also indicated that these values are not-normalised values, requiring normalisation before being used to calculate the averaged kinetic endpoint to be used in GW and SW modelling. That will be done separately further down the Report.

Finally, it shall be also pointed out that because at **Step 2** of the kinetic analysis it was not possible to obtain the robust kinetic fit for FOE Thiadone, RMS decided not to use the proposed by the Applicant default value of the kinetic formation fraction – *ff* = 1 as reliable endpoint in further assessment. Also, because of the lack of reliability of the fit for FOE Thiadone at Step 2, it was not justifiable to use in the further assessment the results of the fitting for Flufenacet obtained at that step. Therefore RMS decided to consider reliable for the further assessment the results for Flufenacet obtained at **Step 1**.

Table B.8.1.1.2.1.1._CA-140: The reliable set of the kinetic parameters determined in the experiment

Determined parameter	Compound	
	Flufenacet	FOE Thiadone
DT ₅₀ [days]	57.63	15.9
DT ₉₀ [days]	191.42	52.9
Kinetic formation fraction <i>ff</i>	Not applicable	Not determined
Precursor	Not applicable	-----
Kinetic model	SFO	SFO – top-down approach

Next fourteen studies, summarised below, are examining the rate of degradation of four degradation products of Flufenacet – FOE Sulfonic acid, FOE Methylsulfone, FOE Thiadone and Trifluoroacetic acid, for which it was either not possible to obtain reliable kinetic endpoints examining the data coming from the route studies, or the obtained results were not sufficient to calculate the reliable kinetic endpoints to be used in modelling. Applicant submitted flowing studies:

- for FOE Sulfonic acid seven studies were submitted, of which three were “old studies” and three new/newly submitted ones; two of them were found by the RMS to be not relevant for the current evaluation;
- for FOE Methylsulfone three studies were submitted, all identified as new/newly submitted studies;
- for FOE Thiadone two studies were submitted, both new/newly submitted studies;
- for Trifluoroacetic acid two studies, both new/newly submitted studies, were submitted.

Study 9:

Report: Hellpointner E., (1996): “Degradation of [Phenyl-UL-¹⁴C]FOE 5043-Sulfonic Acid in Three Soils.”; Bayer AG, Crop Protection Business Group, Crop-Protection Development, Agrochemicals Division, Development, Institute for Metabolism Research and Residue Analysis, D51368 Leverkusen; Germany for Bayer Corporation, Agriculture Division, P. O. Box 4913, Hawthorne Road, Kansas City, MO 64120-0013, USA; unpublished Report No. PF 4110 (Bayer Report Number 107515); 8 January 1996; ; study reference number: M-004098-01-2;

Guidelines: The study was performed to comply with the following Guidelines:

- BBA Guidelines for the Official Testing of Plant Protectants, Part IV, 4-1 (1986);
- SETAC-Europe Procedures for Assessing the Environmental Fate and Ecotoxicology of Pesticides (*ed.* Mark Lynch), March 1995;
- US. EPA Guideline 162-1 Aerobic Soil Metabolism (supplemental);

GLP: Yes;

RMS comments: The study had been evaluated for the previous authorisation of Flufenacet in the EU, by its inclusion into the Annex I of the Directive 91/414/EEC. Its summary can be found under the point B.7.1.2.1.1.2.2., in section B.7 of the Annex B to the Monograph prepared by the RMS – France, for Flufenacet. The study was evaluated for its compliance with OECD Guideline 307 – Aerobic and Anaerobic Transformation in Soil. RMS stated that the study complied with the provisions of the reference Guideline, therefore it can be considered acceptable for the present assessment. It is summarised below.

Summary:

The aim of the study was to examine the degradation of FOE 5043-Sulfonic acid (FOE Sulfonic acid) – the major degradation product of Flufenacet, in soil under aerobic conditions in order to determine its rate of degradation. The experiment was performed on three European (German) soils. Their characteristic is given below in the table B.8.1.1.2.1.1._CA-141. In the study report it was stated that the test soils had been used in several other studies and met the requirements of the registration authorities; the statement provided most probably as a justification of their selection.

The test soils BBA 2.1 and BBA 2.2 were stored prior to the experiment in a wooden boxes, havingh the dimensions of 70 cm x 80 cm x 40 cm (length/width/depth) and wodden bottom plate permeable for water, outdoors during vegetation period and in a greenhouse at T = 16⁰C in winter. Each box was filled with approx. 35-cm layer of soil. Grass was used as crop cover. Third test soil – Laacherhof, was freshly sampled from the nearby field.

Table B.8.1.1.2.1.1._CA-141: The characteristic of soils used in the study.

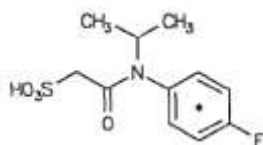
Parameter			Soil		
Soil origin			<i>BBA 2.1</i>	<i>BBA 2.2</i>	<i>Laacherhof</i>
Soil type (in the DAR)			Germany; EU	Germany; EU	Germany; EU
Soil type (USDA; reported in the study)			Sand	Loamy sand	Silt Loam
Particle size distribution	Sand [%]		89.4	80.5	36.9
	Silt [%]		10.5	12.3	51.1
	Clay [%]		0.1	7.2	12.0
pH value in H ₂ O			5.9	Not determined	8.1
pH value in CaCl ₂			5.3	6.3	7.3
Organic carbon content (C _{org}) [%]			0.57	2.48	0.9
Cation Exchange Capacity – CEC [mEq/100g]			5	10	8
Soil moisture at 40% MWHC [g H ₂ O/100 g soil d. w.]			9.0	17.9	14.0
Soil moisture at 75% of ½ bar [g H ₂ O/100 g soil d. w.]			9.2	16.1	15.5
Soil density [mg/cm ³]			2.59	2.45	2.40
Soil biomass expressed in mg microbial C/kg soil ¹⁾	Control (no test compound)	DAT 0	111	390	780
		DAT 100	n. m. ⁴⁾	115	188
	Treated with test compound ³⁾	DAT 0	90	381	812
		DAT 100	n. m. ⁴⁾	138	145
Soil biomass expressed as %OC ²⁾	Control (no test compound)	DAT 0	1.95	1.57	3.25
		DAT 100	----	0.46	0.49
	Treated with test compound ³⁾	DAT 0	1.58	1.56	3.38
		DAT 100	----	0.56	0.60

Footnotes to the table:

- 1) The soil microbial biomass was determined in soil samples using Anderson and Domsch method;
- 2) Values calculated by the RMS using the OC content reported in the study report for each test soil;
- 3) Samples were treated with 375-μL aliquots of application solution containing solely non-radiolabelled test compound; the amount of the test substance introduced was 40 μg/sample;
- 4) Not measurable, Applicant stated that most probably due to the extreme dryness of soil.

The test soils were gently air-dried about 1 week before the experiment began, sieved through 2-mm sieve and analysed for their moisture content. Then 100-g aliquots of each test soil were weighed into 300-mL Erlenmeyer flasks and adjusted to soil moisture level of 75% of ½ bar, roughly corresponding to about 40% MWHC, with the appropriate amount of demineralised water. So prepared test vessels were once again weighed, closed with cotton-wool plug and pre-incubated for 7 days in the dark at T = 20°C. The number of so prepared test vessels was such to obtain for each test soil duplicate samples per each sampling point and samples for determination of soil biomass (further called **Control samples**) at the beginning and the end of the incubation period (lasting 100 days).

The test substance used in the experiment was the ¹⁴C-FOE Sulfonic acid, in form of ammonium (NH₄⁺) salt, radiolabelled uniformly in phenyl ring, as shown below on figure B.8.1.1.2.1.1._CA-55 (RMS noticed that the structure presented on in the study report was that for acid, not its ammonium salt).

**Figure B.8.1.1.2.1.1._CA-55:** The structural formula of the radiolabelled FOE Sulfonic acid used in the experiment (copied from the study report).

The specific activity of the test compound was 2.846 MBq/mg, corresponding to 22.4 mCi/mmol and its radiochemical purity, determined by TLC, was 99.3%.

Also the non-radiolabelled test compound was used, having chemical purity of 93.6% (with 5.79% of water).

The whole delivered amount of radiolabelled test compound was dissolved in 10 mL of the H₂O/CH₃CN 9:1 (v/v) to obtain the stock solution. The concentration of the test compound in that solution, determined by LCS in three 50-μL aliquots, was 92.48 kBq/mL, corresponding to ~0.032 mg/mL. That solution will be further called **Stock solution 1**.

Also the stock solution of the non-radiolabelled test compound was prepared, having the nominal concentration of 1.8 mg/mL. That was done by dissolving 19.23 mg of the technical non-radiolabelled test compound (corresponding to 18.0 mg of the pure compound, assuming the purity of the test compound 93.6%) in 100 mL of the H₂O/CH₃CN 9:1 (v/v). That solution will be further called **Stock solution 2**.

Next the total amount of the **Stock solution 1** was mixed with 10 mL of the **Stock solution 2** to obtain the **Application solution**. The total volume of the **Application solution** was 19.85 mL, and its concentration was 40 µg of FOE Sulfonic acid/375 µL. The specific radioactivity of the test compound in the **Application solution** was 0.4297 kBq/ µg and solution's radiochemical purity – 97.2% when determined by HPLC and 95.4% when determined by TLC.

The characterised above **Application solution** was used to treat test soils in each test vessel. The assumed application dose was 40 µg test compound/100 g of the test soil (d. w.), corresponding to the application rate of 300 g test compound/ha, assuming soil density of 1.5 g/cm³ and the depth of soil layer of 5 cm (standard assumptions). The application rate was calculated assuming the maximum recommended application rate for Flufenacet of 750 g/ha and 40%-conversion of that compound to FOE Sulfonic acid. To obtain the target application dose, to each test vessel 375-µL aliquots of the **Application solution** were introduced by pipetting it in small droplets onto the soil surface. The exact application dose was subsequently verified. It was determined to be 36.8 µg FOE Sulfonic acid/100 g of the test soil (d. w.).

After application the test vessels were closed with tower traps for volatile compounds. The so obtained incubation vessels looked as presented below on the figure B.8.1.1.2.1.1._CA-56.

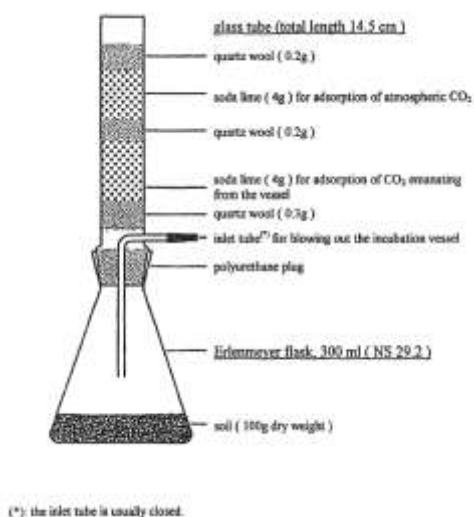


Figure B.8.1.1.2.1.1._CA-56: The example incubation vessel used in the experiment (scheme copied from the study report).

So prepared incubation vessels were placed in the dark, in a temperature-controlled incubation chamber and incubated at $T = 20 \pm 2^{\circ}\text{C}$ for up to 100 days. The temperature in the incubation chamber was recorded continuously with circular charts changed on every 7th day. Treated samples were removed for the analysis at DAT (Days After Treatment) 0, 0.08 (after 2 hours), 3, 7, 14, 30, 63, 80 and 100.

At these time points also soil moisture was adjusted. That was done in all samples not taken to the analysis in a following way: all test vessels were ventilated for 10 minutes with air, introduced for the first 5 minutes at rate 1 mL/s. and then at rate 10 mL/s., to transfer all volatile compounds present in the headspace above the soil surface to the traps for volatile compounds. Then they were dissected the Erlenmayer flasks containing test soil samples weighed to determine the loss of water and replenishing it adequately. Then the tower traps were set and the incubation vessels returned to the incubation chamber.

For each test soil the **Control samples** were set. They were prepared in two variants – as samples not treated with the test compound (Bio-) and treated with the test compound (Bio+) samples. The “BIO+” samples were treated in a way identical to described above for the test samples, with exception that the treatment solution contained solely non-radiolabelled test compound. Two sets of the **Control samples** were prepared – DAT-0 samples analysed at the beginning of the experiment and DAT-100 samples incubated for 100 days as all other samples and analysed for the soil microbial activity at the end of the whole incubation period. The DAT-100 samples were prepared and maintained as all remaining samples, with exception that their soil moisture content was not controlled and corrected during incubation period.

The test vessels removed for analysis were also ventilated for 10 minutes with air, introduced for the first 5 minutes at rate 1 mL/s. and then at rate 10 mL/s., to transfer all volatile compounds present in the headspace above the soil surface to the traps for volatile compounds. Then the test vessels were dissected and the content of volatile traps analysed for the radioactivity content.

Soil samples from the Erlenmeyer flasks were then entirely transferred to the centrifuging beakers and extracted using three-step procedure, looking as follows:

- Step 1: extraction by shaking for 60 minutes at room temperature with 50 mL of water, followed by centrifugation at ~10,000 g for ~15 minutes; clear supernatants were decanted by filtering through paper filters to collect suspended particles (**Filter 1**), their volumes measured and three 100- μ L aliquots analysed by LSC while the remaining extracts stored for further analysis by TLC;
- Step 2: extraction by shaking for 60 minutes at room temperature with 50 mL of $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ solution, followed by centrifugation at ~10,000 g for ~15 minutes; clear supernatants were decanted by filtering through the same paper filters as used at Step 1 to collect suspended particles (**Filter 1**), their volumes measured and three 100- μ L aliquots analysed by LSC while the remaining extracts stored for further analysis by TLC;
- Step 3: extraction by shaking for 60 minutes at room temperature with 50 mL of 0.01N HCl_{aq} in CH_3CN solution, followed by centrifugation at ~10,000 g for ~15 minutes; clear supernatants were decanted by filtering through paper filters to collect suspended particles (**Filter 2**), their volumes measured and three 100- μ L aliquots analysed by LSC while the remaining extracts stored for further analysis by TLC.

The **Filter 1** and **Filter 2** together with retained particles were pressed to pills, combusted and resulting $^{14}\text{CO}_2$ quantified. Also the radioactivity remaining in extracted soil pellets was quantified. That was done by combusting three 1-g aliquots of dried and homogenised soil pellets, and measuring the amount of formed $^{14}\text{CO}_2$ by LSC.

The radioactivity measured for each sample in both **Filters** and extracted soil pellet was subsequently considered to form the NER fraction.

The volatile traps were dissected into polyurethane plugs, which were not further processed (it was stated that they contained no substantial amount of radioactivity), and soda lime filling, processed to determine the amount of captured $^{14}\text{CO}_2$ formed during incubation. That was done by dissolving soda lime in 60 mL of 18% HCl_{aq} in an apparatus presented below on figure B.8.1.1.2.1.1._CA-57. Liberated $^{14}\text{CO}_2$ was absorbed in a suitable scintillation cocktail and analysed by LSC.

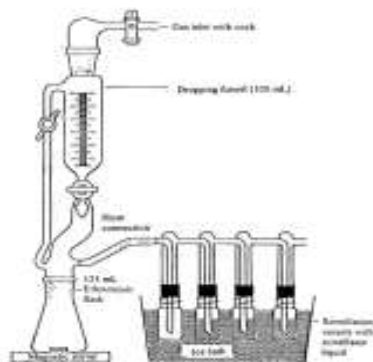


Figure B.8.1.1.2.1.1._CA-57: The apparatus used for the liberation of $^{14}\text{CO}_2$ (scheme copied from the study report).

All liquid samples were analysed for their radioactivity content using LS6000LL (Beckmann 6500) liquid scintillation counter. The scintillation cocktail declared to be used was Instant Scint Gel[®].

In case of the aqueous soil extracts – water extracts and $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ extracts, the volume of analysed sample was 2 mL, the counting time was 10 minutes and the average background (BKGD) – 19 cpm. The minimum sensitivity of LSC analysis for these samples was 2.01 E-4 ppm. When expressed as Lowest Acceptable Gross Count Rate (LAGC) it was 943 cpm, while as Lowest Acceptable Net Count Rate (LANC) – 924 cpm. The greatest probable error GPE = 2.1%. Limit of sensitivity was set to 2*BKGD – 38 cpm.

In case of organic soil extracts – 0.01N $\text{HCl}_{\text{aq}}/\text{CH}_3\text{CN}$ extracts, the volume of analysed sample was 2 mL, the counting time was 10 minutes and the average background (BKGD) – 19 cpm. The minimum sensitivity of LSC analysis for these samples was 1.24 E-5 ppm. When expressed as Lowest Acceptable Gross Count Rate (LAGC)

it was 76 cpm, while as Lowest Acceptable Net Count Rate (LANC) – 57 cpm. The greatest probable error GPE = 9.5%. Limit of sensitivity was set to $2 \times \text{BKGD}$ – 38 cpm.

The $^{14}\text{CO}_2$ generated during the combustion of extracted soil pellets was absorbed in Oxisolve C 400 (Zinsser Analytic) scintillation cocktail and quantified using PW4700 (Raytest Co) LS Counter or LKB 1219 (Wallac Oy.) LS Counter.

The initial amount of the analysed sample was 1.0 g, the counting time was 10 minutes and the average background (BKGD) – 24 cpm. The minimum sensitivity of LSC analysis for these samples was 1.05 E-4 ppm . When expressed as Lowest Acceptable Gross Count Rate (LAGC) it was 236 cpm, while as Lowest Acceptable Net Count Rate (LANC) – 212 cpm. The greatest probable error GPE = 4.1%. Limit of sensitivity was set to $2 \times \text{BKGD}$ – 48 cpm.

Similar parameters were recorded in case of LSC analysis for paper filters. The only difference consisted on initial amount of analysed sample – it was <500 mg.

All extracts were analysed qualitatively and quantitatively – for identification and quantitation of FOE Sulfonic acid, using TLC.

The TLC analysis was performed on silica gel 60 plates coated by F-254 (Merck, Co.) developed in glass chamber with following solvent system: $\text{CH}_3\text{CN}/\text{CH}_3\text{CHOHCH}_3/\text{CH}_3\text{COOC}_2\text{H}_5/\text{H}_2\text{O}$ 60:9:6:3 (v/v/v/v) solution ($\text{CH}_3\text{CHOHCH}_3$ stands for 2-propanol and $\text{CH}_3\text{COOC}_2\text{H}_5$ for ethyl acetate).

The identification of the test compound was performed by means of the comparison of the R_f values for the analysed sample with those of the known standards.

The quantitative analysis – radioactivity counting, was performed using BIO imaging analyser (Fuji Co.). The LOD (determination limit) for a single peak was <0.5% AR.

Results and their discussion:

The results of the determination of soil moisture, soil pH and soil microbial activity in each test soil are presented below in the table B.8.1.1.2.1.1._CA-142. In the study report it was indicated that in samples incubated for 100 days the soil moisture content was not checked and corrected during the incubation period, what resulted in observed decrease in microbial activity. Therefore the results of the soil biomass determination obtained for the DAT-100 samples should be considered with care when used to decide on the validity of the study, as they may not represent the situation in the test samples, adjusted for the soil moisture at each sampling point.

Table B.8.1.1.2.1.1._CA-142: The results of the determination of the soil microbial activity, soil moisture content and soil pH in the **Control samples**.

Test soil	Type of sample	Results obtained for DAT-0 samples				Results obtained for DAT-100 samples			
		Determination of soil biomass		Soil moisture content [%]	Soil pH in KCl	Determination of soil biomass		Soil moisture content [%]	Soil pH in KCl
		[mg microbial C/kg soil]	%OC			[mg microbial C/kg soil]	%OC		
BBA 2.1	BIO- ¹⁾	111	1.95	7.1	4.8	n. m ³⁾	----	0.4	4.5
	BIO+ ²⁾	90	1.58	5.6	4.9	n. m ³⁾	----	0.4	4.5
BBA 2.2	BIO- ¹⁾	390	1.57	12.9	5.5	115	0.46	7.0	4.9
	BIO+ ²⁾	381	1.56	14.0	5.5	138	0.56	7.9	4.9
Laaherhof	BIO- ¹⁾	780	3.25	12.6	6.9	188	0.49	7.6	6.8
	BIO+ ²⁾	812	3.38	14.1	7.1	145	0.60	7.0	6.8

Footnotes to the table:

- 1) Samples not treated with the test compound;
- 2) Samples treated with the non-radiolabelled test compound in amount (nominal) 40 µg/sample;
- 3) Not measurable; in the study report this was attributed to the extreme dryness of the test soil.

The level and uniformity of the application dose was checked at application by LSC in 100-µL aliquots of the **Application solution**. The results are presented below in the table B.8.1.1.2.1.1._CA-143.

Table B.8.1.1.2.1.1._CA-143: The results of the determination of the level and uniformity of application dose.

Parameter determined in/as:	Measured values					
	Radioactivity in sample [Bq/100 μ L]				Statistical evaluation	
	Replicate 1	Replicate 2	Replicate 3	Mean	SD [Bq/100 μ L]	RSD [%]
<i>SAS1 sample¹⁾</i>	165.25	165.45	165.29	165.33	0.11	0.06
<i>SAS2sample²⁾</i>	166.9	164.01	165.21	165.37	1.45	0.88
<i>SAS3 sample³⁾</i>	165.64	166.32	165.85	165.93	0.35	0.21
<i>Mean</i>	165.93	165.26	165.45	165.55	0.64	0.38
<i>SD [Bq/100 μL]</i>	0.86	1.17	0.34	0.34	0.81	----
<i>RSD [%]</i>	0.52	0.71	0.21	0.20	----	----

Footnotes to the table:

- 1) Application solution sampled prior to the first application;
- 2) Application solution sampled after treatment of the half of the test vessels;
- 3) Application solution sampled after all test vessels were treated with the test compound;

The presented above results conformed the uniformity of the application for each test vessel. It was also stated that the level of applied radioactivity was 16.55 kBq/vessel – the value defined as 100% AR. When the radiochemical purity of the test compound was taken into account the treatment level was determined to be 15.79 kBq/vessel, corresponding to 36.8 μ g FOE Sulfonic acid/test vessel.

The value of 16.55 kBq/vessel, determined to be 100% AR was subsequently used in reporting the results as DAT-0 value for all test soils. Other data for DAT-0 samples (e. g. amount of AR extracted from soil) were not reported.

The obtained results showed good recovery of AR, within the limits recommended by the relevant Guidelines (OECD 307). It looked as follows:

- in BBA 2.1 soil the total recovery was in range 91.7% – 103% (mean values); the lowest values were observed for DAT-0.1 samples and were attributed to the fact that the filters were combusted without oxygen, therefore the radioactivity was not released as $^{14}\text{CO}_2$;
- in BBA 2.2 soil the total recovery was in range 96.9 – 102.7% (mean values);
- in Laacherhof soil the total recovery was in range 96.7 – 100.0% (mean values).

It was stated that in none of the test soil the time-dependent tendency was observed.

The level of mineralisation, measured by the amount of $^{14}\text{CO}_2$ formed, was not very high, reaching at the end of the study (DAT 100) 10% in BBA 2.1 soil, 11% in BBA 2.2 soil and 14% in Laacherhof soil.

The amount of NER formed was following:

- in BBA 2.1 soil at the end of the study (DAT 100) – ~15% AR;
- in BBA 2.2 soil at the end of the study (DAT 100) – ~19% AR;
- in Laacherhof soil – ~31% AR.

The values were given as a sum of the radioactivity in extracted soil pellets and that retained on filters. It was stated that while in BBA 2.1 and BBA 2.2 soils NER fraction steadily increased with time, no such tendency was observed in Laacherhof soil.

The Applied Radioactivity was recovered mainly in extracts. In case of the two soils – BBA 2.1 and BBA 2.2, the amount of radioactivity extracted decreased with time to reach at the end of incubation period the level of 75.4% AR in BBA 2.1 soil and 66.5% AR in BBA 2.2 soil. In case of Laacherhof soil the situation was more complex, because on DAT 30 and DAT 63 time points the amount of radioactivity in extracts was higher than recorded in preceding and succeeding time points. RMS having analysed the whole data set came to conclusion that these two points may be analytical artifacts, but that should be verified during the kinetic analysis of the data.

It was also noted that in BBA 2.1 and BBA 2.2 soils the extracted radioactivity was predominantly found in water- and water/acetonitrile- extracts, while in case of Laacherhof soil it was more evenly distributed between the three fractions.

The only identified constituent of extracts was FOE Sulfonic acid, decreasing steadily with time to reach at the end of the study (DAT 100) the level of 62.3% AR in both BBA 2.1 and BBA 2.2 soils. More complex picture, with local maximum on DAT 30 and DAT 63, was observed in Laacherhof soil, the phenomenon identical to that observed in that soil for radioactivity extracted.

The detailed results are presented below, separately for each test soil, in numerical and graphical form. All values were rounded to one digit after the decimal point. RMS noticed that there were several discrepancies between the averages, what may be the result of the applied rounding procedure.

The results obtained in BBA 2.1 (Sand) soil are presented below in numerical form in the table B.8.1.1.2.1.1._CA-144 and in numerical form on figure B.8.1.1.2.1.1._CA-58.

Table B.8.1.1.2.1.1._CA-144: The numerical results of the experiment performed on BBA 2.1 soil.

Radioactivity			Measured on DAT									
			0	0.08	3	7	14	30	63	80	100	
In extract [%AR]	Water extract	Rep. 1	----	37.9	33.1	43.5	39.6	39.6	33.9	33.9	30.5	
		Rep 2.	----	42.1	38.4	43.8	40.1	36.4	36.4	32.9	31.0	
		Mean	----	40.0	35.8	43.6	39.9	38.0	35.2	33.4	30.7	
	CH ₃ CN/H ₂ O extract	Rep. 1	----	31.6	40.9	31.1	35.8	28.5	28.6	25.8	28.9	
		Rep 2.	----	32.4	38.0	30.7	33.2	30.6	26.4	26.0	26.9	
		Mean	----	32.0	39.5	30.9	34.5	29.5	27.5	25.9	27.9	
	0.01M HCl/CH ₃ CN extract	Rep. 1	----	15.4	15.4	22.6	17.6	14.0	17.4	18.1	16.9	
		Rep 2.	----	14.6	14.6	16.7	16.0	14.6	17.9	15.4	16.7	
		Mean	----	15.0	15.0	19.7	16.8	14.3	17.6	16.7	16.8	
	Total extracted	Rep. 1	100	84.9	89.4	97.2	93.0	82.1	79.9	77.8	76.3	
		Rep 2.	100	89.1	91.0	91.2	89.3	81.6	80.7	74.3	74.6	
		Mean	100	87.0	90.3	94.2	91.2	81.8	80.3	76.0	75.4	
	Identified (TLC) as FOE Sulfonic acid [% AR]		Rep. 1	----	84.2	83.6	82.8	77.7	78.3	70.0	64.1	64.3
			Rep 2.	----	94.6	84.6	83.0	80.6	76.6	67.2	66.9	62.1
			Mean	----	89.4	84.1	82.9	79.2	77.5	68.6	65.5	63.2
FOE Sulfonic acid recovered [μg]		Mean	36.8	30.51	32.00	32.26	30.25	29.73	27.32	26.16	25.87	
NER fraction [% AR]		Rep. 1	----	2.9	6.1	4.8	5.5	7.5	10.2	10.7	11.0	
		Rep 2.	----	3.0	3.8	4.5	5.6	8.2	9.6	10.4	10.2	
		Mean	----	3.0	4.9	4.7	5.6	7.8	9.9	10.5	10.6	
On filters [% AR]		Rep. 1	----	1.4 ¹⁾	3.1	3.4	2.2	4.2	3.6	2.7	3.3	
		Rep 2.	----	2.1 ¹⁾	2.5	3.2	2.4	2.8	3.6	4.1	4.6	
		Mean	----	1.7	2.8	3.3	2.3	3.5	3.6	3.4	4.0	
Mineralisation – ¹⁴ CO ₂ [% AR]		Rep. 1	----	0.0	0.5	1.2	2.3	4.0	7.9	8.8	10.9	
		Rep 2.	----	0.0	0.2	1.2	2.2	4.2	7.8	8.5	9.5	
		Mean	----	0.0	0.3	1.2	2.0	4.1	7.9	8.6	10.2	
Total radioactivity recovered [% AR]		Rep. 1	100	89.2	106.3	101.6	99.6	101.2	102.4	98.8	101.3	
		Rep 2.	100	94.2	99.7	99.5	97.9	100.0	99.2	98.6	99.6	
		Mean	100	91.7	103.0	100.5	98.7	100.6	100.8	98.7	100.5	

Footnotes to the table:

1) The filters were combusted without oxygen, so radioactivity on them was probably not fully released;

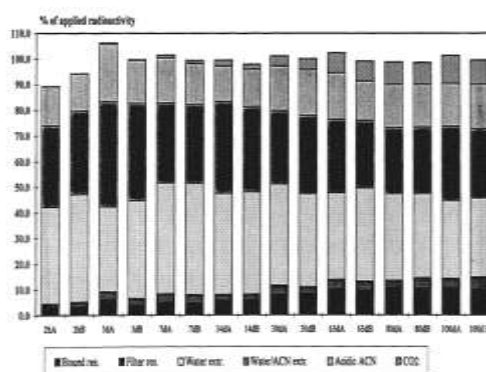


Figure B.8.1.1.2.1.1._CA-58: The graphical results of the determination of the distribution of radioactivity in the test soil BBA 2.1 (scheme copied from the study report).

The results obtained in BBA 2.2 (Loamy sand) soil are presented below in numerical form in the table B.8.1.1.2.1.1._CA-145 and in numerical form on figure B.8.1.1.2.1.1._CA-59.

Table B.8.1.1.2.1.1._CA-145: The numerical results of the experiment performed on BBA 2.2 soil.

Radioactivity			Measured on DAT								
			0	0.08	3	7	14	30	63	80	100
In extract [%AR]	Water extract	Rep. 1	----	30.5	35.1	33.9	31.9	31.7	28.0	24.6	23.2
		Rep 2.	----	33.4	32.5	32.8	33.2	32.1	28.2	23.8	20.9
		Mean	----	32.0	33.8	33.3	32.5	31.9	28.1	24.2	22.1
	CH ₃ CN/H ₂ O extract	Rep. 1	----	33.7	32.4	30.7	31.3	26.7	24.0	21.9	24.5
		Rep 2.	----	38.5	33.5	31.2	30.9	27.0	23.3	23.9	24.2
		Mean	----	36.1	33.0	31.0	31.1	26.9	23.6	22.9	24.4
	0.01M HCl/CH ₃ CN extract	Rep. 1	----	22.2	21.3	22.2	21.2	21.6	19.6	19.5	19.7
		Rep 2.	----	26.9	22.0	22.7	20.4	20.7	19.0	22.0	20.3
		Mean	----	24.6	21.7	22.4	20.8	21.1	19.3	20.7	20.0
	Total extracted	Rep. 1	100	86.4	88.8	86.8	84.1	80.0	71.6	66.0	67.4
		Rep 2.	100	98.8	88.0	86.7	84.5	79.8	70.5	69.7	65.4
		Mean	100	92.7	88.5	86.7	84.4	79.9	71.0	67.8	66.5
Identified (TLC) as FOE Sulfonic acid [% AR]		Rep. 1	----	84.2	83.6	82.8	77.7	78.3	70.0	64.1	64.3
		Rep 2.	----	94.6	84.6	83.0	80.6	76.6	67.2	66.9	62.1
		Mean	----	89.4	84.1	82.9	79.2	77.5	68.6	65.5	63.2
FOE Sulfonic acid recovered [μg]		Mean	36.8	32.89	30.93	30.49	29.13	28.50	25.45	24.09	23.26
NER fraction [% AR]		Rep. 1	----	7.1	7.5	9.2	11.3	12.8	17.2	17.9	16.0
		Rep 2.	----	7.0	8.8	9.1	11.1	12.8	16.1	18.9	16.5
		Mean	----	7.1	8.1	9.1	11.2	12.8	16.6	18.4	16.2
On filters [% AR]		Rep. 1	----	3.1	3.2	3.0	3.1	4.1	2.9	3.6	3.0
		Rep 2.	----	2.7	2.9	3.1	3.0	4.2	3.3	3.5	3.2
		Mean	----	2.9	3.0	3.0	3.0	4.2	3.1	3.6	3.1
Mineralisation – ¹⁴ CO ₂ [% AR]		Rep. 1	----	0.0	0.6	1.3	2.2	3.4	7.8	9.6	10.6
		Rep 2.	----	0.0	0.6	1.3	2.3	3.7	7.7	10.2	11.5
		Mean	----	0.0	0.6	1.3	2.2	3.6	7.7	9.9	11.1
Total radioactivity recovered [% AR]		Rep. 1	100	96.8	100.1	100.2	101.1	100.4	99.6	97.0	97.0
		Rep 2.	100	108.6	100.3	100.1	100.8	100.6	97.6	102.2	96.7
		Mean	100	102.7	100.2	100.2	100.9	100.5	98.6	99.6	96.9

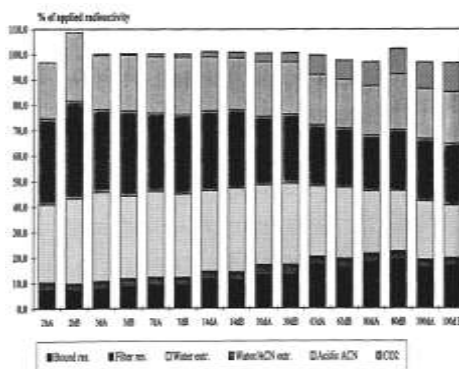


Figure B.8.1.1.2.1.1._CA-59: The graphical results of the determination of the distribution of radioactivity in the test soil BBA 2.2 (scheme copied from the study report).

The results obtained in Laacherhof (Silt loam) soil are presented below in numerical form in the table B.8.1.1.2.1.1._CA-146 and in graphical form on figure B.8.1.1.2.1.1._CA-60.

Table B.8.1.1.2.1.1._CA-146: The numerical results of the experiment performed on Laacherhof soil.

Radioactivity			Measured on DAT								
			0	0.08	3	7	14	30	63	80	100
In extract [%AR]	Water extract	Rep. 1	----	49.4	50.0	46.6	43.3	41.1	35.1	36.0	32.5
		Rep 2.	----	48.0	49.3	46.5	44.5	39.5	34.2	35.8	32.6
		Mean	----	48.7	49.7	46.6	43.9	40.3	34.7	35.9	32.6
	CH ₃ CN/H ₂ O extract	Rep. 1	----	12.7	11.4	12.6	12.7	12.2	25.1	9.4	10.3
		Rep 2.	----	14.2	12.4	12.3	12.0	11.6	23.8	10.4	22.0
		Mean	----	13.4	11.9	12.4	12.4	11.9	24.5	9.9	16.2
	0.01M HCl/CH ₃ CN extract	Rep. 1	----	28.1	8.7	7.5	8.1	26.3	14.6	23.0	7.8
		Rep 2.	----	8.2	8.1	8.1	7.1	27.6	14.0	8.1	11.2
		Mean	----	18.2	8.4	7.8	7.6	26.9	14.3	15.6	9.5
	Total extracted	Rep. 1	100	90.2	70.1	66.7	64.1	79.6	74.8	68.4	50.6
		Rep 2.	100	70.4	69.8	66.9	63.6	78.7	72.0	54.3	65.8
		Mean	100	80.3	70.0	66.8	63.9	79.1	73.5	61.4	58.3
Identified (TLC) as FOE Sulfonic acid [% AR]		Rep. 1	----	85.6	69.6	64.9	63.2	77.7	70.0	66.9	48.0
		Rep 2.	----	66.7	68.8	65.0	62.0	75.8	68.4	54.3	63.5
		Mean	----	76.2	69.2	64.9	62.6	76.8	69.2	60.6	55.7
FOE Sulfonic acid recovered [µg]		Mean	36.8	28.04	25.47	23.89	23.03	28.24	25.46	22.30	20.50
NER fraction [% AR]		Rep. 1	----	7.4	27.1	29.8	29.5	12.3	13.2	16.1	29.4
		Rep 2.	----	28.9	27.8	29.2	31.1	12.5	14.2	29.7	15.8
		Mean	----	18.1	27.5	29.5	30.3	12.4	13.7	22.9	22.6
On filters [% AR]		Rep. 1	----	2.2	1.1	1.0	1.0	2.7	2.1	2.3	0.9
		Rep 2.	----	0.9	1.1	1.1	1.1	2.5	2.1	1.1	1.9
		Mean	----	1.6	1.1	1.0	1.1	2.6	2.1	1.7	1.4
Mineralisation – ¹⁴ CO ₂ [% AR]		Rep. 1	----	0.0	0.7	1.3	2.6	4.8	10.2	12.0	14.1
		Rep 2.	----	0.0	0.7	0.5	2.6	4.7	10.0	12.6	14.8
		Mean	----	0.0	0.7	0.9	2.6	4.8	10.1	12.3	14.4
Total radioactivity recovered [% AR]		Rep. 1	100	99.8	99.0	98.9	97.3	99.4	100.3	98.9	95.0
		Rep 2.	100	100.2	99.4	97.7	98.4	98.4	98.3	97.9	98.4
		Mean	100	100.0	99.2	98.3	97.9	98.9	99.3	98.4	96.7

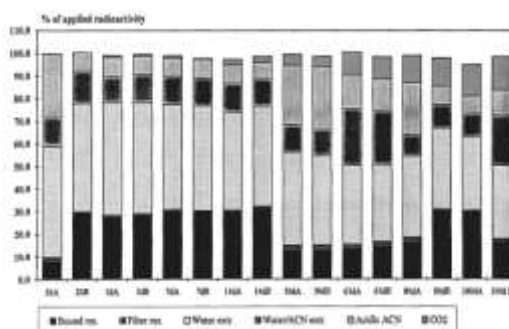


Figure B.8.1.1.2.1.1._CA-60: The graphical results of the determination of the distribution of radioactivity in the test soil Laacherhof (scheme copied from the study report).

The results obtained for FOE Sulfonic acid presented in the tables above were kinetically examined to derive the kinetic endpoints. The kinetic analysis was performed using the linear regression method. As it did not comply with principles set by FOCUS Kinetics Guidance Document, its results will not be presented here.

Additionally the results were kinetically examined by Schäfer in two separate reports – MR-1085/95 and MR-037/98, summarised briefly further down this Renewal Assessment Report as **Study 21** and **Study 22** respectively. Finally, the results of this study were kinetically examined in compliance with provisions of FOCUS Kinetics Guidelines [FOCUS; 2006, 2011]. The results of that exercise are presented further down in the **Study 13**.

Study 10:

Report: Hellpointner E., (2003): “Time-Dependent Sorption of FOE5043-Sulfonic Acid in Soil.”; Bayer Crop Science AG, Development – Global Regulatory Affairs, D-40789 Monheim, Germany; unpublished study Report No. MEF-229/03; 2003-10-13; study reference number: M-111445-01-1;

Guidelines: Due to the aims of the study – examination of the time-dependent sorption of FOE Sulfonic acid, it was declared to be performed in such way, to comply with the following Guidelines:

- examination of soil sorption of the test compound: OECD Guideline for Testing of Chemicals No. 106, Adsorption and Desorption;
- in the area of incubation of the test flasks – ageing and processing of test soils:
 - BBA Guidelines for the Official Testing of Plant Protectants, Part IV, 4-1 (1986);
 - SETAC-Europe Procedures for Assessing the Environmental Fate and Ecotoxicology of Pesticides (*ed.* Mark Lynch), March 1995;
 - US. EPA Guideline 162-1 Aerobic Soil Metabolism (supplemental);

GLP: Yes

RMS comments: This is a newly submitted study. Its was to examine the time-dependent sorption of FOE Sulfonic acid in soil. Although the examination of the degradation kinetics was not its main task, the rate of degradation of the test compound in the test soils had also to be determined as a necessary component of the experiment. Therefore RMS decided to evaluate the study for its compliance with the following Guidelines examining the degradation in soil:

- OECD Guideline 307 – Aerobic and Anaerobic Transformation in Soil for the experimental protocol;
- FOCUS (2006): “Guidance Document on Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration.” Report of the FOCUS Work Group on Degradation Kinetics, EC Document Reference SANCO/10058/2005 version 2.0, 434 pp (main GD) and FOCUS (2011): “Generic guidance for Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration”, version 1.0 issued on 23 November 2011.(supplementary GD) in the area of the kinetic evaluation of the data.

It was verified by the RMS and found acceptable in the area of the examination of the degradation kinetics of FOE Sulfonic acid in soil. It is summarised below. The summary is given only for the part of the study examining the degradation of the test compound in soil.

Summary:

The aim of the study was to examine the phenomenon of the time-dependent sorption, i.e. increase with time of the K_{OC} value, of FOE Sulfonic acid onto soil. That was done in order to clarify the reasons for the observed discrepancies of the results of different studies, namely:

- high mobility and leaching potential of FOE Sulfonic acid in soil demonstrated by the results of the batch equilibrium sorption studies – average K_{OC} = 12.5 mL/g, and modelling GW exposure assessment, with PEC_{GW} for cereals in range of 3.1 – 9.2 µg/L;
- moderate concentrations of the compound in lysimeter studies – up to 1.69 µg/L in the average 1st year leachates when the compound was applied twice in the same year;
- the fact stated in the regulatory study by Hellpointner [1999], examining the degradation of FOE Sulfonic acid in soil (summarised above as **Study 9**), that the compound was not as easily extracted from soil, especially at later time points, as it might be suggested by its K_{OC} value.

The experiment was performed using the [Phenyl-U-¹⁴C] FOE Sulfonic acid in form of ammonium salt. Its structural formula is presented below on figure B.8.1.1.2.1.1._CA-61. The specific activity of the test compound was 2.66 MBq/mg (21.0 mCi/mMole) and its radiochemical purity was 98%.

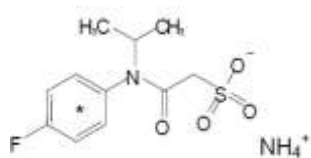


Figure B.8.1.1.2.1.1._CA-61: The structural formula of the test compound (copied from the study report).

The test compound was used to prepare the **Stock solution**, subsequently used in the experiment to treat the test soil. That solution was prepared by dissolving the whole delivered amount of radiolabelled FOE Sulfonic acid in 1 mL of CH₃CN and 19 mL of H₂O. Next the concentration of the test compound in the solution was determined. For that purpose five 50- μ L aliquots of the **Stock solution** were radioassayed. The concentration of the test compound, expressed as radioactivity, was determined to be 9706.3 kBq/20 mL (9.7063 MBq/20 mL), corresponding to 0.1824 mg FOE Sulfonic acid/mL. The radiochemical purity of the solution, determined by TLC, was ~98%. The **Stock solution** was used directly to treat the test soils.

Two test soils were used in the study. The soils were freshly sampled, shortly before the beginning of the experiment, from the 0-20 cm layer. Their characteristics are presented below in the table B.8.1.1.2.1.1._CA-147.

Table B.8.1.1.2.1.1._CA-147: The characteristics of soils used in the study.

Parameter		Soil	
		<i>Laacherhof AXXa</i>	<i>Laacherhof AIII</i>
Soil origin		Monheim, Germany	Monheim, Germany
Soil type (USDA)		Sandy loam	Silt loam
Particle size distribution	Sand (50 μ m – 2 mm) [%]	72.4	36.9
	Silt (2 – 50 μ m) [%]	22.6	51.1
	Clay (< 2 μ m) [%]	5.0	12.0
pH value in CaCl ₂		6.3	6.8
pH value in H ₂ O		6.9	7.6
pH value in KCl		6.3	7.2
Organic carbon content (OC) [%]		1.47	0.88
Organic matter content (OM) [%]		2.53	1.51
Cation Exchange Capacity – CEC [mEq/100g]		10.3	9.8
Water holding capacity	Max. [g H ₂ O/100 g soil]	34.42	36.40
	In air-dried and sieved soil [%]	8.62	7.22
Bulk density [g/cm ³]		2.5	2.55
Soil microbial biomass [mg microbial C/kg soil]	At start of incubation period – DAT 0	242	275
	At the end of incubation period – DAT 100	209	195
Soil microbial biomass [% OC] ¹⁾	At start of incubation period – DAT 0	1.65	3.13
	At the end of incubation period – DAT 100	1.42	2.22

Footnotes to the table:

1) Value calculated by the RMS.

In the laboratory the test soils were air-dried and sieved to a particle size ≤ 2 mm. Then the soil moisture content was measured in sieved soil by drying it at 105°C and determining the loss of weight.

Next 100-g (d.w.) portions of air-dried and sieved test soils (109.43 g in case of Laacherhof AXXa soil and 107.78 g in case of Laacherhof AIII soil) were weighed into 1000-mL centrifuge tubes and brought to 40% MWHC by the addition of the appropriate amount of distilled water – 4.33 g/vessel for Laacherhof AXXa soil and 6.78 g/vessel for Laacherhof AIII. The test vessels were then closed with cotton-wool plugs and pre-incubated for about one week in the darkness and at constant T = 20°C.

At the beginning of the whole experiment the soils in the test vessels were treated with the test compound applied as already described **Stock Solution** in amount 73 μ L/vessel, using a 100- μ L Eppendorf pipette. That gave the treatment dose of 35.5 kBq/vessel when expressed in terms of radioactivity, corresponding to the application dose of 13 μ g FOE Sulfonic acid/100 g soil. It was declared in the study report that such application dose corresponded to the lowest concentration of the test compound – 0.13 μ g/g soil, used in the study examining adsorption of FOE Sulfonic acid onto soil.

RMS recalculated that application dose to obtain the theoretic application rate expressed in g/ha. Standard assumptions were used: soil density $d = 1.5$ g/cm³ and the depth of the soil layer $l = 5$ cm. The resulting

application rate was **A = 99.70 g FOE Sulfonic acid/ha**. It corresponds to ~41% highest application rate of Flufenacet proposed in the current EU-representative GAP – 240 g/ha.

When the experimentally determined soil bulk density values were used, the calculated theoretic application rates were as follows:

- in Laacherhof AXXa soil (bulk density $d = 2.5 \text{ g/cm}^3$) application rate **A = 162.50 g FOE Sulfonic acid/ha**;
- in Laacherhof AIII soil (bulk density $d = 2.55 \text{ g/cm}^3$) application rate **A = 165.75 g FOE Sulfonic acid/ha**.

After treatment of the test soils with the test compound several test were performed, aimed on the determination of adsorption parameters. All they were performed in the same way as typical batch sorption tests described in OECD 106 Guidance document. The main test was performed with treated soil aged for the determined amount of days before the adsorption was examined. All test are briefly characterised, in form of a table copied from the study report, on figure B.8.1.1.2.1.1._CA-62.

Table 2 Applications with each approx. 35.5 kBq of test item

Test	Tubes/soil	Investigations
a) DAT-0: Soil treated prior to shaking	1	Samples taken after 1, 3, 7 and 24 hrs of shaking with 100 mL of 0.01 M CaCl_2 solution LSC and TLC of supernatant
b) DAT-0: Solution treated prior to shaking	1	Samples taken after 1, 3, 7 and 24 hrs of shaking with 100 mL of 0.01 M CaCl_2 solution LSC and TLC of supernatant
c) DAT-0: Reference solution: soil not treated during shaking	1	Processing after 24 hrs of shaking with 100 mL of 0.01 M CaCl_2 solution, then treatment of decanted aqueous 0.01 M CaCl_2 filled into a new empty tube and shaking for 24 hrs, LSC and TLC of solution and LSC of tube extract ^{*)}
d) DAT-0: soil treated prior to shaking	1	Processing after 24 hrs of shaking with 333 mL of 0.01 M CaCl_2 solution LSC and TLC of supernatant and soil extract combustion of soil solids
e) DAT-0: Control without soil Solution treated prior to shaking	1	Samples taken after 1, 3, 7 and 24 hrs of shaking with 100 mL of 0.01 M CaCl_2 solution LSC and TLC of supernatant and LSC of tube extract ^{*)}
Main Test: DAT-X: soil treated then aged prior to shaking	14	Processing after 24 hrs of shaking with 100 mL of 0.01 M CaCl_2 solution, LSC and TLC of supernatant and soil extract, combustion of soil solids

^{*)}: In order to get information on the sorption of radioactivity onto the walls of the testing tubes. The tube was washed (extracted) as it is described for test a or d.

Figure B.8.1.1.2.1.1._CA-62: The table listing and briefly characterising tests performed in the experiment (copied from the study report).

The data possible to be used in the determination of the degradation kinetics of Flufenacet in the test soils were obtained in the main test, so only that stage will be characterised in this summary.

For each test soil 14 pre-incubated test vessels treated with the test compound applied to the soil surface as **Stock solution** in amount 73 $\mu\text{L}/\text{vessel}$, to obtain the application dose of 0.13 mg/kg, corresponding to the theoretic application rate **A = 99.7 g/ha**. Then the test vessels were closed with cotton-wool plugs and all, except DAT-0 samples placed in the darkness in the temperature-controlled room and incubated for up to 100 days at $T = 20^\circ\text{C}$.

For each test soil duplicate samples were removed for further processing at the following time points: DAT 0, DAT 3, DAT 7 DAT 14, DAT 28, DAT 56 and DAT 100. The samples removed from the incubation room were further processed following their procedure presented below on figure B.8.1.1.2.1.1._CA-63.

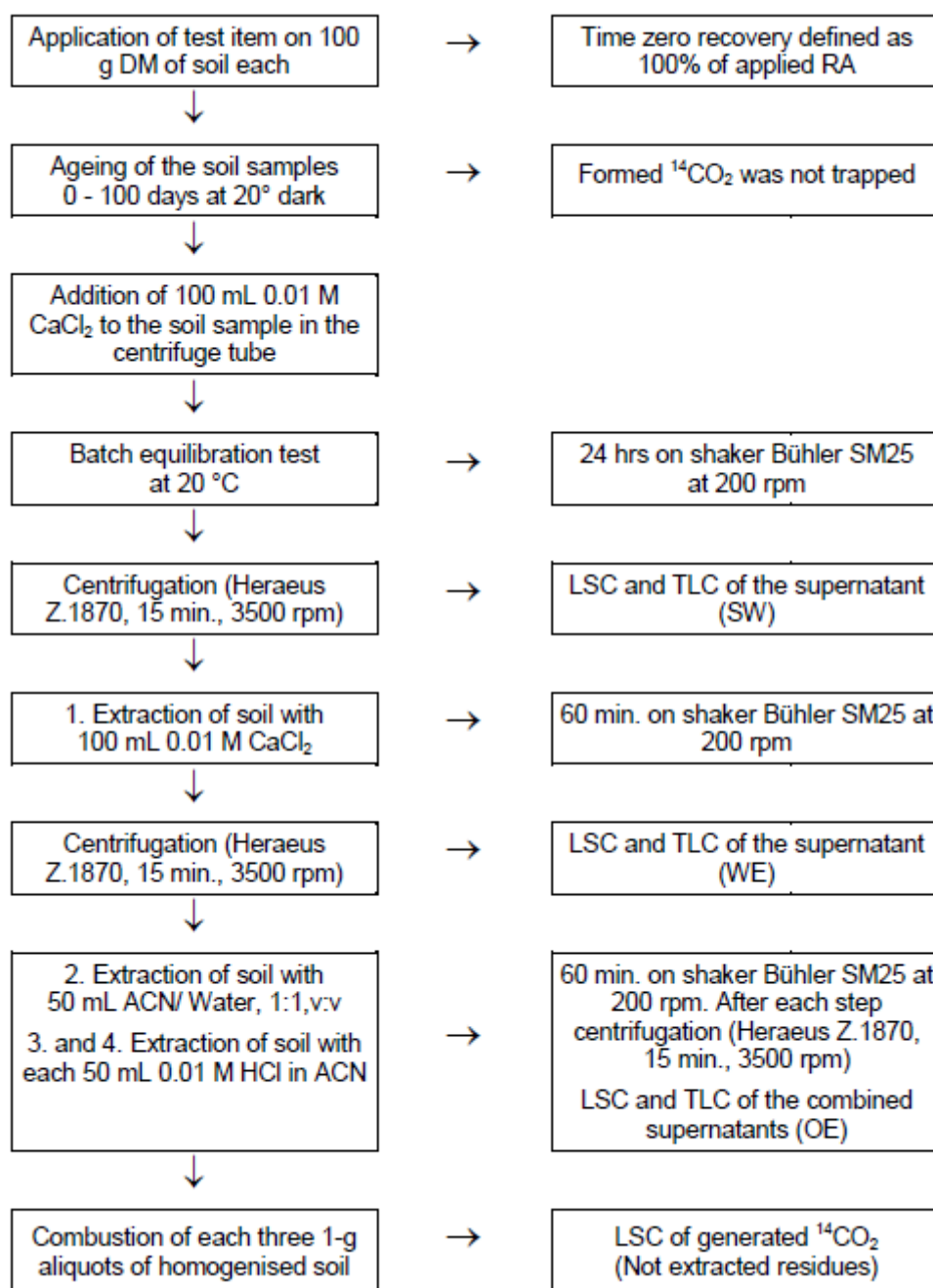


Figure B.8.1.1.2.1.1._CA-63: The flow chart of the processing of samples during the main test of the experiment (copied from the study report).

The 0.01M CaCl_2 solution used at the first stage of extraction, named on the flow chart “batch equilibration test”, was prepared by dissolving 2.94 g of $\text{CaCl}_2 \times \text{H}_2\text{O}$ in 2 L of deionised (Milli-Q) water. Three such solutions were prepared for the purpose of the experiment, having a pH ranging from 5.5 to 6.2. The same solution was also used at 1st step of extraction.

The clear supernatants obtained at each step after centrifugation were collected and their volume determined by weighing. The acetonitrile extracts ($\text{CH}_3\text{CN}/\text{H}_2\text{O}$ and 0.01N $\text{HCl}_{\text{aq}}/\text{CH}_3\text{CN}$ extracts) were combined.

The supernatant obtained during batch equilibration test was further called **Supernatant**, that obtained after extraction with 100 mL of 0.01 M CaCl_2 – **water extract**, while combined supernatants obtained after extraction with solutions containing CH_3CN – **organic extract**.

The extracts were not further processed but their three 200- μ L aliquots analysed for radioactivity content using LSC.

The extracts were also analysed using radio-TLC. For that purpose the following amounts of each fraction were used:

- in case of **Supernatant** one 100- μ L aliquot;
- in case of **Water extract** one 200- μ L aliquot;
- in case of **Organic extract** one 500- μ L aliquot

The extracted soil pellets were air-dried, homogenised and analysed for the content of NER fraction. For that purpose their three 1-g aliquots were combusted in oxidiser and generated $^{14}\text{CO}_2$ quantified using LSC.

The LSC analysis of the liquid samples (200- μ L aliquots) was performed in 2-mL Quicksafe-A scintillation liquid containing 5% of water. The measurements were done on LS 6500 or LS 6000LL counters. Sample counting time was 10 minutes, average counting efficiency ~91% and the background 14-16 cpm.

The $^{14}\text{CO}_2$ generated during the oxidative combustion of the extracted soil pellets was absorbed in Oxysolve C-400 scintillation cocktail and analysed by LSC.

The TLC analysis was performed on crude solutions of each extract in order to determine the concentration of the test compound in each of the fractions. The analysed samples were not enriched or preconditioned prior to the analysis.

The TLC analysis was performed on 200 x 200 mm silica gel Si60 TLC plates. Chromatograms were developed in glass chamber using the following solvent system: $\text{CH}_3\text{CN}/\text{CH}_3\text{CHOHCH}_3/\text{CH}_3\text{COOC}_2\text{H}_5/\text{H}_2\text{O}$ 60:9:6:3 (v/v/v/v) solution ($\text{CH}_3\text{CHOHCH}_3$ stands for 2-propanol and $\text{CH}_3\text{COOC}_2\text{H}_5$ for ethyl acetate).

The identification of the test compound was performed by means of the comparison of the R_f – values for the analysed sample with those of the known standards.

The quantitative analysis – radioactivity counting, was performed using BIO imaging analyser (Fuji Co.). The LOD (determination limit) for a single peak was 0.5% AR. That value however significantly depended on the volume of sample introduced on the plate.

Results and their discussion:

Below are presented the results obtained during the main test. RMS decided to present only the results relevant for the determination of the degradation kinetics of FOE Sulfonic acid in the test soils.

The total recoveries of Applied radioactivity in DAT-0 samples were as follows:

- for Laacherhof AXXa soil: **34.152 kBq**, subsequently used as a reference 100% AR value; it corresponded to 12.23 μg FOE Sulfonic acid/100 g soil;
- for Laacherhof AIII soil: **34.840 kBq**, subsequently used as a reference 100% AR value; it corresponded to 12.40 μg FOE Sulfonic acid/100 g soil.

The temperature in incubation chamber was demonstrated to be constant during the whole incubation period, and maintained at the designated level $T = 20 \pm 1^\circ\text{C}$. The mean temperature during incubation was $T = 19.9^\circ\text{C}$ ranging from 19.8°C to 20.35°C .

The graphical presentation of the changes of incubation temperature are presented below on figure B.8.1.1.2.1.1._CA-56.

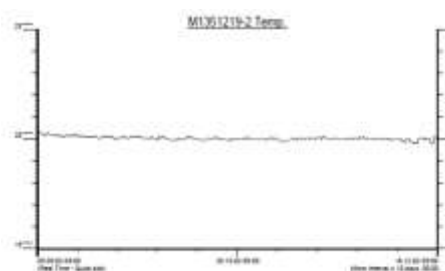


Figure B.8.1.1.2.1.1._CA-56: Temperature recorded in incubation chamber during the experiment (copied from the study report).

In the study report it was stated that both soils were microbiologically viable and that the microbial biomass was within the usual range expected for soils sampled from agricultural fields.

RMS stated that the microbial biomass was above the minimal level recommended by OECD 307 Guideline – 1% OC throughout the whole study duration. It was also noted that, as expected, higher decrease in microbial biomass was observed in soil having lower OC content, but that parameter at the end of the study was still on such level that the test soil may be considered fully viable.

The results of the qualitative and quantitative analysis of the radioactivity in both test systems are presented below. Because of the design of the incubation vessels – the traps for the volatile compounds were not set, it was not possible to determine the level of mineralisation and hence it was also not possible to determine the mass balance.

RMS also noticed that the way the results were reported in the study report made them not fully transparent with regard to their further use in kinetic analysis. In particular, the results of the determination of radioactivity in each fraction was given in [Bq] for individual replicates. When transformed to % AR the values were given as averages of the two replicates.

The concentrations of FOE Sulfonic acid in different fractions at each time point determined by TLC, were expressed as % radioactivity in analysed sample. Only for extracts obtained in Laacherhof AIII soil were given the values for %AR in given fraction, enabling the calculation of the concentration of FOE Sulfonic acid expressed as % AR.

As a result, RMS decided to recalculate all the results provided in the study report in order to:

- a) obtain the results of the quantitation of radioactivity in each fraction, on each time point and for each replicate, expressed as %AR;
- b) obtain the concentrations of FOE Sulfonic acid in each replicate at each time point expressed as %AR.

The repeated calculations were carried out using the raw results presented in the study report. These are shown below, as tables copied from the study report, on figures B.8.1.1.2.1.1._CA-64 and B.8.1.1.2.1.1._CA-65. On figure B.8.1.1.2.1.1._CA-64 are reproduced the results of the determination of radioactivity in each fraction. For calculations were used the values marked bold – amount of radioactivity in the whole sample expressed in [Bq]. The reference value, defined as 100% AR, was “Avg. DAT-0” value reported at the bottom of each table.

On the next figure – B.8.1.1.2.1.1._CA-65 are presented the raw results of the analysis of each fraction by TLC. The following abbreviations were used by the Applicant in the reproduced tables to characterise fractions:

- SW for **Supernatant**;
- WE for **Water extract**;
- OE for **Organic extract**.

The numerical, re-formatted results of the experiment are given in two tables – B.8.1.1.2.1.1._CA-148 for Laacherhof AXXa soil and B.8.1.1.2.1.1._CA-149 for Laacherhof AIII soil. Presenting them the RMS decided to provide the average values for concentration of radioactivity in fractions at each sampling point as they were given in the study report. Also the concentrations of the test compound – FOE Sulfonic acid, expressed in [$\mu\text{g}/100\text{ g soil}$] are taken from the study report.

To maintain the coherence of the reported results RMS decided to present all results in form of a single digit after the decimal coma. The only exception was made when the average concentrations of FOE Sulfonic acid in [$\mu\text{g}/100\text{ g soil}$], reproduced from the study report, were reported – the format used in the study report was kept. Such approach may possibly result in small discrepancies between the averages reported by the Applicant and would –be averages calculated by the RMS, but such differences are estimated to be negligible.

In addition to numerical results RMS presented the graphical results of the determination of the distribution of radioactivity between extractable and non-extractable phases, reproduced from the study report (figures B.8.1.1.2.1.1._CA-66 and B.8.1.1.2.1.1._CA-67).

Finally RMS decided to provide the estimates of the mineralisation level. That was done assuming the theoretical total recovery level of AR at each time point and for each replicate equal to 100% and subtracting from that value the experimentally determined total radioactivity recovered. The resulting value was considered to represent the approximate level of mineralisation. RMS noticed that the obtained values were in line with those obtained in the previously summarised study by [Hellpointner; 1999] (**Study 9**).

Raw results obtained in Laacherhof AXXa soil (LSC analysis)																	
Days	Sample ID DH25	Supernatant after 24h shaking (SW)				Water extract (WE)				organic extract (OE)				Soil not extracted			Recovery Total Bq Total
		V _T [mL]	V _A [mL]	LS [Bq]	Subtotal [Bq]	V _T [mL]	V _A [mL]	LS [Bq]	Subtotal [Bq]	V _T [mL]	V _A [mL]	LS [Bq]	Subtotal [Bq]	M _T [g]	LS [Bq/g]	Subtotal [Bq]	
0	A1T1	76.0	0.2	59.36	22,557	92.4	0.2	16.30	7,531	152	0.2	4.46	3,390	100.3	7.12	714	34,191
	A2T1	77.5	0.2	58.61	22,711	93.4	0.2	15.94	7,444	156	0.2	4.18	3,260	100.6	6.94	698	34,114
3	A1T2	77.1	0.2	56.94	21,950	95.7	0.2	16.02	7,666	152	0.2	4.71	3,580	100.4	10.24	1,028	34,224
	A2T2	75.0	0.2	57.26	21,473	97.1	0.2	15.84	7,690	154	0.2	4.95	3,812	100.4	10.07	1,011	33,985
7	A1T3	76.5	0.2	55.42	21,198	96.6	0.2	15.14	7,313	152	0.2	4.59	3,488	100.4	16.33	1,640	33,639
	A2T3	76.4	0.2	55.22	21,094	96.0	0.2	15.05	7,224	152	0.2	4.58	3,481	100.6	17.61	1,772	33,570
14	A1T4	77.4	0.2	50.73	19,633	94.4	0.2	13.83	6,528	162	0.2	4.59	3,718	100.5	24.27	2,439	32,317
	A2T4	75.9	0.2	51.12	19,400	94.1	0.2	13.85	6,516	156	0.2	4.85	3,783	100.5	24.41	2,453	32,153
28	A1T5	77.4	0.2	41.34	15,999	97.2	0.2	11.68	5,676	156	0.2	4.49	3,502	100.3	49.01	4,916	30,093
	A2T5	77.8	0.2	43.32	16,851	94.4	0.2	11.84	5,588	156	0.2	4.27	3,331	100.3	43.12	4,325	30,095
56	A1T6	76.8	0.2	32.12	12,334	95.1	0.2	8.93	4,246	156	0.2	3.79	2,956	100.5	70.68	7,103	26,640
	A2T6	76.9	0.2	34.20	13,150	93.4	0.2	9.27	4,329	156	0.2	3.90	3,042	100.3	66.61	6,681	27,202
100	A1T7	68.5	0.2	15.68	5,370	100.3	0.2	5.23	2,623	156	0.2	2.62	2,044	101.4	102.22	10,365	20,402
	A2T7	68.5	0.2	15.38	5,268	102.2	0.2	5.24	2,678	156	0.2	2.70	2,106	102.4	103.54	10,602	20,654
Avg. DAT-0:																	34,153
V _T = Total volume V _A = Volume of aliquot LS = Liquid scintillation counting M _T = Total soil weight before exhaustive extraction (dry weight)																	
Raw results obtained in Laacherhof AIII soil (LSC analysis)																	
Days	Sample ID DH25	Supernatant after 24h shaking (SW)				Water extract (WE)				organic extract (OE)				Soil not extracted			Recovery Total Bq Total
		V _T [mL]	V _A [mL]	LS [Bq]	Subtotal [Bq]	V _T [mL]	V _A [mL]	LS [Bq]	Subtotal [Bq]	V _T [mL]	V _A [mL]	LS [Bq]	Subtotal [Bq]	M _T [g]	LS [Bq/g]	Subtotal [Bq]	
0	B1T1	78.3	0.2	61.55	24,097	92.9	0.2	16.10	7,478	160	0.2	3.61	2,888	100.0	8.39	839	35,302
	B2T1	79.3	0.2	59.40	23,552	94.5	0.2	15.40	7,277	160	0.2	3.57	2,856	100.3	6.92	694	34,379
3	B1T2	76.1	0.2	58.43	22,233	97.0	0.2	15.93	7,726	158	0.2	4.08	3,223	100.1	11.78	1,179	34,361
	B2T2	76.3	0.2	57.44	21,913	95.2	0.2	15.93	7,583	158	0.2	3.96	3,128	100.0	11.98	1,198	33,822
7	B1T3	78.3	0.2	56.03	21,396	96.1	0.2	14.35	6,895	158	0.2	3.94	3,113	100.1	15.14	1,516	33,459
	B2T3	77.9	0.2	54.48	21,220	96.4	0.2	14.17	6,830	158	0.2	3.95	3,121	100.1	20.88	2,090	33,260
14	B1T4	77.5	0.2	53.08	20,569	93.8	0.2	13.90	6,519	160	0.2	3.96	3,168	100.4	21.64	2,173	32,428
	B2T4	77.9	0.2	51.03	19,876	95.7	0.2	13.68	6,546	160	0.2	4.11	3,288	100.0	23.68	2,368	32,078
28	B1T5	78.6	0.2	45.14	17,740	96.9	0.2	11.52	5,581	160	0.2	3.64	2,912	100.3	39.28	3,940	30,173
	B2T5	77.4	0.2	43.81	16,954	95.7	0.2	11.71	5,603	160	0.2	3.57	2,856	100.1	43.79	4,383	29,797
56	B1T6	78.4	0.2	33.54	13,148	93.7	0.2	8.92	4,179	162	0.2	3.05	2,471	100.1	62.03	6,209	26,006
	B2T6	76.6	0.2	32.30	12,371	97.7	0.2	8.75	4,274	158	0.2	3.14	2,481	100.2	66.23	6,636	25,762
100	B1T7	71.9	0.2	14.51	5,216	108.6	0.2	4.99	2,710	158	0.2	2.18	1,722	97.0	101.61	9,856	19,504
	B2T7	70.8	0.2	16.96	6,004	99.7	0.2	4.29	2,139	158	0.2	2.04	1,612	95.3	104.25	9,935	19,689
Avg. DAT-0:																	34,840
V _T = Total volume V _A = Volume of aliquot LS = Liquid scintillation counting M _T = Total soil weight before exhaustive extraction (dry weight)																	
108.6 10 mL of solvent had to be added in addition																	

Figure B.8.1.2.1.1_CA-64: Raw results of the LSC quantitation of radioactivity in extracts and extracted soil (copied from the study report).

Raw results of the TLC analysis of extracts obtained in Laacherhof AXXa soil							Raw results of the TLC analysis of extracts obtained in Laacherhof AIII soil							
Analytical Investigation - TLC Distribution of the Spotted Radioactivity - Values in % P&L-BKG Soil: Laacher Hof AXXa							Analytical Investigation - TLC Distribution of the Spotted Radioactivity - Values in % P&L-BKG Soil: Laacher Hof AIII							
Incubation time [d] (Replicate)	Extract	DH25 TLC-No./ Trace	Origin	FOE5043 SA	Diffuse radioact.	Total	Incubation time [d] (Replicate)	Extract	Radioact. (% of applied)	DH25 TLC-No./ Trace	Origin	FOE5043 SA	Diffuse radioact.	Total
0 (A1)	SW	d007/1	0.18	98.40	1.42	100.00	0 (B1)	SW	69.16	d007/3	0.34	97.66	1.80	100.00
	WE	d004/1	0.49	94.47	5.04	100.00		WE	21.46	d004/3	0.67	96.04	3.29	100.00
	OE	d010/1	0.80	90.88	8.32	100.00		OE	8.20	d010/3	2.09	93.15	4.78	100.00
0 (A2)	SW	d007/2	0.26	98.31	1.43	100.00	0 (B2)	SW	67.60	d007/4	0.37	97.26	2.37	100.00
	WE	d004/2	0.56	97.00	2.44	100.00		WE	20.89	d004/4	0.46	95.69	3.85	100.00
	OE	d010/2	0.56	95.70	3.74	100.00		OE	8.20	d010/4	0.58	93.15	6.27	100.00
3 (A1)	SW	d011/1	1.05	97.44	1.51	100.00	3 (B1)	SW	63.81	d011/3	0.94	97.69	1.37	100.00
	WE	d013/1	0.21	98.49	1.30	100.00		WE	22.18	d013/3	0.42	98.81	0.77	100.00
	OE	d012/1	0.32	98.26	1.42	100.00		OE	9.25	d012/3	0.92	99.82	0.18	100.00
3 (A2)	SW	d011/2	1.09	97.63	1.28	100.00	3 (B2)	SW	62.90	d011/4	1.05	98.83	2.12	100.00
	WE	d013/2	0.25	99.02	0.73	100.00		WE	21.76	d006/5		98.31	1.69	100.00
	OE	d012/2		99.54	0.46	100.00		OE	8.98	d012/4		98.90	1.10	100.00
7 (A1)	SW	d026/1	0.56	98.95	0.49	100.00	7 (B1)	SW	62.96	d026/3	0.66	98.92	0.42	100.00
	WE	d018/1	0.21	99.17	0.62	100.00		WE	19.79	d018/3	0.21	98.69	0.90	100.00
	OE	d017/1		98.36	1.64	100.00		OE	8.93	d017/3	0.46	98.20	1.34	100.00
7 (A2)	SW	d026/2	0.41	97.65	1.95	100.00	7 (B2)	SW	60.91	d026/4	0.41	99.27	0.32	100.00
	WE	d018/2		99.35	0.65	100.00		WE	19.60	d018/4	0.41	99.52	0.07	100.00
	OE	d017/2	0.25	98.90	0.85	100.00		OE	8.98	d017/4	2.43	97.15	0.42	100.00
14 (A1)	SW	d019/1	0.63	98.79	0.58	100.00	14 (B1)	SW	59.04	d019/3	0.62	99.38	0.00	100.00
	WE	d021/1	0.49	98.36	1.15	100.00		WE	18.71	d021/3	0.56	98.36	1.08	100.00
	OE	d020/1	0.49	98.52	0.99	100.00		OE	9.09	d020/3	0.46	95.33	4.21	100.00
14 (A2)	SW	d019/2	0.80	98.84	0.56	100.00	14 (B2)	SW	57.05	d019/4	0.51	98.59	0.90	100.00
	WE	d021/2	0.37	98.07	1.56	100.00		WE	18.79	d021/4	0.35	99.24	0.41	100.00
	OE	d020/2	0.63	97.48	1.91	100.00		OE	9.44	d020/4	1.07	93.53	5.40	100.00
28 (A)	SW	d022/1	0.71	99.07	0.22	100.00	28 (B1)	SW	50.92	d022/3	0.58	99.40	0.04	100.00
	WE	d025/1	1.42	96.66	1.92	100.00		WE	16.02	d025/3	1.13	97.55	1.32	100.00
	OE	d023/1	1.49	97.43	1.08	100.00		OE	8.36	d023/3	2.77	95.49	1.74	100.00
28 (B)	SW	d022/2	0.60	98.85	0.55	100.00	28 (B2)	SW	48.66	d022/4	0.55	98.61	0.84	100.00
	WE	d025/2	1.17	96.37	2.46	100.00		WE	16.08	d025/4	0.92	97.54	1.54	100.00
	OE	d023/2	1.23	97.73	1.04	100.00		OE	8.20	d023/4	2.69	96.19	1.12	100.00
56 (A)	SW	d027/1	0.86	98.47	0.67	100.00	56 (A)	SW	37.74	d027/3	0.54	98.69	0.77	100.00
	WE	d028/1	2.31	93.20	4.49	100.00		WE	11.99	d028/3	1.63	93.18	5.19	100.00
	OE	d029/1	4.44	89.91	5.65	100.00		OE	7.09	d029/3	6.60	90.23	3.17	100.00
56 (B)	SW	d027/2	0.77	99.07	0.18	100.00	56 (B)	SW	35.51	d027/4	0.65	98.95	0.40	100.00
	WE	d028/2	1.87	93.87	4.26	100.00		WE	12.27	d028/4	1.54	94.46	4.00	100.00
	OE	d029/2	4.54	91.57	3.89	100.00		OE	7.12	d029/4	6.59	87.35	6.96	100.00
100 (A)	SW	d030/1	1.76	96.88	1.36	100.00	100 (A)	SW	14.97	d030/3	1.16	97.50	1.34	100.00
	WE	d031/1	2.21	96.35	1.44	100.00		WE	7.78	d031/3	0.89	96.76	2.95	100.00
	OE	d032/1	6.80	72.41	20.79	100.00		OE	4.94	d032/3	9.27	70.43	20.30	100.00
100 (B)	SW	d030/2	1.99	95.97	2.04	100.00	100 (B)	SW	17.23	d030/4	1.29	95.53	3.18	100.00
	WE	d031/2	1.83	95.81	2.36	100.00		WE	6.14	d031/4	1.39	96.32	2.29	100.00
	OE	d032/2	7.35	74.61	18.04	100.00		OE	4.63	d032/4	10.99	65.70	23.31	100.00

Figure B.8.1.1.2.1.1_CA-65: Raw results of the TLC analysis of radioactivity in extracts
(copied from the study report).

The results obtained in Laacherhof AXXa (Sandy loam) soil are presented below in numerical form in the table B.8.1.1.2.1.1._CA-148 and in graphical form on figure B.8.1.1.2.1.1._CA-66.

Table B.8.1.1.2.1.1._CA-148: The numerical results of the experiment performed on Laacherhof AXXa soil.

Radioactivity			Measured on DAT						
			0	3	7	14	28	56	100
In extract [%AR]	Supernatant	Rep. 1	66.0	64.3	62.1	57.5	46.8	36.1	15.7
		Rep 2.	66.5	62.9	61.8	56.8	49.3	38.5	15.4
		Mean	66.3	63.6	61.9	57.1	48.1	37.3	15.6
	Water extract	Rep. 1	22.1	22.4	21.4	19.1	16.6	12.4	7.7
		Rep 2.	21.8	22.5	21.2	19.1	16.4	12.7	7.8
		Mean	21.9	22.5	21.3	19.1	16.5	12.6	7.8
	Organic extract	Rep. 1	9.9	10.5	10.2	10.9	10.3	8.7	6.0
		Rep 2.	9.5	11.2	10.2	11.1	9.8	8.9	6.2
		Mean	9.7	10.8	10.2	11.0	10.0	8.8	6.1
	Total extracted	Rep. 1	90.2	97.2	93.7	87.5	73.7	57.2	29.4
		Rep 2.	97.8	96.6	93.2	87.0	75.5	60.1	29.4
		Mean	97.9	96.9	93.4	87.2	74.6	58.6	29.4
Identified (TLC) as FOE Sulfonic acid [% AR]	Supernatant	Rep. 1	65.0	62.6	61.4	56.8	46.4	35.6	15.2
		Rep 2.	65.4	61.4	60.3	55.9	48.8	38.1	14.8
		Mean	65.2	62.0	60.9	56.4	47.6	36.9	15.0
	Water extract	Rep. 1	20.8	22.1	21.2	18.8	16.6	11.6	7.4
		Rep 2.	21.1	22.3	21.0	18.7	15.8	11.9	7.5
		Mean	21.0	22.2	21.1	18.8	16.2	11.7	7.5
	Organic extract	Rep. 1	9.0	10.3	10.0	10.7	10.0	7.8	4.3
		Rep 2.	9.1	11.1	10.1	10.8	9.5	8.2	4.6
		Mean	9.1	10.7	10.1	10.8	9.8	8.0	4.5
	Total extracted	Rep. 1	94.8	95.0	92.7	86.3	73.0	54.9	27.0
		Rep 2.	95.7	94.8	91.4	85.4	74.1	58.2	26.9
		Mean	95.2	94.9	92.1	85.9	73.5	56.6	26.9
FOE Sulfonic acid recovered [µg/100 g soil]		Rep. 1	12.2	12.2	11.9	11.1	9.3	7.1	3.5
		Rep 2.	12.3	12.2	11.7	11.0	9.5	7.5	3.5
		Mean	12.23	12.19	11.82	11.04	9.41	7.26	3.46
NER fraction [% AR]		Rep. 1	2.1	3.0	4.8	7.1	14.4	20.8	30.3
		Rep 2.	2.0	3.0	5.2	7.2	12.7	19.6	31.0
		Mean	2.1	3.0	5.0	7.2	13.5	20.2	30.7
Total radioactivity recovered [% AR]		Rep. 1	100.1	100.2	98.5	94.6	88.1	78.0	59.7
		Rep 2.	99.9	99.5	98.3	94.1	88.1	79.6	60.5
		Mean	100.0	99.9	98.4	94.4	88.1	78.8	60.1
Theoretical level of mineralisation [% AR] ¹⁾		Rep. 1	0.0	0.0	1.5	5.4	11.9	22.0	40.3
		Rep 2.	0.1	0.5	1.7	5.9	11.9	20.4	39.5
		Mean	0.0	0.1	1.6	5.6	11.9	21.2	39.9

Footnotes to the table:

- 1) The theoretical level of mineralisation calculated by the RMS by subtracting the appropriate value representing the “Total radioactivity recovered” from the theoretical level of applied radioactivity – 100%. For DAT-0 samples that value was set to 0, as for that time point no mineralisation was expected to occur. In cases when the amount of radioactivity recovered at the given time point was higher than 100% the level of would-be mineralisation was also set to zero.

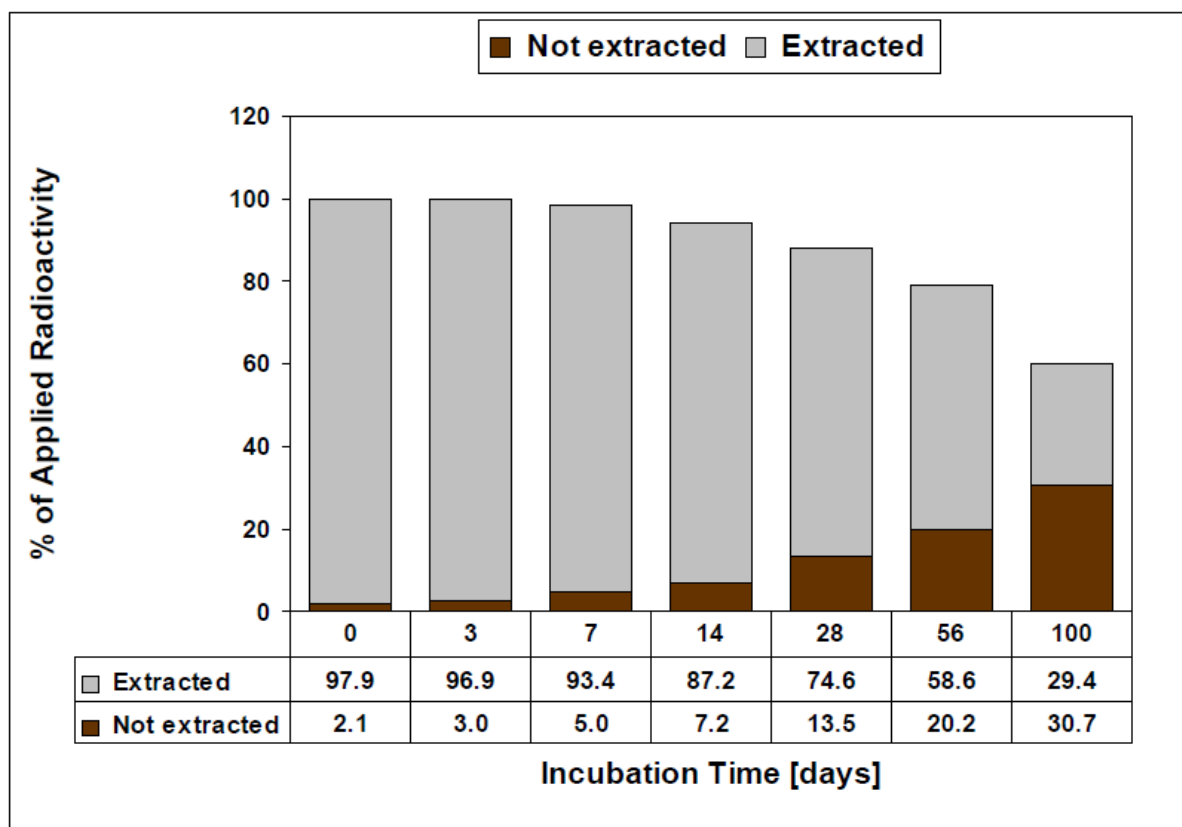


Figure B.8.1.1.2.1.1._CA-66: The graphical results of the determination of the distribution of radioactivity in the test soil Laacherhof AXXa (scheme copied from the study report).

The results obtained in Laacherhof AIII (Silt loam) soil are presented below in numerical form in the table B.8.1.1.2.1.1._CA-149 and in graphical form on figure B.8.1.1.2.1.1._CA-67.

Table B.8.1.1.2.1.1._CA-149: The numerical results of the experiment performed on Laacherhof AIII soil.

Radioactivity			Measured on DAT						
			0	3	7	14	28	56	100
In extract [%AR]	Supernatant	Rep. 1	69.2	63.8	63.0	59.0	50.9	37.7	15.0
		Rep 2.	67.2	62.9	60.9	57.0	48.7	35.5	17.2
		Mean	68.4	63.4	61.9	58.0	49.8	36.6	16.1
	Water extract	Rep. 1	21.5	22.2	19.8	18.7	16.0	12.0	7.8
		Rep 2.	20.9	21.8	19.6	18.8	16.1	12.3	6.1
		Mean	21.2	22.0	19.7	18.7	16.1	12.1	7.0
	Organic extract	Rep. 1	8.3	9.3	8.9	9.1	8.4	7.1	4.9
		Rep 2.	8.2	9.0	9.0	9.4	8.2	7.1	4.6
		Mean	8.2	9.1	8.9	9.3	8.3	7.1	4.8
	Total extracted	Rep. 1	99.0	95.3	91.7	86.8	75.3	56.5	27.7
		Rep 2.	96.7	93.7	89.5	85.2	73.0	54.9	27.9
		Mean	97.8	94.4	90.6	86.1	74.1	55.9	27.8
Identified (TLC) as FOE Sulfonic acid [% AR]	Supernatant	Rep. 1	67.7	62.3	62.3	58.7	50.6	37.2	14.6
		Rep 2.	65.7	60.9	60.5	56.2	48.0	35.1	16.5
		Mean	66.7	61.6	61.4	57.5	49.3	36.2	15.5
	Water extract	Rep. 1	20.6	21.9	19.6	18.4	15.6	11.2	7.5
		Rep 2.	20.0	21.4	19.5	18.6	15.7	11.6	5.9
		Mean	20.3	21.7	19.5	18.5	15.7	11.4	6.7
	Organic extract	Rep. 1	7.7	9.2	8.7	8.7	8.0	6.4	3.5
		Rep 2.	7.6	8.9	8.7	8.8	7.9	6.2	3.0
		Mean	7.7	9.1	8.7	8.7	7.9	6.3	3.3
	Total extracted	Rep. 1	96.0	93.5	90.6	85.7	74.2	54.8	25.6
		Rep 2.	93.4	91.2	88.7	83.7	71.6	52.9	25.4
		Mean	94.7	92.3	84.7	84.70	72.9	53.9	25.5
FOE Sulfonic acid recovered [µg/100 g soil]		Rep. 1	12.6	12.2	11.9	11.2	9.7	7.2	3.4
		Rep 2.	12.2	11.9	11.6	11.0	9.4	6.9	3.3
		Mean	12.40	12.09	11.74	11.10	9.55	7.06	3.34
NER fraction [% AR]		Rep. 1	2.4	3.4	4.4	6.2	11.3	17.8	28.3
		Rep 2.	2.2	3.4	6.0	6.8	12.6	19.0	28.5
		Mean	2.2	3.4	5.2	6.5	11.9	18.4	28.4
Total radioactivity recovered [% AR]		Rep. 1	101.3	98.6	96.0	93.1	86.6	74.6	56.0
		Rep 2.	98.7	97.1	95.5	92.1	85.5	73.9	56.5
		Mean	100.0	97.9	95.8	92.6	86.1	74.3	56.2
Theoretical level of mineralisation [% AR] ¹⁾		Rep. 1	0.0	1.4	4.0	6.9	13.4	25.4	44.0
		Rep 2.	0.0	2.9	4.5	7.9	14.5	26.1	43.5
		Mean	0.0	2.1	4.2	7.4	13.9	25.7	43.8

Footnotes to the table:

- 1) The theoretical level of mineralisation calculated by the RMS by subtracting the appropriate value representing the “Total radioactivity recovered” from the theoretical level of applied radioactivity – 100%. For DAT-0 samples that value was set to 0, as for that time point no mineralisation was expected to occur. In cases when the amount of radioactivity recovered at the given time point was higher than 100% the level of would-be mineralisation was also set to zero.

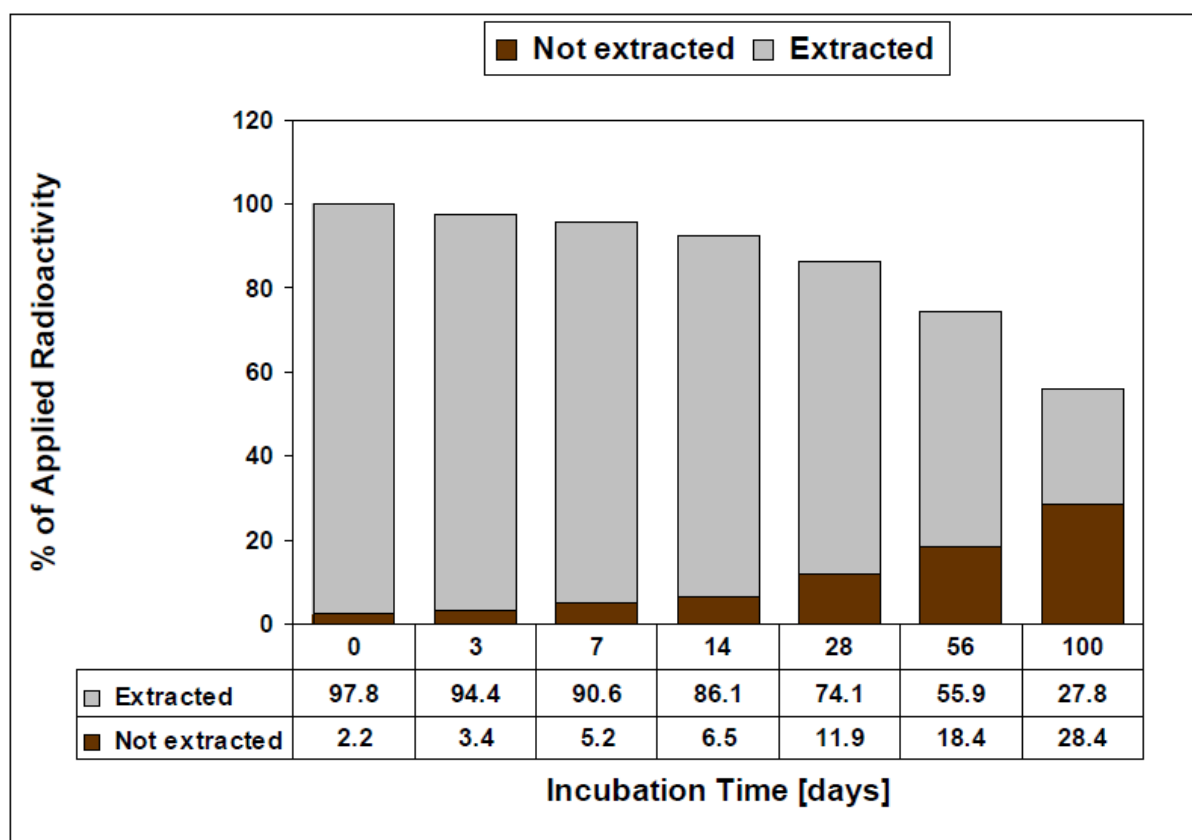


Figure B.8.1.1.2.1.1. CA-67: The graphical results of the determination of the distribution of radioactivity in the test soil Laacherhof AIII (scheme copied from the study report).

The data obtained for FOE Sulfonic acid were kinetically examined in order to obtain the kinetic endpoints – DT_{50} and DT_{90} values, in each of the test soils. The kinetic examination of the data was performed only for SFO model. The data used in the fitting were the average concentrations of FOE Sulfonic acid expressed in [$\mu\text{g}/100 \text{ g soil}$]. RMS stated that the kinetic analysis of the results did not comply with the recommendations of the FOCUS Kinetics Guideline. Therefore, and also because the same data sets were kinetically re-examined fully in line with FOCUS Kinetics recommendations in another study – **Study 13** below, RMS decided not to present them.

Study 11:

Report: Hein E. M., (2013): “FOE sulfonic acid: Aerobic Degradation in Four European Soils.”; Bayer CropScience AG, BCS-D-EnSa-Testing, 40789 Monheim, Germany; unpublished Study Report No. EnSa-13-0442; 2013. 08. 05, updated by the Amendment No. 1 (Hein E. M. (2013): “Amendment No. 1 to: FOE Sulfonic Acid: Aerobic Degradation in Four European Soils.”; Bayer CropScience AG, BCS-D-EnSa-Testing, 40789 Monheim, Germany;) issued on 2013. 08. 22; study reference number: M-461413-02-1;

Guidelines: The study was declared to be performed in line with the provisions of the OECD Guideline for the Testing of Chemicals No. 307 – Aerobic and Anaerobic Transformation in Soil. The Applicant stated that there was no deviations from the declared Guideline. Additionally, as the data obtained in their study were kinetically evaluated and the results presented in the study report, it was declared that the following Guideline was used:

- FOCUS (2006): “Guidance Document on Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration.” Report of the FOCUS Work Group on Degradation Kinetics, EC Document Reference SANCO/10058/2005 version 2.0, 434 pp.;

In this case also no deviations from the Guideline referred to were stated.

GLP: Yes;

RMS comments: This is a new study, submitted specifically for purpose of this assessment. It was verified by the RMS and found acceptable. No deviations from the declared Guidelines were stated. The study is summarised below.

Summary:

The aim of the study was to determine the rate of degradation FOE Sulfonic acid in aerobic soil incubated under laboratory conditions. The experiment was performed on four test soils taken from the agriculturally used areas, representing different geographical origin and different soil properties, in line with the requirement of the relevant Guideline. The characteristic of the test soils is provided below in the table B.8.1.1.2.1.1._CA-150.

Table B.8.1.2.1.1.CA-150: The characteristic of soils used in the study.

Parameter			Soil			
			<i>Laacherhof AXa (AX)</i>	<i>Dollendorf II (DD)</i>	<i>Höfchen am Hohenseh 4a (HH)</i>	<i>Wurmweise (WW)</i>
Soil origin			Monheim/ North Rhine-Westphalia /Germany	Blankenheim/ North Rhine-Westphalia /Germany	Burscheid/ North Rhine-Westphalia /Germany	Monheim/ North Rhine-Westphalia /Germany
Soil type (USDA)			Loamy sand	Loam	Silt loam	Sandy loam
Particle size distribution	Sand [%]		84	48	22	60
	Silt [%]		10	28	62	26
	Clay [%]		6	24	16	14
pH value	in 0.01M CaCl ₂ (1:2)		6.2	7.0	6.1	5.0
	in H ₂ O (1:1)		6.3	7.1	6.3	5.2
	in 1M KCl (1:1)		6.0	6.7	5.8	4.7
Organic Carbon content (OC) [%]			1.7	4.6	2.0	1.8
Organic Matter content (OM) [%] ¹⁾			2.9	7.9	3.4	3.1
Cation Exchange Capacity – CEC [mEq/100g]			9.2	19.5	11.1	10.4
Water holding capacity	MWHC [g H ₂ O/ 100 g soil d. w.]		48.5	79.1	54.8	56.3
	at pF 2.0 (0.1 bar) [%]		12.9	45.4	33.1	19.8
Soil bulk density (disturbed) [g/cm ³]			1.19	1.03	1.09	1.17
Soil biomass [mg microbial C/ kg soil d. w.] ²⁾	DAT-0	BIO- ⁴⁾	924	3883/ 4188 ⁶⁾	1100/ 1192 ⁶⁾	770
	DAT-60	BIO- ⁴⁾	510	2116	657	476
		BIO+ ⁵⁾	517	2057	623	498
	DAT-120	BIO- ⁴⁾	412	n. d. ⁷⁾	472	367
		BIO+ ⁵⁾	399	n. d. ⁷⁾	510	362
	DAT-0	BIO- ⁴⁾	5.43	8.44/9.11	5.50/5.96	4.28
Soil biomass [% OC] ³⁾	DAT-60	BIO- ⁴⁾	3.00	4.60	3.28	2.64
		BIO+ ⁵⁾	3.04	4.47	3.12	2.77
	DAT-120	BIO- ⁴⁾	2.42	----	2.36	2.04
		BIO+ ⁵⁾	2.35	----	2.55	2.01

Footnotes to the table:

- 1) Value calculated from experimentally determined OC content, using the following equation: $OM = 1.724 \text{ OC}$;
- 2) Determined using the SIR method developed by Anderson & Domsch [1978];
- 3) Values recalculated by the RMS using the OC content reported in the table for each test soil;
- 4) Determined in samples not treated with blank application solution – 0.4 mL of 1:1 MeOH/H₂O;
- 5) Determined in samples treated with blank application solution – 0.4 mL of 1:1 CH₃OH/H₂O;
- 6) The second value is given for repeated DAT-0 sample; analysis was performed as it has become necessary to introduce two additional sampling points – DAT 1 and DAT 3;
- 7) Analysis not performed as in this soil, due to the rapid degradation of the test compound, the incubation was terminated on DAT 37.

The test soils were sampled shortly before being used (17 days before the experiment began) with shovel from 0-20 cm layer of grassland plot. No Plant Protection Products were used on the sampling field for 5 years preceding sampling. Sampled test soils were transported to the test facility in plastic bags. There they were sieved through 2-mm sieve and stored in the darkness at either $T = 5^{\circ}\text{C}$ or $T = 20^{\circ}\text{C}$ until being used. The whole soil sampling-and-handling procedure was declared to be performed in accordance with ISO 10381-6.

The experiment was performed using 300-mL Erlenmeyer flasks into which 100-g (d. w.) portions of sieved test soils were weighed. Next the soil moisture content of each sample was adjusted to $55 \pm 5\%$ MWHC by addition of the appropriate amount of deionised water. So prepared incubation flask were then capped with PU plugs to allow free air exchange. The example incubation vessel is presented below on figure B.8.1.1.2.1.1._CA-68. After adjustment of the soil moisture the incubation vessels were pre-conditioned for 3 days in the dark, in a temperature-controlled walk-in climatic chamber at $T = 20 \pm 2^{\circ}\text{C}$, until being treated with the test compound. The number of incubation vessels prepared for each test soils was such to grant at least to have duplicate treated samples at each sampling point and those for the determination of soil biomass in soil samples not treated and treated with blank application solution.

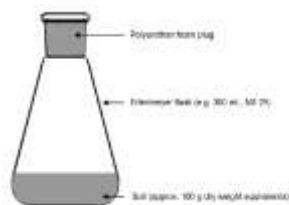


Figure B.8.1.1.2.1.1._CA-68: The example incubation vessel (copied from the study report).

The test compound was a non-radiolabelled FOE Sulfonic acid in form of Na^+ salt, having the chemical purity, determined by ^{19}F -NMR, of 86% (RMS noticed that the chemical purity of the test compound was 9-% lower than recommended minimum, but that had no impact on the validity of the study, as that factor was taken into account in all calculations). Its structural formula is shown below on figure B.8.1.1.2.1.1._CA-69.

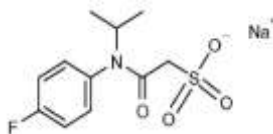


Figure B.8.1.1.2.1.1._CA-69: The structural formula of the test compound used in the experiment (copied from the study report).

It was delivered as a solid sample, in form of a white powder, weighing 16.48 mg. That sample was used entirely to prepare first a **Stock solution** and next **Application solutions**.

The **Stock solution** was prepared by dissolving the whole delivered sample of FOE Sulfonic acid Na^+ salt in 14.44 mL of $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (1:1 v/v), to obtain a solution having a nominal concentration 1.0 mg FOE Sulfonic acid/mL, taking into account the chemical purity of the test compound being 86%. The so prepared **Stock solution**, labelled **Ja66 SS**, was stored in the darkness at $T < 8^{\circ}\text{C}$ until being used.

Three diluted solutions were prepared from the **Stock Solution**:

- **Dilution solution 1**, labelled **Ja66 SS D1**, by transferring 0.43 mL of the **Stock solution Ja66 SS** into 50-mL volumetric flask and bringing it to a volume with the appropriate amount of $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (1:1 v/v). The so prepared solution had a nominal concentration 8600 ng/mL and was used to prepare the series of calibration solutions;

- **Dilution solution 2**, labelled **Ja66 SS D2**, by transferring 5 mL mL of the **Ja 66 SS D1** solution into 50-mL volumetric flask and bringing it to a volume with the appropriate amount of CH₃CN/H₂O (1:1 v/v). The so prepared solution had a nominal concentration 860 ng/mL and was used to prepare the series of calibration solutions;
- **Dilution solution 3**, labelled **Ja66 SS D3**, by transferring 0.5 mL mL of the **Ja 66 SS D1** solution into 50-mL volumetric flask and bringing it to a volume with the appropriate amount of CH₃CN/H₂O (1:1 v/v). The so prepared solution had a nominal concentration 86 ng/mL.

Next two following application solutions were prepared:

- **Application solution Ja66 AS AR**, to treat samples used in validation of the analytical procedure, concurrent recovery samples and the degradation samples;
- **Application solution Ja66 AS LOQ**, to treat concurrent recovery samples and those used in the determination of LOQ.

The application solution **Ja66 AS AR** was prepared by transferring 8.6 mL of the **Stock solution Ja66 SS** into 100-mL volumetric flask and evaporating it to dryness under the constant stream of N₂. The residue was reconstituted and brought to volume with the appropriate amount of 1:1 (v/v) CH₃OH/H₂O. The nominal concentration of so prepared application solution was 0.086 mg FOE Sulfonic acid/mL.

The application solution **Ja66 AS LOQ** was prepared by transferring 0.43 mL of the **Stock solution Ja66 SS** into 100-mL volumetric flask and evaporating it to dryness under the constant stream of N₂. The residue was reconstituted and brought to volume with the appropriate amount of 1:1 (v/v) CH₃OH/H₂O. The nominal concentration of so prepared application solution was 0.0043 mg FOE Sulfonic acid/mL.

The **Ja66 AS AR** solution was used to treat degradation samples. To do that 0.4 mL of it was applied dropwise onto soil surface in each incubation vessel to obtain the application dose of 34.4 µg FOE Sulfonic acid/100 g soil (d. w.). That application dose – equal to 0.344 mg/kg soil was determined using the following assumptions:

- field application rate of Flufenacet (parent compound, precursor of FOE Sulfonic acid): 600 g/ha;
- maximum occurrence of FOE Sulfonic acid in aerobic soil (determined in the laboratory studies): 26.3%;
- molar weight of Flufenacet M = 363.3 g/mol;
- molar weight of FOE Sulfonic acid M' = 297.3 g/mol;
- soil bulk density: 1.5 g/cm³;
- thickness of the soil layer: 2.5 cm.

RMS analysing the calculations noticed that the assumed soil layer was ½ of that routinely used to calculate field application rate (in [g/ha]) from that expressed in mg/kg soil. Therefore the RMS back calculated the would-be field application rate for FOE Sulfonic acid using the standard assumptions:

- soil bulk density: 1.5 g/cm³;
- thickness of the soil layer: 5 cm.

The so calculated field application rate **A = 258.0 g FOE Sulfonic acid/ha**.

Using the measured soil bulk density of each test soil used in the experiment that value would be:

- for Laacherhof AXXa soil: **A = 204.68 g/ha**;
- for Dollendorf II soil: **A = 177.16 g/ha**;
- for Höfchen am Hohenseh 4a soil: **A = 187.48 g/ha**;
- for Wurmwielse soil: **A = 201.24 g/ha**

The verification of application rate and homogeneity of application was performed using **Ja66 AS AR** solution at the beginning and at the end of the whole application cycle. That was done by transferring of 0.4-mL portions of the application solution into 500-mL graduated cylinders. Next the solution was brought to the volume of 400 mL using 1:1 (v/v) CH₃OH/H₂O solution and analysed using HPLC-MS/MS.

The same solution was used to treat the Concurrent Recovery Samples. The application dose was the same as for degradation samples – 0.4 mL/100 g soil, resulting in fortification level of 0.344 mg/kg soil. The samples were freshly prepared at each sampling point using Laacherhof AXXa soil.

Application solution **Ja66 AS LOQ** was used to treat another set of Concurrent Recovery Samples, in amount 0.4 mL/100 g soil (d.w.), what resulted in application rate 1.72 µg/100 g soil (0.072 mg/kg soil) – 5% of the nominal application rate. The samples were freshly prepared at each sampling point using Laacherhof AXXa soil.

The verification of application rate and homogeneity of application in Concurrent Recovery Samples was performed in the same manner as for degradation samples.

Immediately after treatment the incubation vessels designated as degradation samples were closed with PU plugs to grant free access of air, placed in the darkness in temperature-controlled walk-in climatic chamber and incubated for up to 120 days under aerobic conditions at $T = 20 \pm 2^{\circ}\text{C}$. Duplicate samples were removed from incubation chamber at following time-points (DAT stands for “Days After Treatment”):

- for Laacherhof AXXa soil: DAT 0, DAT 7, DAT 14, DAT 21, DAT 37, DAT 58, DAT 86 and DAT 120;
- for Dollendorf II soil: DAT 0, DAT 1, DAT 3, DAT 7, DAT 14, DAT 21, DAT 37;
- for Höfchen am Hohenseh 4a soil: DAT 0, DAT 1, DAT 3, DAT 7, DAT 14, DAT 21, DAT 37, DAT 58, DAT 86 and DAT 120;
- for Wurmwielse soil: DAT 0, DAT 7, DAT 14, DAT 21, DAT 37, DAT 58, DAT 86 and DAT 120;

The soil moisture content in incubation vessels was controlled by weighing them at designated time points and replenishing lost water with adequate amount of deionised water. That was done 3 days before application and on the following time points: DAT 0, DAT 7, DAT 14, DAT 21, DAT 37, DAT 51, DAT 58, DAT 65, DAT 79, DAT 86, DAT 93, DAT 102, DAT 112 and DAT 120 for all test vessels remaining in the incubation chamber.

Samples removed from the incubation chamber were processed and analysed immediately after sampling. That was done using the entire portions of the test soil recovered at each sampling point, using the procedure presented below on figure B.8.1.1.2.1.1_CA-70. The same procedure was applied to Concurrent Recovery Samples.

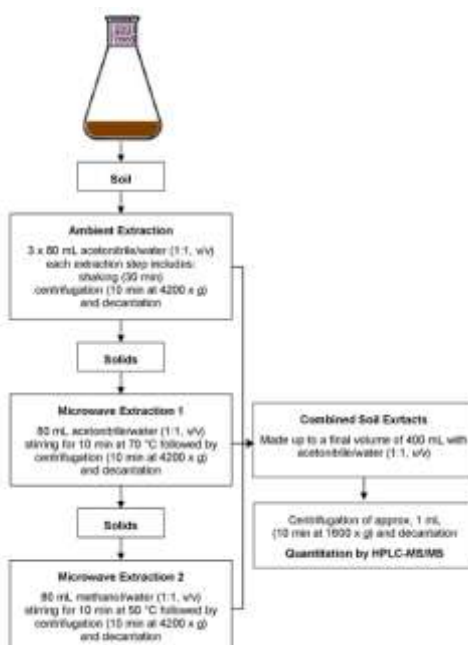


Figure B.8.1.1.2.1.1_CA-70: The sample-processing procedure used in the experiment (scheme copied from the study report, slightly modified by the RMS to increase its transparency).

The samples for the determination of soil biomass were set alongside the degradation samples. The soil biomass was determined in pre-conditioned test soil samples sampled on DAT 0 (beginning of the incubation period), DAT 60 (middle of the incubation period) and DAT 120 (end of incubation period). The experiment was performed in two variants:

- “BIO-” samples, not treated with blank application solution; these samples were taken for the analysis on DAT 0, DAT 60 and DAT 120;
- “BIO+” samples, treated with 0.4 mL of blank application solution ($\text{CH}_3\text{OH}/\text{H}_2\text{O}$ 1:1 v/v); these samples were taken for the analysis on DAT 60 and DAT 120.

The quantitative and qualitative analysis of combined soil extracts and other liquid samples was performed by means of HPLC-MS/MS. The analysis was performed using HP1200 chromatography workstation equipped with UV absorption detector and Finnigan TSQ Vantage (Thermo Electron Corporation, San Jose, CA, USA) MS detector. The chromatographic separation was performed on Nucleodur Gravity C8 50*2 mm * 5 μm

chromatographic column working in a gradient mode. The column was maintained at constant temperature $T = 40^{\circ}\text{C}$. The gradient elution programme is presented below in the table B.8.1.1.2.1.1._CA-151.

Table B.8.1.1.2.1.1._CA-151: The HPLC gradient mode used in the study.

Time [min]	Solvent ratio	
	<i>Solvent A – Water + 0.1% HCOOH</i>	<i>Solvent B – Acetonitrile + 0.1% HCOOH</i>
0	95	5
1	95	5
2	50	50
5	40	60
6	5	95

The elution lasted for 6 minutes and the flow rate of the mobile phase was 0.3 mL/min.

The identification of the test compound was performed by means of MS analysis using the following MS signals: $m/z = 276.1$ as parent ion and $m/z = 234.1$ as product ion (quantifier). Additional identification parameter for FOE Sulfonic acid was the retention time $R_t = 3.4$ min. (approx.).

The quantitative analysis was performed using the external calibration curve constructed with a series of calibration solutions having concentrations: 1% SAR (0.86 μg FOE Sulfonic acid/L), 5% SAR (4.3 μg FOE Sulfonic acid/L), 10% SAR (8.6 μg FOE Sulfonic acid/L), 50% SAR (43 μg FOE Sulfonic acid/L), 100% SAR (86 μg FOE Sulfonic acid/L) and 150% SAR (129 μg FOE Sulfonic acid/L), where SAR stands for Standard Application Rate defined as 34.4 μg test compound/400 mL of extract. Two types of calibration curves were constructed:

- in CH_3CN ;
- in respective blank soil matrix for each test soil.

The calibration curves in blank soil matrices were prepared in the following way:

- to obtain blank soil matrix solutions 100-g (d.w.) portions of each test soil were weighed into 1-L centrifuge beakers and extracted in a way identical to that presented on figure B.8.1.1.2.1.1._CA-70; in that way the following blank soil matrix solutions were prepared: AX (Laacherhof AXXa soil), DD (Dollendorf II soil), HH (Höfchen am Hohenseh 4a soil) and WW (Wurmweise soil);
- next, each of listed above calibration solutions was prepared by:
 - pipetting 0.375 mL of the **Ja 66 SS D1** solution into 25-mL volumetric flask and bringing it to volume with the adequate amount of the given blank soil matrix solution to obtain 150% SAR calibration solution,
 - pipetting 0.25 mL of the **Ja 66 SS D1** solution into 25-mL volumetric flask and bringing it to volume with the adequate amount of the given blank soil matrix solution to obtain 100% SAR calibration solution,
 - pipetting 1.25 mL of the **Ja 66 SS D2** solution into 25-mL volumetric flask and bringing it to volume with the adequate amount of the given blank soil matrix solution to obtain 50% SAR calibration solution,
 - pipetting 0.25 mL of the **Ja 66 SS D2** solution into 25-mL volumetric flask and bringing it to volume with the adequate amount of the given blank soil matrix solution to obtain 10% SAR calibration solution
 - pipetting 0.5 mL of the **Ja 66 SS D2** solution into 100-mL volumetric flask and bringing it to volume with the adequate amount of the given blank soil matrix solution to obtain 5% SAR calibration solution,
 - pipetting 0.1 mL of the **Ja 66 SS D2** solution into 100-mL volumetric flask and bringing it to volume with the adequate amount of the given blank soil matrix solution to obtain 1% SAR calibration solution.

That resulted in four calibration curves, one for extracts from each test soil – AX calibration curve, DD calibration curve, HH calibration curve and WW calibration curve.

Additionally the calibration curve in CH_3CN – ACN calibration curve, was prepared in the same way as described above, with exception that the appropriate amounts of the solutions containing the test compound were diluted with CH_3CN instead of the appropriate blank soil matrix solution. That calibration curve was used in the quantitative analysis aimed on the verification of application rate and homogeneity of application.

The obtained results – concentrations of FOE Sulfonic acid in each test soil at each time point, were subjected to the kinetic analysis in order to identify the best-fit kinetic model and determine persistence and modelling kinetic endpoints for FOE Sulfonic acid in each test soil.

The kinetic analysis was performed in line with the recommendations of the FOCUS Kinetics Guidance Document [FOCUS; 2006], using KinGUI 2 modelling tool. It followed the procedure used in several already summarised studies, in particular **Study 4** and **Study 5**. Three kinetic models were used in the assessment –

SFO, FOMC and DFOP. The obtained fits were evaluated using the same principles as presented in the summaries of **Studies 2 – 8**.

The results of the study are presented below.

Results and their discussion:

The results of the determination of soil physicochemical properties and soil microbial activity in each test soil are presented in the table B.8.1.1.2.1.1._CA-150 at the beginning of this summary. On their basis it can be stated that the soils were appropriately selected, in line with the recommendations of OECD 307 Guideline, and were biologically viable throughout the experiment.

The results of the monitoring of the incubation temperature are presented below on figure B.8.1.1.2.1.1._CA-71. In the study report it was stated that the main incubation temperature was 19.6°C and it ranged from 18.9°C to 20.3°C.

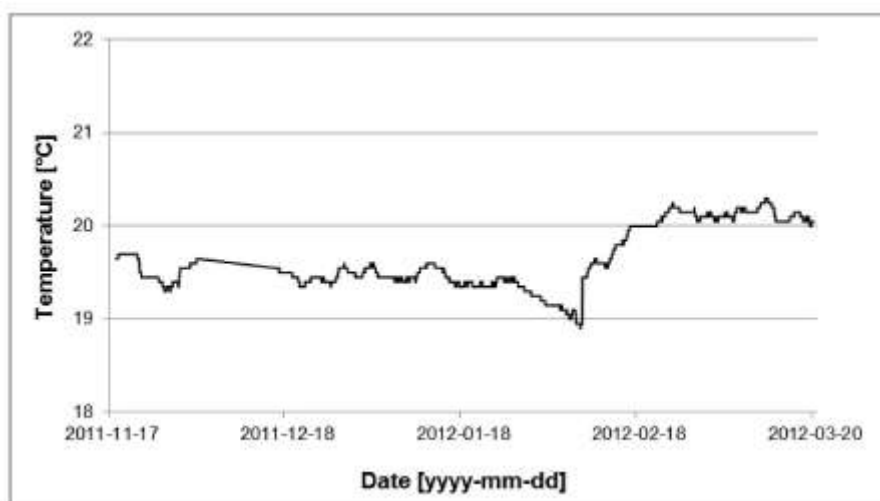


Figure B.8.1.1.2.1.1._CA-71: The temperature recorded during soil pre-conditioning and samples incubation period (copied from the study report).

The results of the monitoring of soil moisture during the experiment are presented below, in the table B.8.1.1.2.1.1._CA-152. On their basis it may be stated that this parameter was maintained on the assumed level during the whole experiment.

Table B.8.1.1.2.1.1._CA-152: The results of the determination of soil moisture content

Test soil	Soil moisture content [g H ₂ O/100 g soil]			Soil moisture during incubation [% MWHC]		
	MWHC	55% MWHC	Actual – in sieved soil	mean	min.	max.
Laacherhof AXXa	48.9	26.7	15.6	55.0	50.5	59.4
Dollendorf II	79.1	43.5	21.9	54.9	52.2	58.3
Höfchen am Hohenseh 4a	54.8	30.1	18.7	54.5	50.5	58.2
Wurmweise	56.3	31.0	18.5	55.2	50.6	59.9

The results of the determination of application rate and the homogeneity of application for DAT 0 – DAT 120 samples were following:

- the amount of the test compound applied per test system at the beginning of application cycle was 34.06 µg (99.0% Standard Application Rate);
- the amount of the test compound applied per test system in the middle of application cycle was 35.26 µg (102.5% Standard Application Rate);
- the amount of the test compound applied per test system at the end of application cycle was 35.00 µg (101.7% Standard Application Rate);

- the mean amount of the test compound applied per test system was 34.77 µg (101.1% Standard Application Rate) with RSD = 1.5%.

In case of additional DAT-1 samples it was 34.54 µg (100.4% Standard Application Rate) with RSD = 1.3% and for DAT-3 samples – 33.15 µg (96.4% Standard Application Rate) with RSD = 1.0%.

On that basis it was stated that the application was homogenous and in good agreement with assumed theoretical application rate of 34.4 µg/100 g soil (d. w.).

The LOQ – limit of quantification, was defined as 5% of nominal study application rate of 344 µg/kg soil, and was equal to 17.2 µg/kg soil. The corresponding LOD was set to $\frac{1}{5}$ LOQ – 1% of the nominal study application rate of 344 µg/kg soil, and was equal to 3.44 µg/kg soil. The values were determined experimentally by examining the linearity of the response of MS/MS detector to the calibration curve built on Blank Soil Matrix AX (Laacherhof AXXa soil). Only the curve based on that Blank Soil Matrix was used because it was stated that the matrix effects were of the same order of magnitude for all investigated soils. The numerical results of that examination are presented below in the table B.8.1.1.2.1.1._CA-153. In the study report it was stated that the excellent correlation between the concentration of the test item and the detector's response was achieved, with $R^2 = 0.9999$. As the graphical presentation of the results caused some problems with its interpretation, RMS repeated the analysis using the CurveExpert Professional 1 tool. The results are presented in graphical form below on figure B.8.1.1.2.1.1._CA-72, conforming the excellent linearity of the detector's response and hence the correctness of the determined LOQ and LOD values.

Table B.8.1.1.2.1.1._CA-153: The numerical results of the determination of the linearity of the response of MS/MS detector.

Calibration sample No.	Nominal concentration		Peak area [a.u.]			RSD [%]
	[% AA]	[ng/mL]	Replicate 1	Replicate 2	Mean	
1	1	0.86	654731	661032	657882	0.5
2	5	4.3	3275334	3237584	3256459	0.6
3	10	8.6	6581627	6467002	6524315	0.9
4	50	43.0	31740125	32235509	31987817	0.8
5	100	86.0	63011508	63058516	63035012	0.0
6	150	129.0	90028439	91279930	90654185	0.7

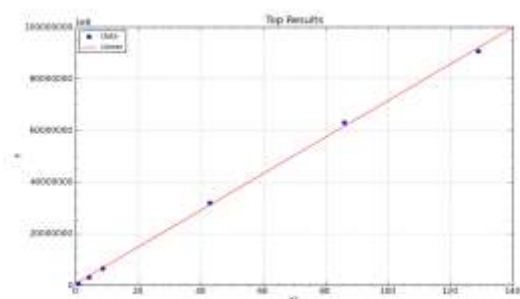


Table B.8.1.1.2.1.1._CA-72: The graphical results of the determination of the linearity of the response of MS/MS detector – calibration curve.

The determination of the accuracy and precision of the method, assessed on the basis of the recovery rates at LOQ level (5% SAR) and application level (100% SAR), looked as follows:

- for Laacherhof AXXa soil mean recovery at LOQ and AR level was 99.3% (96.4 – 102.9%) with RSD = 1.9%;
- for Dollendorf II soil mean recovery at LOQ and AR level was 99.3% (97.6 – 101.1%) with RSD = 1.2%;
- for Höfchen am Hohenseh 4a soil mean recovery at LOQ and AR level was 100.7% (96.6 – 104.0%) with RSD = 2.4%;
- for Wurmwielse soil mean recovery at LOQ and AR level was 98.1% (95.5 – 101.9%) with RSD = 1.9%;
- the mean recovery at LOQ and AR level was 99.4% with RSD = 2.1%.

The results of the experiment – concentrations of FOE Sulfonic acid in soil in function of time, are presented below in the table B.8.1.1.2.1.1._CA-154. For each test soil the concentrations of the test compound are reported

as % of applied amount – [% AA] and in [µg/kg soil]. The values expressed as [%AA] were calculated using the following assumptions:

- for all samples, except DAT-1 and DAT-3 samples, the application rate was determined to be 347.7 µg/kg soil and that value was set to 100% AA (Applied Amount);
- for DAT-1 samples the application rate was determined to be 345.3 µg/kg soil and that value was set to 100% AA (Applied Amount);
- for DAT-3 samples the application rate was determined to be 331.5 µg/kg soil and that value was set to 100% AA (Applied Amount).

The graphic presentation of the results is given on figure B.8.1.1.2.1.1._CA-73.

Table B.8.1.1.2.1.1._CA-154: Concentration of FOE Sulfonic acid in test soils in function of time.

Results obtained in Laacherhof AXXa soil							Results obtained in Wurmwielse soil						
DAT [days]	Concentration of FOE Sulfonic acid						DAT [days]	Concentration of FOE Sulfonic acid					
	[% AA]			[µg/kg soil]				[% AA]			[µg/kg soil]		
	Rep. 1	Rep. 2	Mean	Rep. 1	Rep. 2	Mean		Rep. 1	Rep. 2	Mean	Rep. 1	Rep. 2	Mean
0	103.2	103.2	103.2	358.80	358.92	358.9	0	102.9	101.1	102.1	357.86	352.57	355.2
7	93.0	94.1	93.5	323.48	327.06	325.3	7	92.5	92.1	92.3	321.50	320.44	321.0
14	90.2	88.9	89.5	313.61	309.11	311.4	14	86.4	85.5	85.9	300.28	297.39	298.8
21	85.7	84.5	85.1	298.01	293.71	295.9	21	78.6	78.1	78.4	273.34	271.69	272.5
37	70.9	70.6	70.7	246.48	245.51	246.0	37	58.2	56.2	57.2	202.22	195.41	198.8
58	58.1	58.0	58.1	201.97	201.80	201.9	58	43.1	42.6	42.9	149.85	148.17	149.0
86	44.4	46.0	45.2	154.25	159.81	157.0	86	29.3	29.6	29.5	102.04	102.99	102.5
120	33.9	34.0	33.9	117.77	118.16	118.0	120	25.1	25.6	25.3	87.22	88.92	88.1
Results obtained in Dollendorf II soil							Results obtained in Höfchen am Hohenseh 4a soil						
DAT [days]	Concentration of FOE Sulfonic acid						DAT [days]	Concentration of FOE Sulfonic acid					
	[% AA]			[µg/kg soil]				[% AA]			[µg/kg soil]		
	Rep. 1	Rep. 2	Mean	Rep. 1	Rep. 2	Mean		Rep. 1	Rep. 2	Mean	Rep. 1	Rep. 2	Mean
0	93.7	95.9	94.8	326.00	333.36	363.7	0	104.2	104.9	104.6	362.24	364.92	363.6
1	90.5	92.6	91.5	312.36	319.69	316.0	1	100.9	101.8	101.3	348.53	351.43	350.0
3	67.4	63.5	65.4	223.41	210.44	216.9	3	94.4	95.1	94.8	312.90	315.36	314.1
7	39.2	47.6	43.4	136.45	165.61	151.0	7	69.9	75.5	72.7	243.10	262.55	252.8
14	31.2	22.6	26.9	108.43	78.66	93.5	14	56.4	66.4	61.4	196.21	231.02	213.6
21	6.9	16.0	11.5	24.06	55.59	39.8	21	60.7	60.4	60.5	210.91	210.16	210.5
37	3.7	1.5	2.6	12.87	5.10	9.0	37	46.3	46.9	46.6	161.15	163.26	162.2
							58	28.2	25.5	26.8	97.92	88.70	93.3
							86	12.9	15.2	14.0	44.76	52.78	48.8
							120	3.6	3.1	3.3	12.44	10.85	11.6

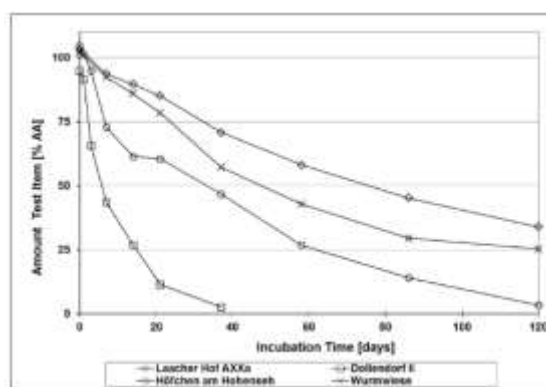


Figure B.8.1.1.2.1.1._CA-73: The graphic presentation of the obtained results (copied from the study report).

The data presented in the table B.8.1.1.2.1.1._CA-1543 were subjected to the kinetic analysis aimed on the determination of the best kinetic fit and derivation of the kinetic endpoints representing persistence of the test compound and suitable for modelling. For that purpose the values obtained for replicates, expressed as [%AA] were used. The values were inserted to the model as they are given in the table above. The results of the kinetic analysis are presented below, separately for each test soil.

- 1) The results of the kinetic analysis of the data obtained for FOE Sulfonic acid in Laacherhof AXXa soil.

The results of the kinetic analysis performed by the Applicant are presented below, in graphical form on figure B.8.1.1.2.1.1._CA-74 and in numerical form in the table B.8.1.1.2.1.1._CA-155. Additionally the table B.8.1.1.2.1.1._CA-156 provides the kinetic endpoints obtained with each of the kinetic models tested.

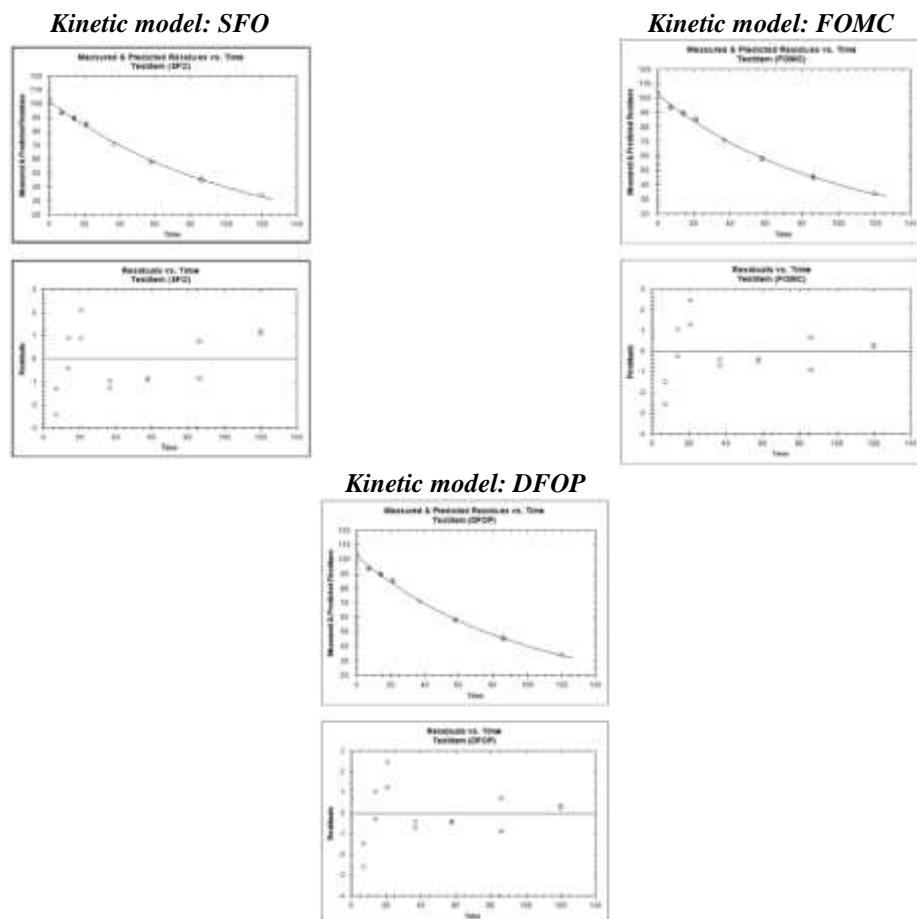


Figure B.8.1.1.2.1.1._CA-74: The graphical results of the kinetic analysis (copied from the study report).

Table B.8.1.1.2.1.1._CA-155: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	Visual assessment ¹⁾
				Lower	Upper			
SFO	M_0	101.9	0.586	100.8	103.09	< 2 E-16	1.275	Good fit
	k	0.009446	1.678 E-4	0.009117	0.017	< 2 E-16		
FOMC	M_0	102.555	0.695	101.193	103.92	< 2 E-16	1.232	Good fit
	α	6.6259	4.61635	-2.4218	15.67	0.0874		
	β	655.8761	4876.5089	-299.624	1611.38	0.1008		
DFOP	M_0	102.511	0.752	101.037	103.985	< 2 E-16	1.325	Good fit
	k_1	0.01227	0.00510	0.00228	0.022	0.01654		
	k_2	0.004977	0.00372	-0.00233	0.012	0.1034		
	g	0.6916	0.5529	-0.3921	1.775	0.1174		

Footnotes to the table:

- 1) Visual assessment of the kinetic curve as proposed by the Applicant.

Table B.8.1.1.2.1.1._CA-156: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested		
		<i>SFO</i>	<i>FOMC</i>	<i>DFOP</i>
<i>FOE Sulfonic acid</i>	DT ₅₀ [days]	73.38	72.33	72.31
	DT ₉₀ [days]	243.77	272.55	278.41

Conclusion:

All three models returned visually and statistically good fits. In terms of χ^2 error the best fit was obtained using FOMC model, although it shall be pointed out that the value of that parameter was very close for all three models tested. At the same time only SFO model returned fully reliable kinetic parameters. In case of FOMC the calculated α and β were not reliable because CI for them passed through zero. In case of DFOP not fully reliable were k_2 and g – for both of them *prob. > t* was higher than 0.1. Therefore the Applicant stated that SFO model shall be considered as returning the best fit for FOE Sulfonic acid in Laacherhof AXXa soil and hence appropriate to derive persistence and modelling endpoints for that compound in that test soil. RMS accepted that proposal.

- 2) The results of the kinetic analysis of the data obtained for FOE Sulfonic acid in Dollendorf II soil.

The results of the kinetic analysis performed by the Applicant are presented below, in graphical form on figure B.8.1.1.2.1.1._CA-75 and in numerical form in the table B.8.1.1.2.1.1._CA-157. Additionally the table B.8.1.1.2.1.1._CA-158 provides the kinetic endpoints obtained with each of the kinetic models tested.

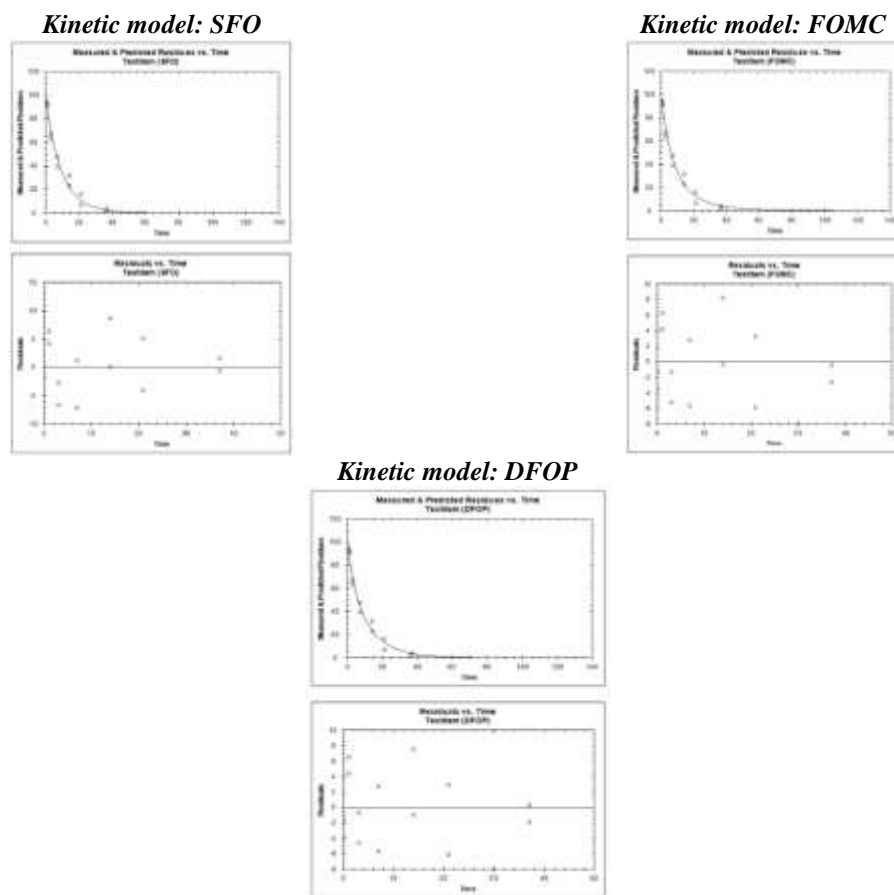


Figure B.8.1.1.2.1.1._CA-75: The graphical results of the kinetic analysis (copied from the study report).

Table B.8.1.1.2.1.1._CA-157: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	Visual assessment ¹⁾
				Lower	Upper			
SFO	M_0	95.683	2.528	90.728	100.638	3.72 E-14	5.586	Good fit
	k	0.1033	0.00754	0.08850	0.118	5.45 E-9		
FOMC	M_0	97.140	2.898	91.460	102.8	9.95 E-13	5.449	Good fit
	α	4.944	4.876	-4.612	14.50	0.166		
	β	41.378	46.947	-50.537	133.40	0.198		
DFOP	M_0	97.633	3.039	91.676	103.589	1.01 E-11	5.804	Good fit
	k_1	0.2706	0.2397	-0.1993	0.740	0.1427		
	k_2	0.08274	0.02501	0.03373	0.132	0.00395		
	g	0.2460	0.3295	-0.3999	0.892	0.2363		

Footnotes to the table:

- 1) Visual assessment of the kinetic curve as proposed by the Applicant.

Table B.8.1.1.2.1.1_CA-158: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested		
		<i>SFO</i>	<i>FOMC</i>	<i>DFOP</i>
<i>FOE Sulfonic acid</i>	DT ₅₀ [days]	6.71	6.23	6.15
	DT ₉₀ [days]	22.30	24.55	24.46

Conclusion:

All three models returned visually and statistically good fits. In terms of χ^2 error the best fit was obtained using FOMC model, although it shall be pointed out that the value of that parameter was very close for all three models tested. At the same time only SFO model returned fully reliable kinetic parameters. In case of FOMC the calculated α and β were not reliable because CI for them passed through zero. In case of DFOP not fully reliable were k_I and g – for both of them *prob. > t* was higher than 0.1. Therefore the Applicant stated that SFO model shall be considered as returning the best fit for FOE Sulfonic acid in Dollendorf II soil and hence appropriate to derive persistence and modelling endpoints for that compound in that test soil. RMS accepted that proposal.

- 3) The results of the kinetic analysis of the data obtained for FOE Sulfonic acid in Höfchen am Hohenseh 4a soil.

The results of the kinetic analysis performed by the Applicant are presented below, in graphical form on figure B.8.1.1.2.1.1._CA-76 and in numerical form in the table B.8.1.1.2.1.1._CA-159. Additionally the table B.8.1.1.2.1.1._CA-160 provides the kinetic endpoints obtained with each of the kinetic models tested.

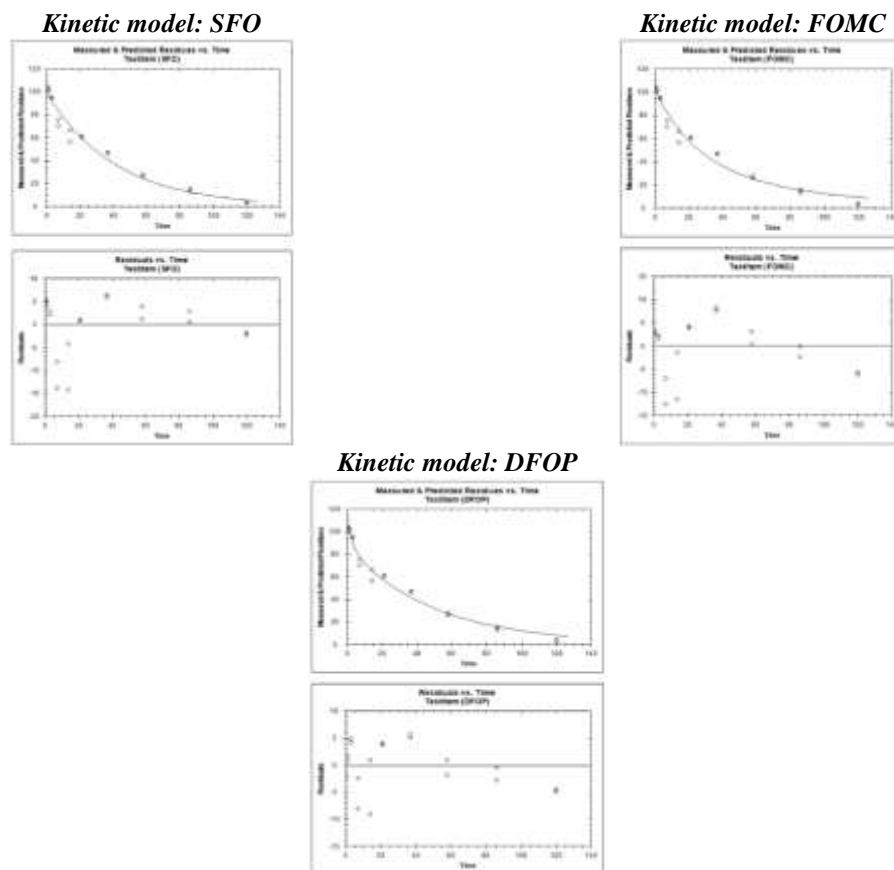


Figure B.8.1.1.2.1.1._CA-76: The graphical results of the kinetic analysis (copied from the study report).

Table B.8.1.1.2.1.1._CA-159: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	Visual assessment ¹⁾
				Lower	Upper			
SFO	M ₀	99.206	2.467	94.372	104.041	< 2 E-16	7.684	Good fit
	k	0.02425	0.00184	0.02064	0.028	5.53 E-11		
FOMC	M ₀	101.693	3.118	95.582	107.804	< 2 E-16	7.557	Good fit
	α	2.896	2.110	-1.239	7.031	0.0939		
	β	93.374	84.918	-73.062	259.810	0.1434		
DFOP	M ₀	106.6	2.598	101.5	111.701	< 2 E-16	5.654	Good fit
	k ₁	0.2587	0.09197	0.07848	0.439	0.00625		
	k ₂	0.019673	1.704 E-3	0.01633	0.023	1.81 E-9		
	g	0.1985	0.04972	0.1011	0.296	5.24 E-4		

Footnotes to the table:

- 1) Visual assessment of the kinetic curve as proposed by the Applicant.

Table B.8.1.1.2.1.1._CA-160: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested		
		<i>SFO</i>	<i>FOMC</i>	<i>DFOP</i>
<i>FOE Sulfonic acid</i>	DT ₅₀ [days]	28.58	25.25	24.03
	DT ₉₀ [days]	94.95	113.44	105.82

Conclusion:

All three models returned visually and statistically good fits. In terms of χ^2 error the best fit was obtained using DFOP model, which also returned, as it was in case of SFO model, fully reliable kinetic parameters. It was noted that both tested bi-phasic models returned the fits that were statistically superior to SFO fit. At the same time in case of FOMC the calculated α and β were not reliable because CI for them passed through zero. Applicant identified DFOP as the model returning the best fit, fully reliable in terms of determined kinetic parameters for FOE Sulfonic acid in Höfchen am Hohenseh 4a soil.

RMS, agreeing in principle with that proposal, noticed that SFO returned fit that was visually and statistically good. The χ^2 error was well below the threshold value of 15%, the distribution of experimental points well correlated with the decline curve (it was comparable to what was obtained using DFOP model), and the residuals on the similar level to that determined for DFOP fit, with also comparable distribution.

All that taken into account, RMS is of the opinion that SFO fit may be considered appropriate as returning persistence and modelling kinetic endpoints. Such selection may be also supported by recommendation given by the relevant Guidelines that whenever it is possible SFO should be selected as first choice, also in order to avoid overparametrisation during the model exposure assessment.

Therefore the final conclusion from that fitting is following: the SFO is of the sufficient quality to be considered as fully appropriate to derive persistence and modelling endpoints for FOE Sulfonic acid in Höfchen am Hohenseh 4a soil.

- 4) The results of the kinetic analysis of the data obtained for FOE Sulfonic acid in Wurmwiese soil.

The results of the kinetic analysis performed by the Applicant are presented below, in graphical form on figure B.8.1.1.2.1.1._CA-77 and in numerical form in the table B.8.1.1.2.1.1._CA-161. Additionally the table B.8.1.1.2.1.1._CA-162 provides the kinetic endpoints obtained with each of the kinetic models tested.

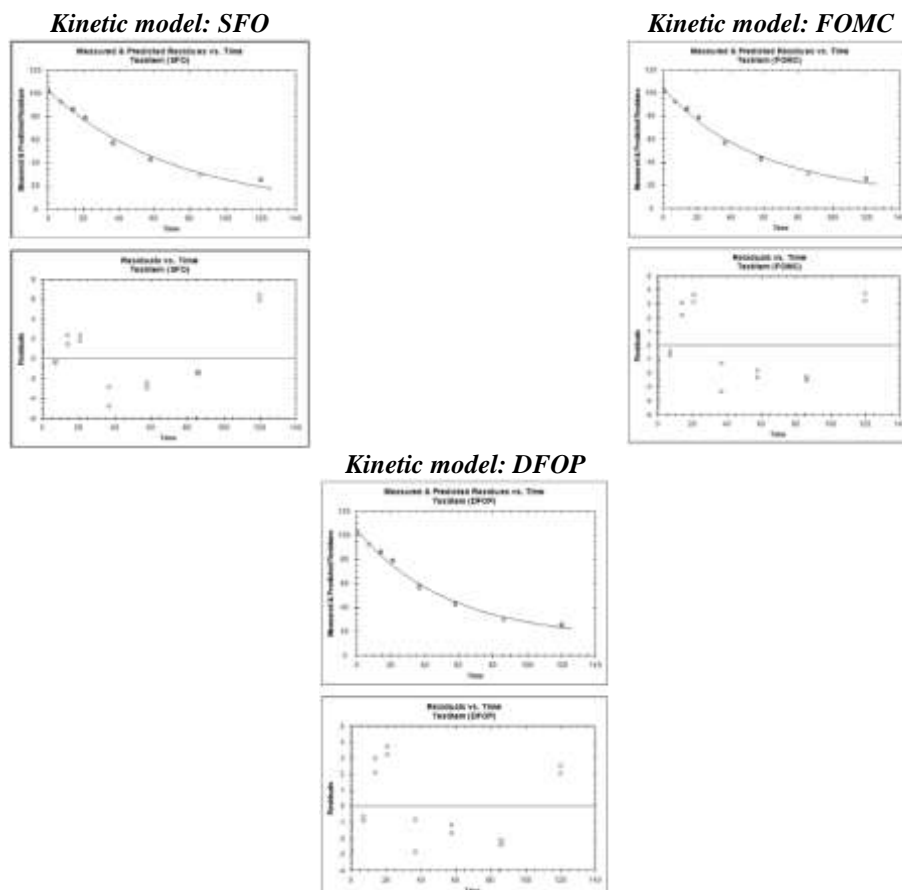


Figure B.8.1.1.2.1.1._CA-77: The graphical results of the kinetic analysis (copied from the study report).

Table B.8.1.1.2.1.1._CA-161: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	Visual assessment ¹⁾
				Lower	Upper			
SFO	M_0	102.2	1.521	99.20	105.161	< 2 E-16	3.662	Good fit
	k	0.01393	5.539 E-4	0.01284	0.015	2.36 E-13		
FOMC	M_0	103.992	1.604	100.847	107.136	< 2 E-16	3.304	Good fit
	α	3.5269	1.63475	0.3228	6.731	0.0251		
	β	215.7837	115.7458	-11.0739	442.641	0.0425		
DFOP	M_0	104.20	1.399	101.4	106.917	< 2 E-16	3.164	Moderate fit
	k_1	0.01852	4.373 E-3	9.946 E-3	0.027	5.79 E-4		
	k_2	2.402 E-9	0.01392	-0.02729	0.027	0.500		
	g	0.8733	0.2748	0.3347	1.412	3.977 E-3		

Footnotes to the table:

- 1) Visual assessment of the kinetic curve as proposed by the Applicant.

Table B.8.1.1.2.1.1._CA-161: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested		
		<i>SFO</i>	<i>FOMC</i>	<i>DFOP</i>
<i>FOE Sulfonic acid</i>	DT ₅₀ [days]	49.77	46.86	45.90
	DT ₉₀ [days]	165.32	198.75	Not determined

Conclusion:

All three models returned visually and statistically good fits, although DFOP fit was classified in the study report as moderate. However, in RMS's opinion it visually did not significantly differ from other two fits, classified as "good". In terms of χ^2 error the best fit was obtained using DFOP model, although it shall be pointed out that the value of that parameter was very close for all three models tested. At the same time only SFO model returned fully reliable kinetic parameters. In case of FOMC the calculated β was not reliable because CI for it passed through zero. In case of DFOP not fully reliable was k_2 – for that parameter the *prob. > t* was much higher than 0.1, reaching the level of 0.5. Therefore the Applicant stated that SFO model shall be considered as returning the best fit for FOE Sulfonic acid in Wurmwiese soil and hence appropriate to derive persistence and modelling endpoints for that compound in that test soil. RMS accepted that proposal.

Final conclusion of the study:

On the basis of the results of the kinetic analysis presented above was determined the definitive set of the reliable kinetic parameters, presented below in the table B.8.1.1.2.1.1._CA-163.

Table B.8.1.1.2.1.1._CA-163: The definitive set of the kinetic endpoints determined in the study.

Soil		Soil properties		Incubation conditions	Selected best-fit model	Evaluation of the fit		Kinetic parameters		Kinetic endpoints	
Soil name	Soil type (USDA)	OC [%]	pH ¹⁾			χ^2 error	Visual fit ²⁾	Par.	Value	DT ₅₀ [days]	DT ₉₀ [days]
<i>Laacherhof AXXa</i>	Loamy sand	1.7	6.2	19.6°C/ 55% MWHC	SFO	1.275	G	<i>k</i>	9.45 E-3	73.38	243.77
<i>Dollendorf II</i>	Loam	4.6	7.0	19.6°C/ 55% MWHC	SFO	5.586	G	<i>k</i>	0.1033	6.71	22.30
<i>Hoefchen Am Hohenseh 4a;</i>	Silt loam	2.0	6.1	19.6°C/ 55% MWHC	SFO	7.684	G	<i>k</i>	0.0242	28.58	94.95
<i>Wurmwiese</i>	Sandy loam	1.8	5.0	19.6°C/ 55% MWHC	SFO	3.662	G	<i>k</i>	0.0139	49.77	165.32

Footnotes to the table:

1) Measured in 0.01M CaCl₂.

2) The abbreviations used to describe the visual fit: G. – good, A. – acceptable, P. – poor;

Study 12:

Report: Ströch K., Junge T., (2013): „FOE sulfonic acid: Degradation in Four Aerobic Soils.”; Bayer CropScience AG, BCS-D-EnSa-Testing, 40789 Monheim, Germany; unpublished Study Report No. EnSa-13-0618; 2013. 10. 24; ; study reference number: M-467862-01-1;

Guidelines: The study was declared to be performed in line with the provisions of the OECD Guideline for the Testing of Chemicals No. 307 – Aerobic and Anaerobic Transformation in Soil. The Applicant stated that there was no deviations from that Guideline. Additionally, as the data obtained in the study were kinetically evaluated and the results presented in the study report, it was declared that the following Guideline was used:

- FOCUS (2006): “Guidance Document on Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration.” Report of the FOCUS Work Group on Degradation Kinetics, EC Document Reference SANCO/10058/2005 version 2.0, 434 pp.;

In this case also no deviations from the Guideline referred to were stated.

GLP: Yes;

RMS comments: This is a new study submitted specifically for purpose of this assessment. It was verified by the RMS and found acceptable. No deviations from the declared Guidelines were stated. The study is summarised below.

Summary:

The aim of the study was to determine the kinetic degradation rate of FOE Sulfonic acid in aerobic soil incubated under laboratory conditions. The experiment was performed on four test soils taken from the agriculturally used areas representing different geographical origin and different soil properties, in line with the requirements of the relevant Guideline. Their characteristic is provided in the table B.8.1.2.1.1._CA-164.

Table B.8.1.2.1.1.CA-164: The characteristic of soils used in the study.

Parameter		Soil			
		<i>Hanscheider Hof</i>	<i>Frankenforst</i>	<i>LUFA 2.3</i>	<i>LUFA 6S</i>
Soil origin		Burscheid/ North Rhine-Westphalia/ Germany	Vinxel/ North Rhine-Westphalia/ Germany	Offenbach/ Rheinland-Palatinate/ Germany	Siebelingen/ Rheinland-Palatinate/ Germany
Soil type (USDA)		Loam	Silt loam	Sandy loam	Clay
Particle size distribution	Sand [%]	42	30	63	35
	Silt [%]	45	51	27	23
	Clay [%]	13	19	10	42
pH value	in 0.01M CaCl ₂ (1:2)	5.6	6.8	6.8	7.0
	in H ₂ O (1:1)	5.8	7.0	7.1	7.2
	in 1M KCl (1:1)	5.3	6.3	6.7	6.6
Organic Carbon content (OC) [%]		2.8	1.8	1.1	1.9
Organic Matter content (OM) [%] ¹⁾		4.8	3.1	1.9	3.3
Cation Exchange Capacity – CEC [mEq/100g]		10.8	15.4	8.9	21.5
Water holding capacity	MWHC [g H ₂ O/ 100 g soil d. w.]	64.4	56.7	39.3	48.3
	at pF 2.0 (0.1 bar) [%]	30.1	30.5	17.8	32.8
Soil bulk density (disturbed) [g/cm ³]		1.04	1.15	1.28	1.22
Soil biomass [mg microbial C/ kg soil d. w.] ²⁾	<i>DAT-0</i>	BIO- ⁴⁾	870	1065	398
		BIO- ⁴⁾	813	999	736
	<i>DAT-58</i>	BIO+ ⁵⁾	787	1024	671
		BIO+ ⁵⁾	787	1024	671
	<i>DAT-121</i>	BIO- ⁴⁾	601	800	227
		BIO+ ⁵⁾	566	757	242
Soil biomass [% OC] ³⁾	<i>DAT-0</i>	BIO- ⁴⁾	3.11	5.92	3.62
		BIO- ⁴⁾	2.90	5.55	6.69
	<i>DAT-58</i>	BIO+ ⁵⁾	2.81	5.69	6.10
		BIO+ ⁵⁾	2.81	5.69	6.10
	<i>DAT-121</i>	BIO- ⁴⁾	2.15	4.44	2.06
		BIO+ ⁵⁾	2.02	4.37	2.20

Footnotes to the table:

- 1) Value calculated from experimentally determined OC content, using the following equation: OM = 1.724 OC;
- 2) Determined using the SIR method developed by Anderson & Domsch [1978];
- 3) Values recalculated by the RMS using the OC content reported in the table for each test soil;
- 4) Determined in samples not treated with blank application solution – 0.4 mL of 1:1 CH₃OH/H₂O; instead 0.2 mL of distilled water was added;
- 5) Determined in samples treated with blank application solution – 0.4 mL of 1:1 CH₃OH/H₂O;

The test soils were sampled shortly before being used (14 days before the experiment began) with shovel from 0-20 cm layer of grassland plot. No Plant Protection Products were used on the sampling fields for 5 years preceding sampling. The sampled test soils were transported to the test facility in plastic bags. There they were sieved through 2-mm sieve and stored in the darkness at either $T < 8^{\circ}\text{C}$ or $T = 20^{\circ}\text{C}$ until being used. The whole soil sampling-and-handling procedure was declared to be performed in accordance with ISO 10381-6.

The experiment was performed using 300-mL Erlenmeyer flasks into which 100-g (d. w.) portions of sieved test soils were weighed. Next the soil moisture content of each sample was adjusted to $55 \pm 5\%$ MWHC by addition of the appropriate amount of deionised water. So prepared incubation flasks were capped with PU plugs to allow free air exchange. The example incubation vessel is presented below on figure B.8.1.1.2.1.1._CA-78. After adjustment of the soil moisture the incubation vessels were pre-conditioned for 3 days in the dark, in a temperature-controlled walk-in climatic chamber at $T = 20 \pm 2^{\circ}\text{C}$, until being treated with the test compound. The number of incubation vessels prepared for each test soils was such to grant at least to have duplicate treated samples at each sampling point and those for the determination of soil biomass in soil samples not treated and treated with blank application solution.

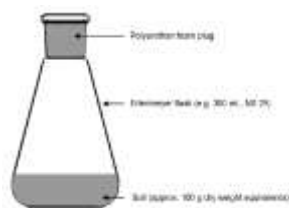


Figure B.8.1.1.2.1.1._CA-78: The example incubation vessel (copied from the study report).

The test compound was non-radiolabelled FOE Sulfonic acid in form of Na^+ salt, having the chemical purity (determined by ^{19}F -NMR) of 87.6%. Its structural formula is shown below on figure B.8.1.1.2.1.1._CA-79.

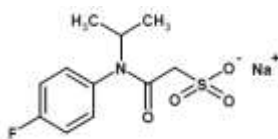


Figure B.8.1.1.2.1.1._CA-79: The structural formula of the test compound used in the experiment (copied from the study report).

It was delivered as a solid sample, in form of a white powder. The whole delivered amount of the test compound was used to prepare first a **Stock solution** and then **Application solutions**.

The **Stock solution** was prepared by dissolving the whole delivered sample of FOE Sulfonic acid Na^+ salt in 2.0 mL of $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (1:1 v/v) sonicated for 10 minutes, to obtain a solution having a nominal concentration 8.8 mg FOE Sulfonic acid/mL. The so prepared **Stock solution**, labelled **TM109_SS**, was stored in the darkness at $T \leq -18^{\circ}\text{C}$ until being used.

The **Stock solution TM109_SS** was subsequently used to prepare the Application solution of Test Item at Application Rate Level, labelled **TM109_AS_AR**, further called **Application solution TM 109_AS_AR**. The **Application solution TM 109_AS_AR** was in turn used to prepare the Application solution of Test Item at LOQ Level, labelled **TM109_AS_LOQ**, further called **Application solution TM 109_AS_LOQ**.

The **Application solution TM 109_AS_AR** was used to treat degradation samples and method validation samples, and to create the calibration curve used in quantitative HPLC-MS/MS analysis. The **Application solution TM 109_AS_LOQ** was used for treatment of concurrent recovery samples at LOQ and for method validation.

The **Application solution TM 109_AS_AR** was prepared by transferring 0.982 mL of the **Stock solution TM109_SS** into 100-mL volumetric flask and evaporating it to dryness under the constant gentle stream of N_2 . The residue was redissolved in 100 mL of $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ 1:1 (v/v) and sonicated for 10 minutes. The obtained solution had a nominal concentration 86.4 $\mu\text{g}/\text{mL}$. The identity of the test compound in so prepared solution was conformed by HPLC-MS/MS. The **Application solution TM 109_AS_AR** was stored in the dark at $T \leq 8^{\circ}\text{C}$.

The **Application solution TM 109_AS_LOQ** was prepared from **Application solution TM 109_AS_AR** by diluting it. That was done in the following way: 2.5 mL of the **Application solution TM 109_AS_AR** was transferred to the 50-mL volumetric flask, brought to volume with the adequate amount of $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ 1:1 (v/v)

and sonicated for 10 minutes. The obtained solution had a nominal concentration 4.3 µg/mL. That solution was also stored in the dark at $T \leq 8^{\circ}\text{C}$.

Additionally the stable-labelled test compound was used in the experiment. The labelling was performed in isopropyl group and consisted on replacing ^1H (*protium*) atoms with ^2H (*deuterium*; marked with symbol D) atoms. Its structural formula is presented below on figure B.8.1.1.2.1.1._CA-80. The compound's chemical purity was 84.8%. It was used as an internal standard in quantitative analysis of FOE Sulfonic acid performed using HPLC-MS/MS method.

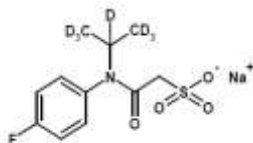


Figure B.8.1.1.2.1.1._CA-80: The structural formula of the deuterised test compound (internal standard) used in the experiment (copied from the study report).

It was delivered as a solid sample, in form of a white powder. The whole delivered amount of the test compound was used to prepare first a **Stock solution** and then a set of **Internal standard solutions**.

The **Stock solution** was prepared by dissolving the whole delivered sample of ^2H - FOE Sulfonic acid Na^+ salt in 5.0 mL of $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (1:1 v/v) sonicated for 10 minutes, to obtain a solution having a nominal concentration 0.848 mg ^2H - FOE Sulfonic acid /mL. The so prepared **Stock solution**, labelled **TM109IS_SS**, was stored in the dark at $T \leq -18^{\circ}\text{C}$ until being used.

The prepared from **TM109IS_SS** solution **Internal standard solutions** were following:

- **Internal standard solution TM109IS_AR**, prepared by transferring 2.028 mL of the **Stock solution TM109IS_SS** into 50-mL volumetric flask, bringing it to the volume with the appropriate amount of $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ 1:1 (v/v) and sonicating it for 10 minutes; the nominal concentration of so prepared solution was 0.0344mg/mL;
- **Internal standard solution TM109IS_D1**, prepared by transferring 0.203 mL of the **Stock solution TM109IS_SS** into 20-mL volumetric flask, bringing it to the volume with the appropriate amount of $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ 1:1 (v/v) and sonicating it for 10 minutes; the nominal concentration of so prepared solution was 0.0086mg/mL;
- **Internal standard solution TM109IS_D2**, prepared by transferring 5 mL of the **Internal standard solution TM109IS_D1** into 50-mL volumetric flask, bringing it to the volume with the appropriate amount of $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ 1:1 (v/v) and sonicating it for 10 minutes; the nominal concentration of so prepared solution was 0.0022mg/mL;

All listed above **Internal standard solutions** were stored in the darkness at $T \leq -18^{\circ}\text{C}$. **Internal standard solution TM109IS_AR** was added to soil extracts and was used in the verification of application rate and homogeneity of application. The **Internal standard solution TM109IS_D2** was added to the standard solutions used to construct calibration curve.

The **Application solution TM 109_AS_AR** was used to treat degradation samples. To do that 0.4 mL of it was applied dropwise onto soil surface in each incubation vessel to obtain the target application dose of 34.4 µg FOE Sulfonic acid/100 g soil (d. w.). That application dose – equal to 0.344 mg/kg soil was determined using the following assumptions:

- field application rate of Flufenacet (parent compound, precursor of FOE Sulfonic acid): 600 g/ha;
- maximum occurrence of FOE Sulfonic acid in aerobic soil (determined in the laboratory studies): 26.3%;
- molar weight of Flufenacet $M = 363.3$ g/mol;
- molar weight of FOE Sulfonic acid $M' = 297.3$ g/mol;
- soil bulk density: 1.5 g/cm^3 ;
- thickness of the soil layer: 2.5 cm.

RMS analysing the calculations noticed that the assumed soil layer was $\frac{1}{2}$ of that routinely used to calculate field application rate (in [g/ha]) from that expressed in mg/kg soil. Therefore the RMS back calculated the would-be field application rate for FOE Sulfonic acid using the standard assumptions:

- soil bulk density: 1.5 g/cm^3 ;
- thickness of the soil layer: 5 cm.

The so calculated theoretic field application rate **A = 258.0 g FOE Sulfonic acid/ha**.

Using the measured soil bulk density of each test soil used in the experiment that value would be:

- for Hanscheider Hof soil: **A = 178.88 g/ha**;
- for Frankfirst soil: **A = 197.80 g/ha**;
- for LUFA 2.3 soil: **A = 220.16 g/ha**;
- for LUFA 6S soil: **A = 209.84 g/ha**

The verification of application rate and homogeneity of application was performed using **Application solution TM 109_AS_AR**, at the beginning of application procedure and after treatment of each test soil. That was done by transferring of 0.4-mL portions of the **Application solution TM 109_AS_AR** into 250-mL volumetric flasks, to which 0.1-mL portions of the **Internal standard solution TM109IS_AR** were added next. The solutions were then brought to volume with the appropriate amount of CH₃OH/H₂O 1:1 (v/v) and mixed thoroughly.

The same **Application solution** and the **Application solution TM 109_AS_LOQ** were used to treat the Concurrent Recovery Samples. The dosing of each application solution was the same as for degradation samples – 0.4 mL/100 g soil. That resulted in fortification level of 0.344 mg/kg soil for samples treated with **Application solution TM 109_AS_AR** and 1.72 µg/100 g/soil (0.072 mg/kg soil) – 5% of the nominal application rate, for samples treated with **Application solution TM 109_AS_LOQ**. The samples were freshly prepared at each sampling point using LUFA 2.3 soil.

The verification of application rate and homogeneity of application was performed in the same way as for degradation samples.

Immediately after treatment the incubation vessels designated as degradation samples were closed with PU plugs to grant free access of air, placed in the darkness in temperature-controlled walk-in climatic chamber and incubated for up to 120 days under aerobic conditions at $T = 20 \pm 2^{\circ}\text{C}$. Duplicate samples were removed from incubation chamber at following time-points (DAT stands for “Days After Treatment”): DAT 0, DAT 2, DAT 4, DAT 7, DAT 14, DAT 30, DAT 58, DAT 91 and DAT 120 (last time point was set only for LUFA 2.3 and LUFA 6S soils).

The soil moisture content in incubation vessels was controlled by weighing them at designated time points: DAT 0, DAT 2, DAT 4, DAT 7, DAT 11, DAT 14, DAT 23, DAT 30, DAT 38, DAT 45, DAT 52, DAT 58, DAT 67, DAT 79, DAT 91, DAT 107 and DAT 120. Soil moisture in the test vessels was adjusted to the designated level, by addition of appropriate amount of deionised water at following time-points: DAT 4, DAT 14, DAT 23, DAT 30, DAT 38, DAT 45, DAT 52, DAT 67, DAT 79 and DAT 107.

The samples for the determination of soil biomass were set alongside the degradation samples. The soil biomass was determined in pre-conditioned test soil samples sampled on DAT 0 (beginning of the incubation period), DAT 58 (middle of the incubation period) and DAT 121 (end of incubation period). The experiment was performed in two variants:

- “BIO-” samples, not treated with blank application solution (instead, 0.2 mL of distilled water was added to each test vessel) ; these samples were taken for the analysis on DAT 0, DAT 58 and DAT 121;
- “BIO+” samples, treated with 0.4 mL of blank application solution (CH₃OH/H₂O 1:1 v/v); these samples were taken for the analysis on DAT 58 and DAT 121.

Samples removed from the incubation chamber were processed and analysed immediately after sampling. That was done using the entire portions of the test soil recovered at each sampling point, using the procedure presented below on figure B.8.1.1.2.1.1._CA-81. The same procedure was applied to Concurrent Recovery Samples.

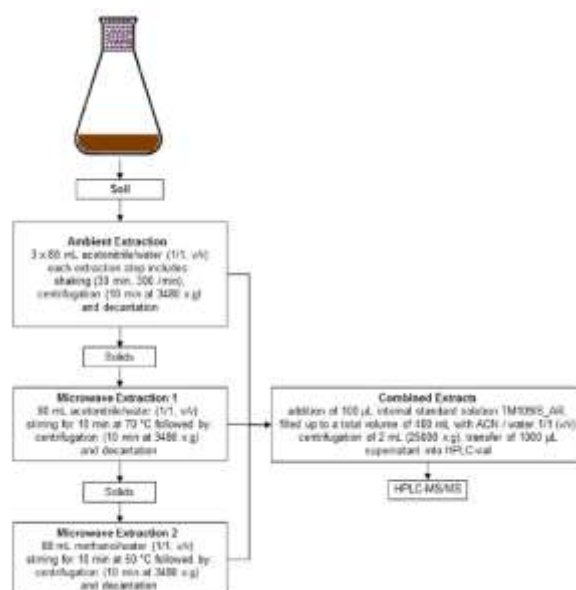


Figure B.8.1.1.2.1.1_CA-81: The sample-processing procedure used in the experiment (scheme copied from the study report, slightly modified by the RMS to increase its transparency).

The quantitative and qualitative analysis of combined soil extracts and other liquid samples was performed by means of HPLC-MS/MS. The analysis was performed using HP1200 chromatography workstation equipped with UV absorption detector and Finnigan TSQ Vantage (Thermo Electron Corporation, San Jose, CA, USA) MS detector. The chromatographic separation was performed on Nucleodur Gravity C8 50*2 mm * 5 µm chromatographic column working in a gradient mode. The column was maintained at constant temperature $T = 40^{\circ}\text{C}$. The gradient elution programme is presented below in the table B.8.1.1.2.1.1_CA-165.

Table B.8.1.1.2.1.1_CA-165: The HPLC gradient modes used in the study.

Time [min]	Solvent ratio	
	<i>Solvent A – Water + 0.1% HCOOH</i>	<i>Solvent B – Acetonitrile + 0.1% HCOOH</i>
0	95	5
1	95	5
2	50	50
5	40	60
6	5	95

The elution lasted for 6 minutes and the flow rate of the mobile phase was 0.3 mL/min.

The identification of the test compound was performed by means of MS analysis using the following MS signals:

- for non-labelled test item: $m/z = 276.1$ as parent ion and $m/z = 234.1$ as product ion (quantifier);
- for ^2H -labelled internal standard: $m/z = 283.1$ as parent ion and $m/z = 2354.1$ as product ion (quantifier).

Additional identification parameter for FOE Sulfonic acid was the retention time $R_t = 3.5$ min. (approx.).

The quantitative analysis was performed using the external calibration curve constructed using the calibration solutions having concentration: 1% SAR (0.86 µg FOE Sulfonic acid/L), 5% SAR (4.3 µg FOE Sulfonic acid/L), 10% SAR (8.6 µg FOE Sulfonic acid/L), 50% SAR (43 µg FOE Sulfonic acid/L), 100% SAR (86 µg FOE Sulfonic acid/L) and 150% SAR (129 µg FOE Sulfonic acid/L), where SAR stands for Standard Application Rate, defined as 34.4 µg test compound in 400 mL of extract. The calibration curve was constructed using $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ 1:1 (v/v) as a solvent.

The procedure of the preparation of calibration curve is described below.

Firstly the **Standard solution TM109_SS_D1** was prepared by transferring 2 mL of the **Application solution TM 109_AS_AR** to 20-mL volumetric flask, filling it to the volume with the appropriate amount of $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ 1:1 (v/v) and sonicating for 10 minutes. The nominal concentration of so obtained solution was 8.6 µg/mL. That solution was used to prepare next dilute – **Standard solution TM109_SS_D2**. That was done by

transferring 2 mL of the **Standard solution TM109_SS_D1** to 20-mL volumetric flask, filling it to the volume with the appropriate amount of CH₃CN/H₂O 1:1 (v/v) and sonicating for 10 minutes. The nominal concentration of so obtained solution was 0.86 µg/mL. These two **Standard solutions** were stored in the dark at T ≤ -18°C until being used.

The solutions used to build calibration curve were freshly prepared on the day of measurements in the following way:

- 0.375 mL of the **Standard solution TM109_SS_D1** and 0.1 mL of the **Internal standard solution TM109IS_D2** were transferred into 25-mL volumetric flask, the resulting solution was brought up to the volume with the appropriate amount of CH₃CN/H₂O 1:1 (v/v) and sonicated for 10 minutes to obtain 150% SAR calibration solution,
- 0.25 mL of the **Standard solution TM109_SS_D1** and 0.1 mL of the **Internal standard solution TM109IS_D2** were transferred into 25-mL volumetric flask, the resulting solution was brought up to the volume with the appropriate amount of CH₃CN/H₂O 1:1 (v/v) and sonicated for 10 minutes to obtain 100% SAR calibration solution,
- 0.125 mL of the **Standard solution TM109_SS_D1** and 0.1 mL of the **Internal standard solution TM109IS_D2** were transferred into 25-mL volumetric flask, the resulting solution was brought up to the volume with the appropriate amount of CH₃CN/H₂O 1:1 (v/v) and sonicated for 10 minutes to obtain 50% SAR calibration solution,
- 0.25 mL of the **Standard solution TM109_SS_D2** and 0.1 mL of the **Internal standard solution TM109IS_D2** were transferred into 25-mL volumetric flask, the resulting solution was brought up to the volume with the appropriate amount of CH₃CN/H₂O 1:1 (v/v) and sonicated for 10 minutes to obtain 10% SAR calibration solution
- 0.125 mL of the **Standard solution TM109_SS_D2** and 0.1 mL of the **Internal standard solution TM109IS_D2** were transferred into 25-mL volumetric flask, the resulting solution was brought up to the volume with the appropriate amount of CH₃CN/H₂O 1:1 (v/v) and sonicated for 10 minutes to obtain 5% SAR calibration solution,
- 0.025 mL of the **Standard solution TM109_SS_D2** and 0.1 mL of the **Internal standard solution TM109IS_D2** were transferred into 25-mL volumetric flask, the resulting solution was brought up to the volume with the appropriate amount of CH₃CN/H₂O 1:1 (v/v) and sonicated for 10 minutes to obtain 1% SAR calibration solution.

The obtained results – concentrations of FOE Sulfonic acid in each test soil at each time point, were subjected to the kinetic analysis in order to identify the best-fit kinetic model and determine persistence and modelling kinetic endpoints for FOE Sulfonic acid in each test soil.

The kinetic analysis was performed in line with the recommendations of the FOCUS Kinetics Guidance Document [FOCUS; 2006], using KinGUI 2 modelling tool. It followed the procedure used in several already summarised studies, in particular **Study 4** and **Study 5**. Two kinetic models were used in the assessment – SFO and FOMC. The obtained fit were evaluated using the same principles as presented in the summaries of **Studies 2 – 8**.

The results of the study are presented below.

Results and their discussion:

The results of the determination of soil physicochemical properties and soil microbial activity in each test soil are presented in the table B.8.1.1.2.1.1._CA-164 at the beginning of this summary. On their basis it can be stated that the soils were appropriately selected, in line with the recommendations of OECD 307 Guideline, and were biologically viable throughout the experiment.

The results of the monitoring of the incubation temperature are presented below on figure B.8.1.1.2.1.1._CA-82. In the study report it was stated that the main incubation temperature was 19.9°C and it ranged from 19.4°C to 20.7°C.

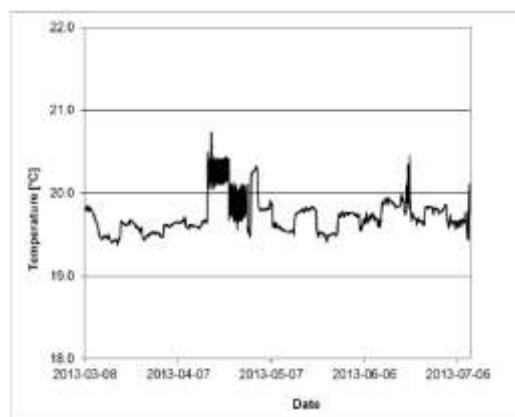


Figure B.8.1.1.2.1.1_CA-82: The temperature recorded during soil pre-conditioning and samples incubation period (copied from the study report).

The results of the monitoring of soil moisture content during the experiment are presented below, in the table B.8.1.1.2.1.1_CA-166. On their basis it may be stated that this parameter was maintained on the assumed level during the whole experiment.

Table B.8.1.1.2.1.1_CA-166: The results of the determination of soil moisture content

Test soil	Soil moisture content [g H ₂ O/100 g soil]			Soil moisture during incubation [% MWHC]		
	MWHC	55% MWHC	Actual – in sieved soil	mean	min.	max.
Herscheider Hof	64.4	35.4	27.6	55.4	51.8	58.0
Frankenforst	56.7	31.2	17.1	55.2	52.2	58.1
LUFA 2.3	39.3	21.6	8.0	54.5	50.2	58.1
LUFA 6S	48.3	26.6	8.5	54.9	51.0	58.0

The results of the determination of application rate and the homogeneity of application for DAT 0 – DAT 120 samples were following:

- the application rate at the beginning of the process was determined to be 422.4 µg/kg;
- the application rate at the end of the 1st series was determined to be 420.4 µg/kg;
- the application rate at the end of the 2nd series was determined to be 418.3 µg/kg;
- the application rate at the end of the 3rd series was determined to be 415.6 µg/kg;
- the application rate at the end of the 4th series was determined to be 420.4 µg/kg;
- the mean application rate was determined to be 419.4 µg/kg with RSD = 0.6%.

On that basis it was stated that the application was homogenous and in good agreement with assumed theoretical application rate.

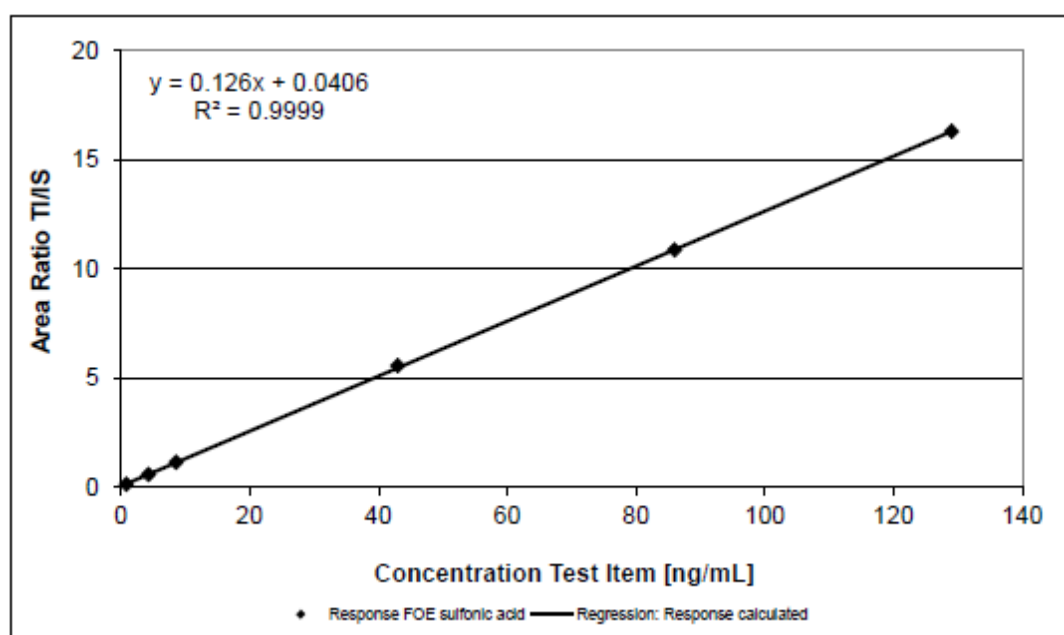
The LOQ – limit of quantification, was defined as 5% of nominal study application rate of 344 µg/kg soil, and was equal to 17.2 µg/kg soil. The corresponding LOD was set to $\frac{1}{5}$ LOQ – 1% of the nominal study application rate of 344 µg/kg soil, and was equal to 3.44 µg/kg soil. The values were determined experimentally by examining the linearity of the response of MS/MS detector to the calibration curve. The numerical results of this examination presented below in the table B.8.1.1.2.1.1_CA-167 and in the graphical form on figure B.8.1.1.2.1.1_CA-83. They conform the good linearity of the detector's response and hence the correctness of the determined LOQ and LOD values.

Table B.8.1.1.2.1.1._CA-167: The numerical results of the determination of the linearity of the response of MS/MS detector.

Calibration sample No.	Nominal concentration		Peak area ratio TI ¹⁾ /IS ²⁾				RSD [%]
	[% AA]	[ng/mL]	Replicate 1	Replicate 2	Replicate 3	Mean	
1	1	0.86	0.1078	0.1085	0.1147	0.1104	2.8
2	5	4.3	0.5582	0.5570	0.5764	0.5639	1.6
3	10	8.6	1.0982	1.1375	1.1465	1.1274	1.9
4	50	43.0	5.4422	5.4795	5.7470	5.5562	2.4
5	100	86.0	10.6867	10.7507	11.1143	10.8503	1.7
6	150	129.0	16.3284	16.1822	16.3563	16.2890	0.5

Footnotes to the table:

- 1) TI – Test Item,
- 2) IS – Internal standard; its amount is always 10% of the nominal study application rate

**Table B.8.1.1.2.1.1._CA-83:** The graphical results of the determination of the linearity of the response of MS/MS detector – calibration curve (copied from the study report).

The determination of the accuracy and precision of the method, assessed on the basis of the recovery rates at LOQ level (5% SAR) and application level (100% SAR), looked as follows:

- for Hanscheider Hof soil mean recovery at LOQ and AR level was 97.4% (93.6 – 100.0%) with RSD = 2.1%;
- for Frankenforst soil mean recovery at LOQ and AR level was 97.9% (95.3 – 102.5%) with RSD = 2.4%;
- for LUFA 2.3 soil mean recovery at LOQ and AR level was 103.9% (97.4 – 103.9%) with RSD = 4.7%;
- for LUFA 6S soil mean recovery at LOQ and AR level was 100.7% (95.9 – 108.3%) with RSD = 4.2%;
- the mean recovery at LOQ and AR level was 100.0% (93.6 – 112.1%) with RSD = 2.1%.

The results of the experiment – concentrations of FOE Sulfonic acid in soil in function of time, are presented below in the table B.8.1.1.2.1.1._CA-168. For each test soil the concentrations of the test compound are reported as % of applied amount – [% AA] and in [µg/kg soil]. The values expressed as [%AA] were calculated using the following assumptions:

- for all samples the application rate was determined to be 41.9 µg/ test system, corresponding to 419 µg/kg soil, and that value was set to 100% AA (Applied Amount);

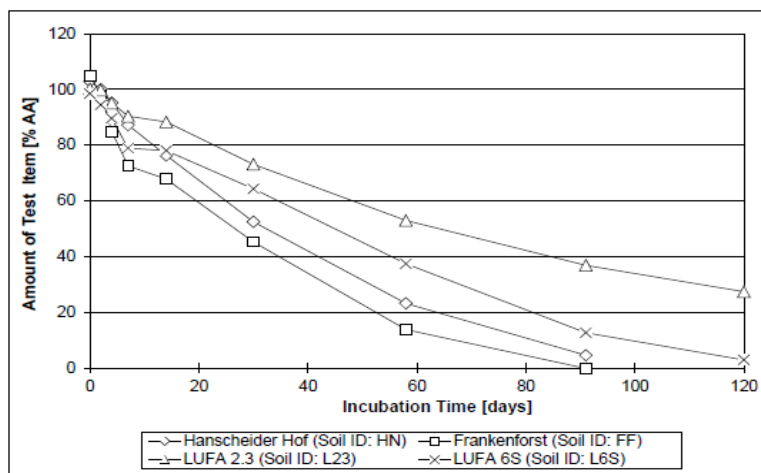
The graphic presentation of the results is given on figure B.8.1.1.2.1.1._CA-84.

Table B.8.1.1.2.1.1._CA-168: Concentration of FOE Sulfonic acid in tets soils in function of time.

Results obtained in Hanscheider Hof soil							Results obtained in Frankenforst soil						
DAT [days]	Concentration of FOE Sulfonic acid						DAT [days]	Concentration of FOE Sulfonic acid					
	[% AA]			[µg/kg soil]				[% AA]			[µg/kg soil]		
	Rep. 1	Rep. 2	Mean	Rep. 1	Rep. 2	Mean		Rep. 1	Rep. 2	Mean	Rep. 1	Rep. 2	Mean
0	101.3	104.4	102.9	425.0	437.9	431.4	0	103.1	106.9	105.0	432.6	448.2	440.3
2	98.3	102.0	100.1	412.2	427.9	419.8	2	97.8	98.3	98.1	410.4	412.3	411.4
4	92.2	98.3	95.3	386.9	412.4	399.5	4	84.2	85.4	84.8	353.2	358.1	355.7
7	88.6	85.9	87.2	371.6	360.2	365.9	7	73.9	71.4	72.6	309.9	299.3	304.6
14	76.5	76.2	76.3	321.0	319.4	320.2	14	66.3	69.5	67.9	277.9	291.7	284.7
30	53.3	51.8	52.5	223.6	217.1	220.4	30	45.1	45.6	45.3	189.1	191.1	190.1
58	22.4	23.1	23.3	94.1	97.1	95.6	58	14.2	13.6	13.9	59.5	56.9	58.1
91	4.7	4.3	4.5	19.8	18.8	19.3	91	<LOD ³⁾	<LOD ³⁾	<LOD ³⁾	<LOD ⁴⁾	<LOD ⁴⁾	<LOD ⁴⁾
120	n. d. ¹⁾	n. d. ¹⁾	n. a. ²⁾	n. d. ¹⁾	n. d. ¹⁾	n. a. ²⁾	120	n. d. ¹⁾	n. d. ¹⁾	n. a. ²⁾	n. d. ¹⁾	n. d. ¹⁾	n. a. ²⁾
Results obtained in LUFA 2.3 soil							Results obtained in LUFA 6S soil						
DAT [days]	Concentration of FOE Sulfonic acid						DAT [days]	Concentration of FOE Sulfonic acid					
	[% AA]			[µg/kg soil]				[% AA]			[µg/kg soil]		
	Rep. 1	Rep. 2	Mean	Rep. 1	Rep. 2	Mean		Rep. 1	Rep. 2	Mean	Rep. 1	Rep. 2	Mean
0	102.5	98.0	100.2	430.0	411.0	420.4	0	98.9	98.0	98.5	414.9	411.1	413.0
2	99.6	100.1	99.8	417.6	419.9	418.8	2	91.4	97.4	94.5	383.4	408.4	396.2
4	94.8	95.4	95.1	397.6	399.9	398.8	4	86.6	92.7	89.6	363.3	388.7	375.9
7	91.5	89.3	90.4	383.6	374.5	379.1	7	80.1	77.8	78.9	335.9	326.4	331.0
14	87.7	89.0	88.3	367.6	373.5	370.5	14	76.8	79.4	78.1	322.0	332.8	327.4
30	72.8	73.6	73.2	305.1	308.7	306.9	30	64.2	64.5	64.4	269.3	270.5	269.9
58	53.3	52.7	53.0	223.7	220.9	222.3	58	37.7	37.2	37.5	158.1	156.2	157.1
91	36.4	37.5	36.9	152.7	157.1	155.0	91	13.8	11.7	12.7	57.9	49.0	53.4
120	27.4	27.6	27.5	114.9	115.7	115.2	120	2.5	3.6	3.0	10.5	14.9	12.7

Footnotes to the table:

- 1) Value not determined – sample not analysed;
- 2) Not available – not calculated;
- 3) LOD – Limit of Detection – 1% AA;
- 4) LOD – Limit of Detection – 3.44 µg/kg soil

**Figure B.8.1.1.2.1.1._CA-84:** The graphic presentation of the obtained results (copied from the study report).

The data presented in the table B.8.1.1.2.1.1._CA-168 were subjected to the kinetic analysis aimed on the determination of the best kinetic fit and derivation of the kinetic endpoints representing persistence of the test compound and suitable for modelling. For that purpose the values obtained for replicates, expressed as [% AA], were used. The values were inserted to the model as they are presented in the table above. The results of the kinetic analysis are presented below, separately for each test soil.

- 1) The results of the kinetic analysis of the data obtained for FOE Sulfonic acid in Hanscheider Hof soil.

The results of the kinetic analysis performed by the Applicant are presented below, in graphical form on figure B.8.1.1.2.1.1._CA-85 and in numerical form in the table B.8.1.1.2.1.1._CA-169. Additionally the table B.8.1.1.2.1.1._CA-170 provides the kinetic endpoints obtained with each of the kinetic models tested.

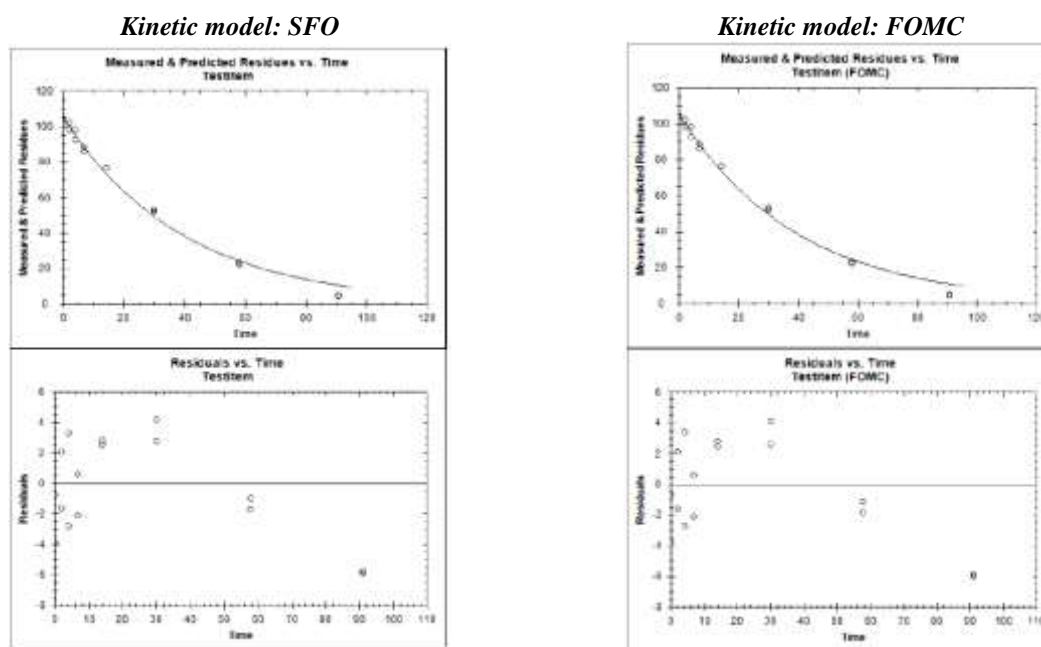


Figure B.8.1.1.2.1.1._CA-85: The graphical results of the kinetic analysis (copied from the study report).

Table B.8.1.1.2.1.1._CA-169: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	Visual assessment ¹⁾
				Lower	Upper			
SFO	M_0	105.2	1.363	102.5	107.833	< 2 E-16	3.247	Good fit
	k	0.025396	1.049 E-3	0.02333	0.027	3.99 E-13		
FOMC	M_0	105.101	1.184	102.780	107.400	< 2 E-16	3.475	Good fit
	α	732.652	632.078	-506.198	1971.5	0.134		
	β	28946.583	25008.052	-20068.298	77961.5	0.134		

Footnotes to the table:

- 1) Visual assessment of the kinetic curve as proposed by the Applicant.

Table B.8.1.1.2.1.1._CA-170: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested	
		SFO	FOMC
FOE Sulfonic acid	DT ₅₀ [days]	27.30	27.40
	DT ₉₀ [days]	90.70	91.12

Conclusion:

Both models returned visually and statistically good fits. In terms of χ^2 error better fit was obtained using SFO model, although it shall be pointed out that the value of that parameter was very close for both models tested. At the same time only SFO model returned fully reliable kinetic parameters. In case of FOMC the calculated α and β were not reliable because CI for them passed through zero. Therefore the Applicant stated that SFO model shall be considered as returning the best fit for FOE Sulfonic acid in Hanscheider Hof soil and hence appropriate to derive persistence and modelling endpoints for that compound in that test soil. RMS accepted that proposal.

- 2) The results of the kinetic analysis of the data obtained for FOE Sulfonic acid in Frankenforst soil.

The results of the kinetic analysis performed by the Applicant are presented below, in graphical form on figure B.8.1.1.2.1.1._CA-86 and in numerical form in the table B.8.1.1.2.1.1._CA-171. Additionally the table B.8.1.1.2.1.1._CA-172 provides the kinetic endpoints obtained with each of the kinetic models tested.

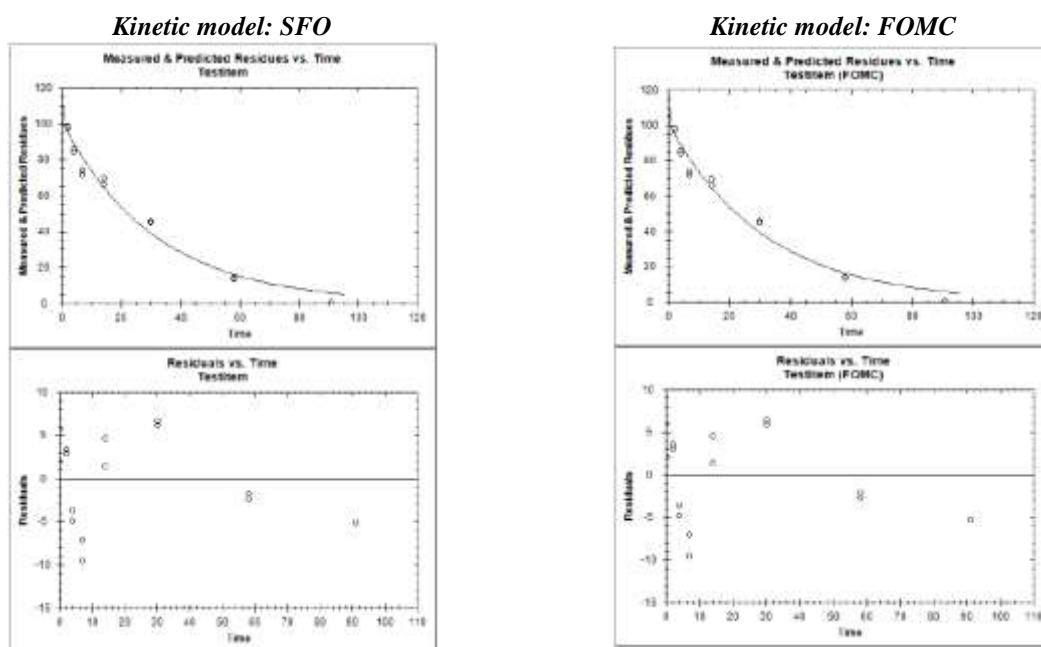


Figure B.8.1.1.2.1.1._CA-86: The graphical results of the kinetic analysis (copied from the study report).

Table B.8.1.1.2.1.1._CA-171: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	Visual assessment ¹⁾
				Lower	Upper			
SFO	M_0	101.2	2.319	99.66	105.751	< 2 E-16	6.412	Good fit
	k	0.03181	2.328 E-3	0.02724	0.036	8.69 E-10		
FOMC	M_0	100.969	2.155	96.745	105.2	3.48 E-16	6.849	Good fit
	α	471.952	1395.635	-2263.443	3207.3	0.370		
	β	14979.798	44387.211	-72017.538	101977.1	0.371		

Footnotes to the table:

- 1) Visual assessment of the kinetic curve as proposed by the Applicant.

Table B.8.1.1.2.1.1._CA-172: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested	
		SFO	FOMC
FOE Sulfonic acid	DT ₅₀ [days]	21.79	22.02
	DT ₉₀ [days]	72.39	73.26

Conclusion:

Both models returned visually and statistically good fits. In terms of χ^2 error better fit was obtained using SFO model, although it shall be pointed out that the value of that parameter was very close for both models tested. At the same time only SFO model returned fully reliable kinetic parameters. In case of FOMC the calculated α and β were not reliable because CI for them passed through zero. Therefore the Applicant stated that SFO model shall be considered as returning the best fit for FOE Sulfonic acid in Frankenforst soil and hence appropriate to derive persistence and modelling endpoints for that compound in that test soil. RMS accepted that proposal.

3) The results of the kinetic analysis of the data obtained for FOE Sulfonic acid in LUFA 2.3 soil.

The results of the kinetic analysis performed by the Applicant are presented below, in graphical form on figure B.8.1.1.2.1.1._CA-87 and in numerical form in the table B.8.1.1.2.1.1._CA-173. Additionally the table B.8.1.1.2.1.1._CA-174 provides the kinetic endpoints obtained with each of the kinetic models tested.

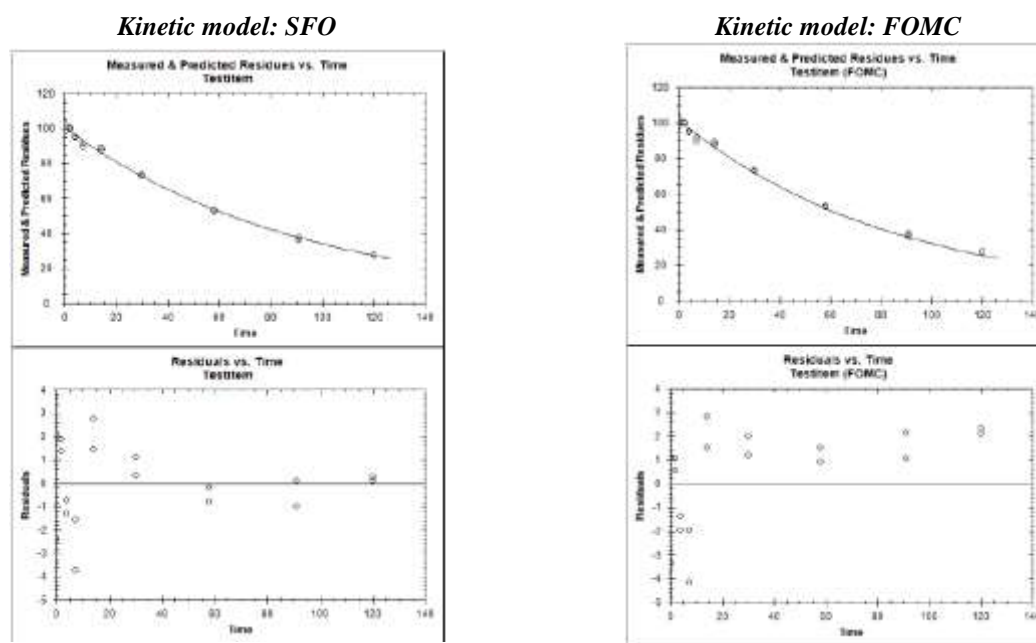


Figure B.8.1.1.2.1.1._CA-87: The graphical results of the kinetic analysis (copied from the study report).

Table B.8.1.1.2.1.1._CA-173: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	Visual assessment ¹⁾
				Lower	Upper			
SFO	M_0	100.4	0.604	99.20	101.567	< 2 E-16	1.450	Good fit
	k	0.01085	2.28 E-4	0.01041	0.011	< 2 E-16		
FOMC	M_0	101.4	0.643	100.1	102.6	< 2 E-16	2.099	Good fit
	α	362.5	62.63	239.7	485.2	1.79 E-5		
	β	3.127 E4	5.411 E3	2.066 E4	41873.0	1.82 E-5		

Footnotes to the table:

1) Visual assessment of the kinetic curve as proposed by the Applicant.

Table B.8.1.1.2.1.1._CA-174: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested	
		SFO	FOMC
FOE Sulfonic acid	DT ₅₀ [days]	63.87	59.85
	DT ₉₀ [days]	212.16	199.27

Conclusion:

Both models returned visually and statistically good fits, although residuals for SFO were more randomly distributed (in case of FOMC the distribution was systematic). In terms of χ^2 error better fit was obtained using SFO model, although it shall be pointed out that the value of that parameter was very close for both models tested. Both models returned full reliable kinetic parameters. As a result, the Applicant stated that SFO model shall be considered as returning the best fit for FOE Sulfonic acid in in LUFA 2.3 soil, hence appropriate to derive persistence and modelling endpoints for that compound in that test soil. RMS accepted that proposal.

- 4) The results of the kinetic analysis of the data obtained for FOE Sulfonic acid in LUFA 6S soil.

The results of the kinetic analysis performed by the Applicant are presented below, in graphical form on figure B.8.1.1.2.1.1._CA-88 and in numerical form in the table B.8.1.1.2.1.1._CA-175. Additionally the table B.8.1.1.2.1.1._CA-176 provides the kinetic endpoints obtained with each of the kinetic models tested.

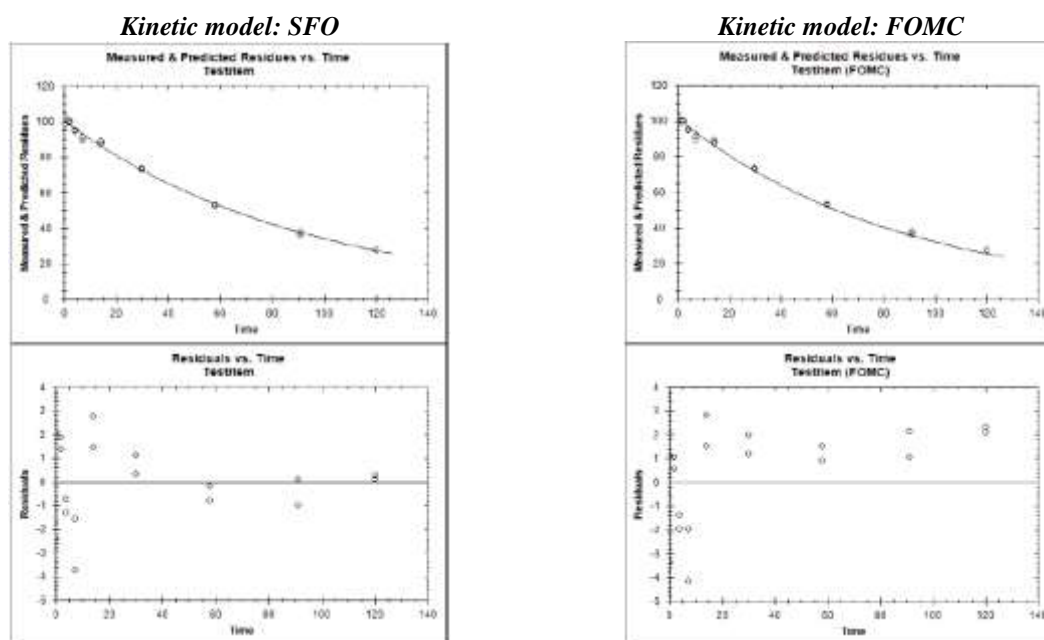


Figure B.8.1.1.2.1.1._CA-88: The graphical results of the kinetic analysis (copied from the study report).

Table B.8.1.1.2.1.1._CA-175: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	Visual assessment ¹⁾
				Lower	Upper			
SFO	M_0	97.664	2.103	93.542	101.786	< 2 E-16	6.49	Good fit
	k	0.01838	0.00122	0.01599	0.0021	3.42 E-11		
FOMC	M_0	98.75	10.16	78.83	118.7	3.64 E-8	7.123	Good fit
	α	1566.39	1671.79	-1710.26	4843.0	0.182		
	β	79448.94	84831.76	-86818.25	245716.1	0.182		

Footnotes to the table:

- 1) Visual assessment of the kinetic curve as proposed by the Applicant.

Table B.8.1.1.2.1.1._CA-176: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested	
		SFO	FOMC
FOE Sulfonic acid	DT ₅₀ [days]	37.71	35.17
	DT ₉₀ [days]	125.28	116.88

Conclusion:

Both models returned visually and statistically good fits. In terms of χ^2 error better fit was obtained using SFO model, although it shall be pointed out that the value of that parameter was very similar for both models tested. At the same time only SFO model returned fully reliable kinetic parameters. In case of FOMC the calculated α and β were not reliable because CI for them passed through zero. Therefore the Applicant stated that SFO model shall be considered as returning the best fit for FOE Sulfonic acid in LUFA 6S soil and hence appropriate to derive persistence and modelling endpoints for that compound in that test soil. RMS accepted that proposal.

Final conclusion of the study:

On the basis of the results of the kinetic analysis presented above was determined the definitive set of the reliable kinetic parameters, presented below in the table B.8.1.1.2.1.1._CA-177.

Table B.8.1.1.2.1.1._CA-177: The definitive set of the kinetic endpoints determined in the study.

Soil		Soil properties		Incubation conditions	Selected best-fit model	Evaluation of the fit		Kinetic parameters		Kinetic endpoints	
Soil name	Soil type (USDA)	OC [%]	pH ¹⁾			χ^2 error	Visual fit ²⁾	Par.	Value	DT ₅₀ [days]	DT ₉₀ [days]
<i>Hanscheider Hof</i>	Loam	2.8	5.6	19.9°C/ 55% MWHC	SFO	3.247	G	<i>k</i>	0.02540	27.30	90.70
<i>Frankenforst</i>	Silt loam	1.8	6.8	19.9°C/ 55% MWHC	SFO	6.412	G	<i>k</i>	0.03181	21.79	72.39
<i>LUFA 2.3</i>	Sandy loam	1.1	6.8	19.9°C/ 55% MWHC	SFO	1.450	G	<i>k</i>	0.01085	63.87	212.16
<i>LUFA 6Se</i>	Clay	1.9	7.0	19.9°C/ 55% MWHC	SFO	6.49	G	<i>k</i>	0.01838	37.71	125.28

Footnotes to the table:

1) Measured in 0.01M CaCl₂.

2) The abbreviations used to describe the visual fit: G. – good, A. – acceptable, P. – poor;

Study 13:

Report: Reinken G., Partsch S., (2014): “Kinetic Evaluation of the Degradation of Flufenacet Degradation Product FOE sulfonic acid under Aerobic Soil conditions in Laboratory according to FOCUS Kinetics Using the KinGUI 2 Tool. FOE sulfonic acid.”; Bayer CropScience AG, Environmental Safety, Alfred-Nobel-Strasse 50, 40789 Monheim, Germany; unpublished Study Report No. EnSa-12-580; 2014. 02. 17; ; study reference number: M-477844-01-1;

Guidelines: The study was declared to be performed to comply with the following guidelines:

- FOCUS (2006): “Guidance Document on Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration.” Report of the FOCUS Work Group on Degradation Kinetics, EC Document Reference SANCO/10058/2005 version 2.0, 434 pp.;
- FOCUS (2011): “Generic guidance for Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration”, version 1.0 (issued on 23 November 2011).

GLP: No, not applicable – this is a modelling study;

RMS comments: RMS verified the study for its compliance with the provisions of the Guidelines listed above.

It was stated that the study generally complied with the two evoked Guidance Documents. The study was aimed on the derivation of the modelling kinetic endpoints for FOE Sulfonic acid. It followed modelling approach outlined already in other studies summarised above – **Study 2**, **Study 7** and **Study 8**. The analysis was performed for the results of the two summarised above studies – by [Hellpointner; 1999] (**Study 9**) and by [Hellpointner; 2003] (**Study 10**). Analysing the data sets declared to be derived from the above source studies and subsequently used in the kinetic analysis RMS noticed that in case of the input data coming from the source **Study 9** the concentrations were given in %. It was also noticed that these values were different from those reported in the tables B.8.1.1.2.1.1._CA-148 for Laacherhof AXXa soil and B.8.1.1.2.1.1._CA-149 for Laacherhof AIII as total radioactivity in extracts identified by TLC as the test compound (values calculated from the raw results by the RMS). In the study report it was not explained how these values were obtained. However, the thorough comparative analysis of the results presented in the source study and this one, enabled to identify the way the input values for Laacherhof AXXa and Laacherhof AIII were derived. That will be explained in details in the summary below. RMS stated that the approach adopted by the authors of the study may be considered acceptable, hence the kinetic analysis presented in the study report did not require to be repeated using different data sets. In general, the study was found to be acceptable and is summarised below.

Summary:

The aim of the study was to kinetically examine the data for FOE Sulfonic acid obtained in two studies summarised above - **Study 9** [Hellpointner; 1999] and **Study 10** [Hellpointner; 2003] in order to derive the kinetic endpoints suitable for use in modelling exposure assessment.

In these two studies the degradation of FOE Sulfonic acid in aerobic soil was examined in five soils – three in **Study 9** and two in **Study 10**. The characteristic of test soils used in these experiments is provided in the table B.8.1.1.2.1.1._CA-141 for **Study 9** and table B.8.1.1.2.1.1._CA-147 for **Study 10**. As their summaries immediately precede the summary of this study, RMS decided not to reproduce these tables in order to not overburden the Assessment Report. However, in the table B.8.1.1.2.1.1._CA-178 are presented key soil properties of each test soil, relevant for the reporting of the results of the kinetic analysis. The experimental conditions used in each experiment are summarised further down, in the table B.8.1.1.2.1.1._CA-179.

Table B.8.1.1.2.1.1._CA-178: The brief characteristic of the test soils.

Study	Soil name	Soil type (USDA classification)	Soil properties			
			pH in CaCl ₂	OC [%]	Soil microbial biomass at the beginning of the study	
					mg microbial C/kg soil	% OC
<i>Hellpointner; 1996</i>	BBA 2.1	Sand	5.3	0.57	111	1.95
	BBA 2.2	Loamy sand	6.3	2.48	390	1.57
	Laacherhof AIII	Silt loam	7.3	0.9	780	3.25
<i>Hellpointner; 2003</i>	Laacherhof AXXa	Sandy loam	6.3	1.47	242	1.65
	Laacherhof AIII	Silt loam	6.8	0.88	275	3.13

Table B.8.1.1.2.1.1._CA-179: The experimental conditions used in each experiment.

Study	Test soil		Incubation temperature $T [^{\circ}\text{C}]$	Experimental conditions		
	Name	Type (USDA classification)		In experiment [% MWHC]	Soil moisture	
					Reference value [g/100g soil]	
Hellpointner; 1999	BBA 2.1	Sand	20 ± 2	31	----	9.2
	BBA 2.2	Loamy sand	20 ± 2	29	----	16.1
	Laacherhof AIII	Silt loam	20 ± 2	44	----	15.1
Hellpointner; 2003	Laacherhof AXXa	Sandy loam	20 ± 2	40	34.42	----
	Laacherhof AIII	Silt loam	20 ± 2	40	36.40	----

The not-processed input data used in the kinetic analysis are presented below in the table B.8.1.1.2.1.1._CA-180. In case of the data derived from the study by [Hellpointner; 2003] the values were transformed to be expressed as [% of the initial dose]. That was done using the results reported in the tables B.8.1.1.2.1.1._CA-148 for Laacherhof AXXa soil and B.8.1.1.2.1.1._CA-149 for Laacherhof AIII as “FOE Sulfonic acid recovered [$\mu\text{g}/100 \text{ g soil}$]”. The data were processed in a following way:

- the DAT-0 average value was defined as 100%;
- the values for each replicate at each time point were recalculated into % initial by dividing them by the DAT-0 average value; the resulting value was multiplied by a factor of 100 to obtain the value expressed in %.

RMS checked the correctness of the calculations and accepted them. It was noted that the values differed from those calculated by the RMS as results of the TLC quantification of the test compound in extracts. However, as the values proposed in the study report were higher, what resulted in longer $\text{DT}_{50}/\text{DT}_{90}$ values, the proposed approach was accepted by the RMS.

Table B.8.1.1.2.1.1._CA-180: The non-processed data obtained in the test soils used as input in kinetic analysis.

The data obtained in the study by [Hellpointner; 1999]								
Soil: BBA 2.1			Soil: BBA 2.2			Soil: Laacherhof		
Time Point – DAT [days]	Concentration [%] of FOE Sulfonic acid		Time Point – DAT [days]	Concentration [%] of FOE Sulfonic acid		Time Point – DAT [days]	Concentration [%] of FOE Sulfonic acid	
	Replic. 1	Replic. 2		Replic. 1	Replic. 2		Replic. 1	Replic. 2
0	100.0	100.0	0	100.0	100.0	0	100.0	100.0
0.08	80.6	85.2	0.08	84.2	94.6	0.08	85.6	66.7
3	86.3	87.6	3	83.6	84.6	3	69.6	68.8
7	87.3	88.0	7	82.8	83.0	7	64.9	65.0
14	83.0	81.4	14	77.7	80.6	14	63.2	62.0
30	80.4	81.2	30	78.3	76.6	30	77.7	75.8
63	73.6	74.9	63	70.0	67.2	63	70.0	68.4
80	70.5	71.7	80	64.1	66.9	80	66.9	54.3
100	70.3	70.3	100	64.3	62.1	100	48.0	63.5

The data obtained in the study by [Hellpointner; 2003]					
Soil: Laacherhof AXXa			Soil: Laacherhof AIII		
Time Point – DAT [days]	Concentration [%] of FOE Sulfonic acid		Time Point – DAT [days]	Concentration [%] of FOE Sulfonic acid	
	Replic. 1	Replic. 2		Replic. 1	Replic. 2
0	99.75	100.57	0	101.61	98.39
3	99.75	99.75	3	98.39	95.97
7	97.30	95.67	7	95.97	93.55
14	90.76	89.94	14	90.32	88.71
28	76.04	77.68	28	78.23	75.81
56	58.05	61.32	56	58.06	55.65
100	28.62	28.62	100	27.42	26.61

The data presented above were subjected to a multistep evaluation procedure, almost identical to that already presented in the summary of the **Study 2**, for convenience repeated below. It consisted of the following steps:

- **Step 1:** Processing of the raw input data;
- **Step 2:** Kinetic evaluation of the processed data using the following 1st order kinetic models: SFO, FOMC and DFOP, and KinGUI 2 as a modelling tool, in order to determine the appropriate kinetic model.
- **Step 3:** Evaluation of the results of kinetic examination of the data;
- **Step 4:** Reporting of the obtained results, in particular kinetic parameters recommended for modelling.

The data-processing to obtain the input values for kinetic analysis (**Step 1**) was identical to the procedure described in the summary of the **Study 2**, on page 166. The processed data used as input in the kinetic examination are presented below in the table B.8.1.1.2.1.1._CA-181.

Table B.8.1.1.2.1.1._CA-181: The processed residue data used in the kinetic analysis.

The data obtained in the study by [Hellpointner; 1999]								
Soil: BBA 2.1			Soil: BBA 2.2			Soil: Laacherhof		
Time Point – DAT [days]	Concentration [%] of FOE Sulfonic acid		Time Point – DAT [days]	Concentration [%] of FOE Sulfonic acid		Time Point – DAT [days]	Concentration [%] of FOE Sulfonic acid	
	Replic. 1	Replic. 2		Replic. 1	Replic. 2		Replic. 1	Replic. 2
0	100.0	100.0	0	100.0	100.0	0	100.0	100.0
0.08	80.6	85.2	0.08	84.2	94.6	0.08	85.6	66.7
3	86.3	87.6	3	83.6	84.6	3	69.6	68.8
7	87.3	88.0	7	82.8	83.0	7	64.9	65.0
14	83.0	81.4	14	77.7	80.6	14	63.2	62.0
30	80.4	81.2	30	78.3	76.6	30	77.7	75.8
63	73.6	74.9	63	70.0	67.2	63	70.0	68.4
80	70.5	71.7	80	64.1	66.9	80	66.9	54.3
100	70.3	70.3	100	64.3	62.1	100	48.0	63.5

The data obtained in the study by [Hellpointner; 2003]					
Soil: Laacherhof AXa			Soil: Laacherhof AIII		
Time Point – DAT [days]	Concentration [%] of FOE Sulfonic acid		Time Point – DAT [days]	Concentration [%] of FOE Sulfonic acid	
	Replic. 1	Replic. 2		Replic. 1	Replic. 2
0	100.11	99.89	0	101.33	98.68
3	99.75	99.75	3	98.39	95.97
7	97.30	95.67	7	95.97	93.55
14	90.76	89.94	14	90.32	88.71
28	76.04	77.68	28	78.23	75.81
56	58.05	61.32	56	58.06	55.65
100	28.62	28.62	100	27.42	26.61

The processed data were kinetically examined using KinGUI ver. 2 modelling tool, developed by Bayer. The optimisation was performed using IRLS (Iteratively Reweighed Nonlinear Least Squares) algorithm. The fitting procedure consisted on the determination of the appropriate kinetic model for FOE Sulfonic acid.

The conceptual metabolic pathway built in the modelling tool was based on the transformation pathway which, in form of simplified scheme, is presented below on figure B.8.1.1.2.1.1._CA-89.

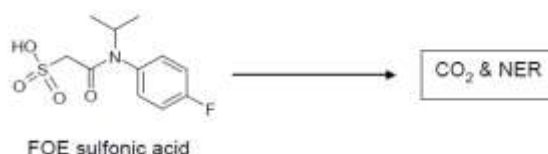


Figure B.8.1.1.2.1.1._CA-89: The simplified transformation pathway used to create conceptual transformation scheme assumed in the modelling tool (copied from the study report).

The obtained results of the kinetic analysis of the data were evaluated by the Applicant. That was done by means of a detailed statistical analysis comprising the following components:

- visual assessment of the fit;
- χ^2 -error statistics;
- t-test significance;
- correlation analysis.

The detailed characteristic of the evaluation procedure was presented in the summary of the **Study 2** on pages 168 – 169. RMS decided not to repeat it here in order to not overburden the Renewal Assessment Report.

On that basis the following multistep assessment procedure was followed:

- **Step 1:** bearing in mind the aim of the kinetic evaluation of the data – determination of the kinetic parameters used in modelling, the SFO kinetic model was tested as first option and if passed the acceptance criteria (visually acceptable, χ^2 -error not exceeding or not significantly exceeding 15%, *prob. > t* value in t-test less than 0.05 for parent and 0.10 for the degradation products), it was considered acceptable;
- **Step 2:** in case the χ^2 -error was significantly greater than 15%, model parameters were fixed and fitting repeated using SFO model;
- **Step 3:** if the **Step-2** fitting failed the χ^2 -error test, bi-phasic models were included. These were FOMC, DFOP and, possibly HS. The model with smaller error was indicated as the most appropriate;
- **Step 4:** if none of the bi-phasic model returned significantly improved fit, SFO model was selected if visually acceptable; that was done in order to avoid of an over-parameterised model based on a marginally better fit.

Analysing the proposed assessment procedure RMS stated that it complied with the procedure for determination of the kinetic endpoints for modelling, presented in FOCUS Kinetics Guidance Document [FOCUS; 2006].

The results of the kinetic analysis are presented below, individually for each test soil.

- 1) The results of the kinetic analysis of the data obtained for FOE Sulfonic acid in BBA 2.1 soil (study by [Hellpointner; 1999]):

The results of the kinetic analysis performed by the Applicant are presented below, in graphical form on figure B.8.1.1.2.1.1._CA-90 and in numerical form in the table B.8.1.1.2.1.1._CA-182. Additionally the table B.8.1.1.2.1.1._CA-183 provides the kinetic endpoints obtained with each of the kinetic models tested.

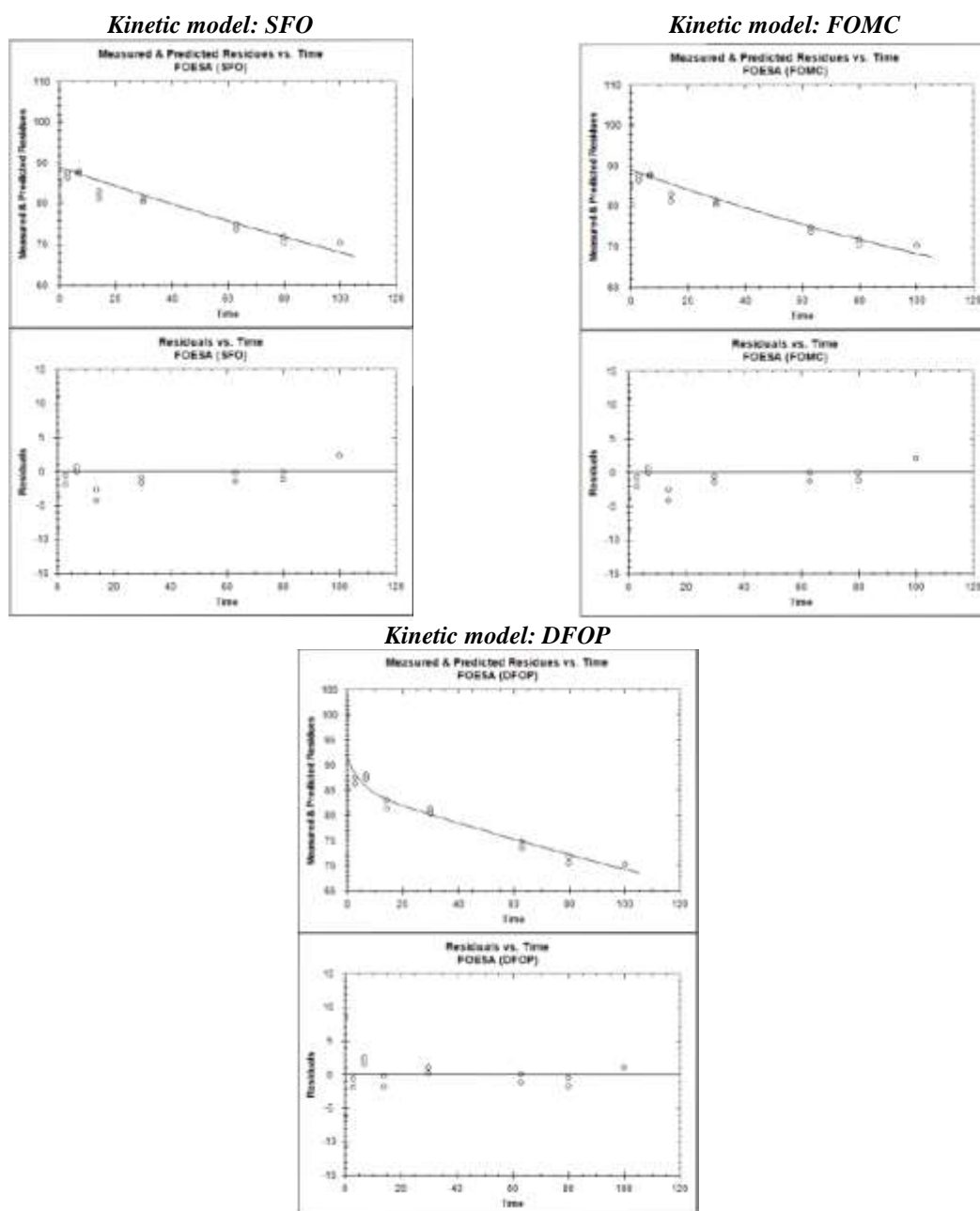


Figure B.8.1.1.2.1.1._CA-90: The graphical results of the kinetic analysis (copied from the study report).

Table B.8.1.1.2.1.1._CA-182: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment ¹⁾
				Lower	Upper			
SFO	M ₀	88.954	1.589	85.840	92.069	< 2 E-16	4.377	0.73; Good fit
	k	2.682 E-3	4.22 E-4	1.855 E-3	0.004	4.77 E -6		
FOMC	M ₀	89.108	1.638	85.899	92.318	< 2 E-16	4.577	0.77; Good fit
	α	1.4819	0.2446	1.0024	1.961	1.1 E-5		
	β	506.8549	9.1175	488.985	524.725	< 2 E-16		
DFOP	M ₀	91.449	2.233	87.072	95.8267	2.81 E-16	4.561	0.74; Good fit
	k ₁	0.1937	0.4986	-0.7834	1.171	0.3517		
	k ₂	2.084 E-3	9.771 E-4	1.689 E-4	0.004	0.0256		
	g	0.06756	0.06248	-0.05490	0.190	0.1489		

Footnotes to the table:

1) Visual assessment of the kinetic curve as proposed by the Applicant.

Table B.8.1.1.2.1.1._CA-183: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested		
		SFO	FOMC	DFOP
FOE Sulfonic acid	DT ₅₀ [days]	258.44	302.29	299.05
	DT ₉₀ [days]	858.51	1890.3	Not determined

Conclusion:

All three models returned visually and statistically good fits. In terms of χ^2 error the best fit was obtained using SFO model, although it shall be pointed out that the value of that parameter was very close for all three models tested. Two models – SFO and FOMC, returned fully reliable kinetic parameters. In case of DFOP not fully reliable were k_2 and g – for these parameterers the *prob. > t* was higher than 0.1.

The Applicant stated that SFO model shall be considered as returning the best fit for FOE Sulfonic acid in BBA 2.1. soil and hence appropriate to derive persistence and modelling endpoints for that trial. RMS consider that proposal acceptable.

At the same time RMS noticed that there was a significant difference in concentration of the test item between the DAT-0 and DAT-0.08 samples, what might have influenced the shape of the kinetic curve in its initial phase, especially in case of bi-phasic models (FOMC and DFOP). Thorough analysis of the data showed that true DAT-0 samples were not processed and analysed. Instead for that tim point the 100% level, based on the results of verification of the level and homogeneity of application, was set. on. The concentrations in DAT 0.08 samples are therefore first truly measured concentrations of FOE Sulfonic acid in soil. As a result, because the two time points are located very close to each other, RMS decided to repeat the kinetic analysis removing the values for DAT-0 time point from the data set. That was done in order to verify would such action improve the fitting results. The outcome is presented further down the report under the point 6).

- 2) The results of the kinetic analysis of the data obtained for FOE Sulfonic acid in BBA 2.2 soil Study by [Hellpointner; 1999]:

The results of the kinetic analysis performed by the Applicant are presented below, in graphical form on figure B.8.1.1.2.1.1._CA-91 and in numerical form in the table B.8.1.1.2.1.1._CA-184. Additionally the table B.8.1.1.2.1.1._CA-185 provides the kinetic endpoints obtained with each of the kinetic models tested.

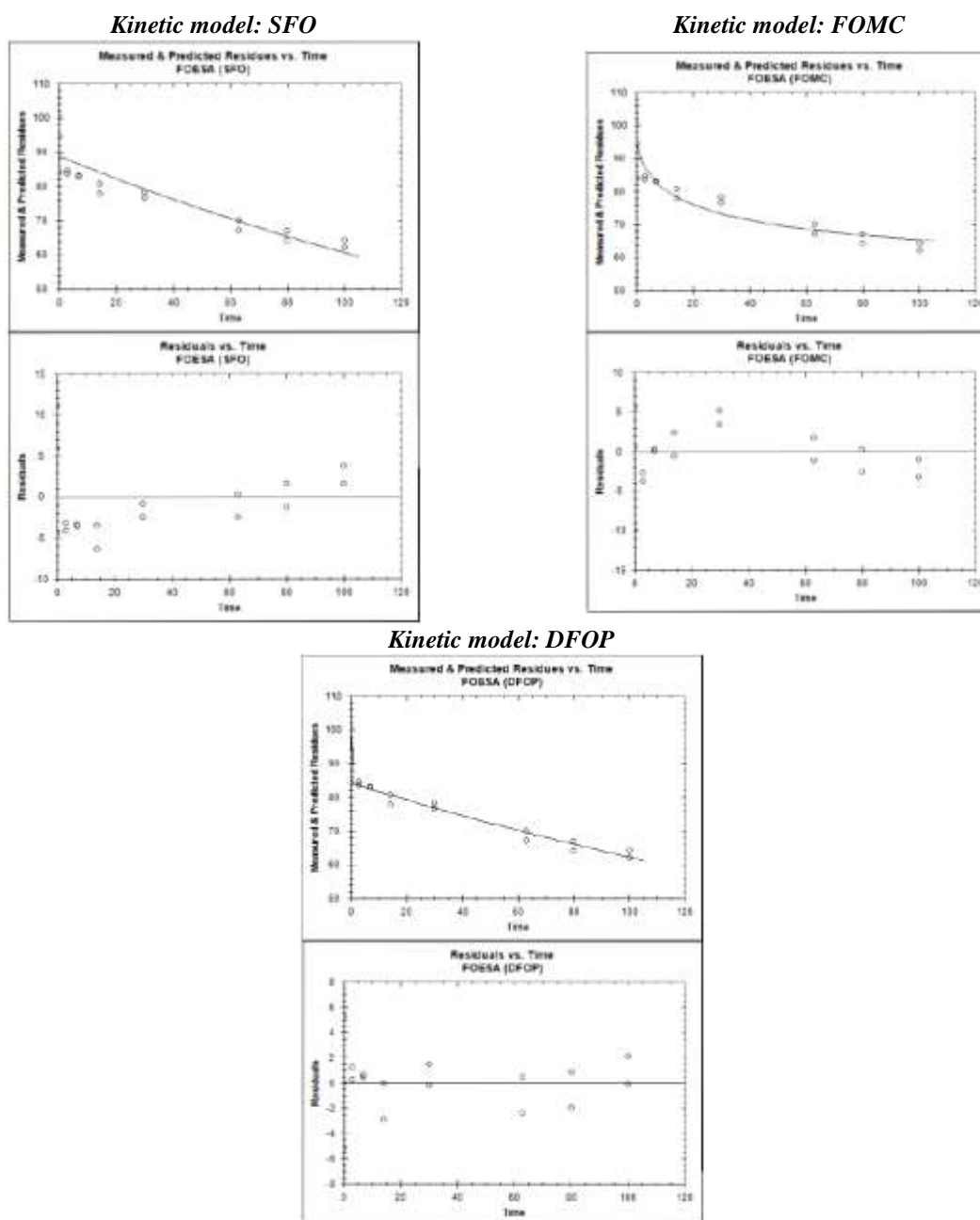


Figure B.8.1.1.2.1.1._CA-91: The graphical results of the kinetic analysis (copied from the study report).

Table B.8.1.1.2.1.1._CA-184: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment ¹⁾
				Lower	Upper			
SFO	M ₀	88.73	1.757	85.29	92.175	< 2 E-16	4.638	0.81; Acceptable fit
	k	3.833 E-3	5.037 E-4	2.846 E-3	0.005	5.26 E-7		
FOMC	M ₀	94.418	2.267	89.975	98.862	< 2 E-16	3.363	0.94; Acceptable fit
	α	0.09969	0.02777	0.045526	0.154	0.00134		
	β	2.5286	2.5026	-2.3764	7.433	0.1642		
DFOP	M ₀	100.0	1.581	96.90	103.098	< 2 E-16	0.905	0.97; Good fit
	k ₁	13.73	4.381	5.140	22.314	0.00367		
	k ₂	3.028 E-3	2.616 E-4	2.515 E-3	0.004	7.44 E-9		
	g	0.1587	0.01736	0.1247	0.193	1.40 E-7		

Footnotes to the table:

1) Visual assessment of the kinetic curve as proposed by the Applicant.

Table B.8.1.1.2.1.1._CA-185: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested		
		SFO	FOMC	DFOP
FOE Sulfonic acid	DT ₅₀ [days]	180.82	2643.3	171.85
	DT ₉₀ [days]	600.67	27168313490	703.43

Conclusion:

Of the three tested models DFOP returned visually and statistically good fit, while the fits obtained using FOMC and SFO were, according to the Applicant, statistically good, but visually only acceptable. RMS noticed that in case of FOMC model the visual fit may also be considered good. Of all three models tested DFOP returned the superior fit, while that for SFO was the poorest. In terms of the reliability of kinetic parameters, SFO and DFOP may be considered fully reliable, while in case of FOMC the calculated β was not reliable because CI for it passed through zero. It was also noticed that the kinetic endpoints returned by the modelling tool for FOMC were unrealistically long.

The Applicant stated that despite displayed deficiencies, the fit obtained with SFO was robust enough to be considered appropriate to derive persistence and modelling endpoints for FOE Sulfonic acid in BBA 2.2. soil. RMS is of the opinion that the proposal is acceptable.

At the same time RMS noticed that there was a significant difference in concentration of the test item between the DAT-0 and DAT-0.08 samples, what might have influenced the shape of the kinetic curve in its initial phase, especially in case of bi-phasic models (FOMC and DFOP). Thorough analysis of the data showed that true DAT-0 samples were not processed and analysed. Instead for that time point the 100% level, based on the results of verification of the level and homogeneity of application, was set. on. The concentrations in DAT 0.08 samples are therefore first truly measured concentrations of FOE Sulfonic acid in soil. As a result, because the two time points are located very close to each other, RMS decided to repeat the kinetic analysis removing the values for DAT-0 time point from the data set. That was done in order to verify would such action improve the fitting results. The outcome is presented further down the report under the point 7).

- 3) The results of the kinetic analysis of the data obtained for FOE Sulfonic acid in Laacherhof soil (study by [Hellpointner; 1999]):

The results of the kinetic analysis performed by the Applicant are presented below, in graphical form on figure B.8.1.1.2.1.1._CA-92 and in numerical form in the table B.8.1.1.2.1.1._CA-186. Additionally the table B.8.1.1.2.1.1._CA-187 provides the kinetic endpoints obtained with each of the kinetic models tested.

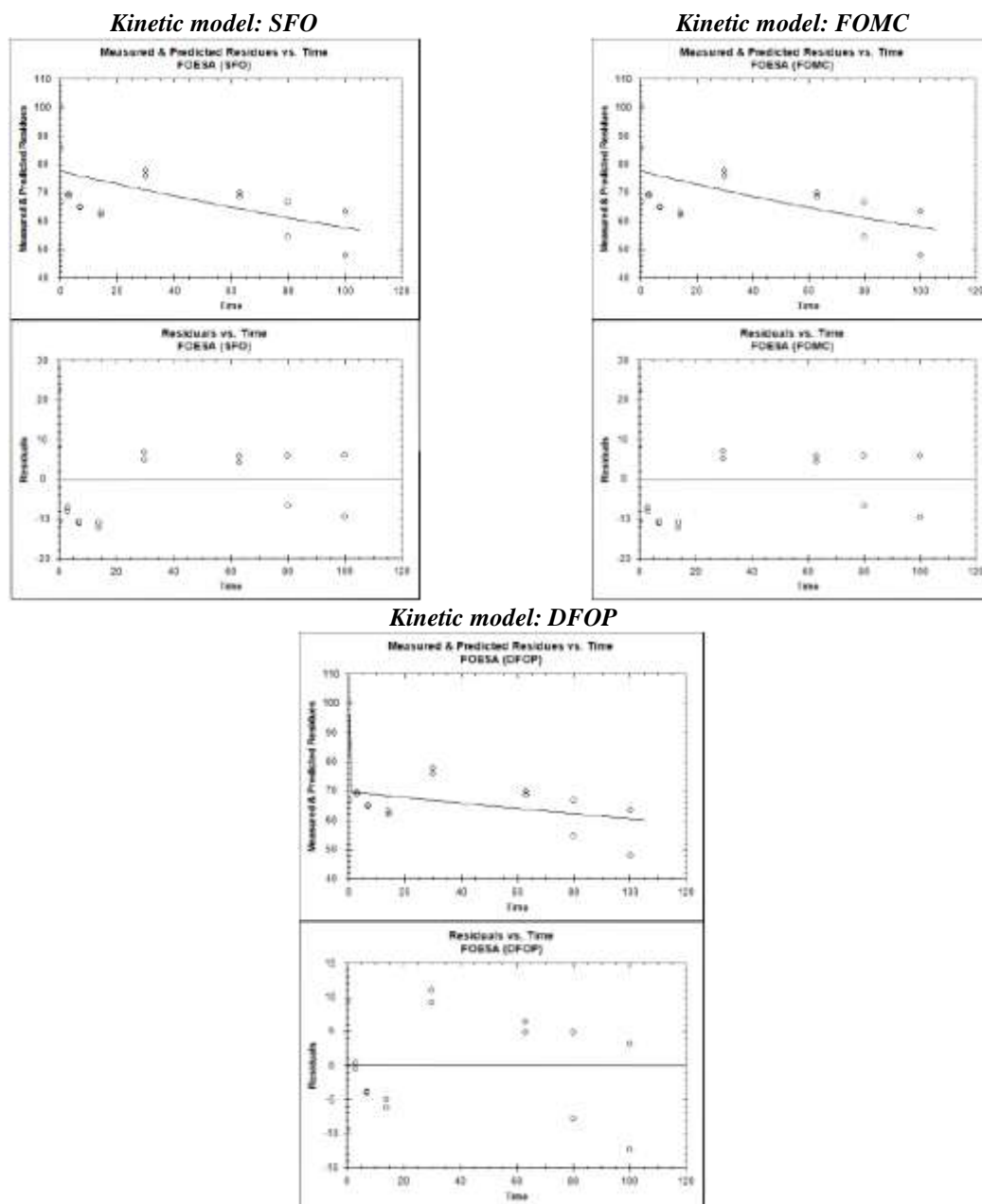


Figure B.8.1.1.2.1.1._CA-92: The graphical results of the kinetic analysis (copied from the study report).

Table B.8.1.1.2.1.1._CA-186: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment ¹⁾
				Lower	Upper			
SFO	M ₀	77.37	3.812	69.90	84.84	3.81 E-13	11.24	0.30; Acceptable fit
	k	2.95 E-3	1.177 E-3	6.432 E-4	0.005	0.0117		
FOMC	M ₀	77.454	3.953	69.706	85.201	2.12 E-12	11.88	0.30; Acceptable fit
	α	2.5601	1.0448	0.5123	4.608	0.0135		
	β	822.5645	43.1441	738.0035	907.125	3.15 E-12		
DFOP	M ₀	100.0	4.866	90.46	109.536	3.72 E-12	6.07	0.75; Acceptable fit
	k ₁	19.11	11.01	-2.460	40.678	0.0522		
	k ₂	1.417 E-3	7.778 E-4	-1.074 E-4	0.003	0.0449		
	g	0.3044	0.04429	0.2176	0.391	3.82 E-63		

Footnotes to the table:

1) Visual assessment of the kinetic curve as proposed by the Applicant.

Table B.8.1.1.2.1.1._CA-187: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested		
		SFO	FOMC	DFOP
FOE Sulfonic acid	DT ₅₀ [days]	234.92	255.78	232.98
	DT ₉₀ [days]	780.40	1199.4	Not determined

Conclusion:

All three models returned fits acceptable visually and statistically fits, with DFOP the best of the three. Also the determined kinetic parameters were reliable for all three models.

The Applicant proposed to consider SFO model to return the fit robust enough to be appropriate to derive from it persistence and modelling endpoints for FOE Sulfonic acid in Laacherhof soil.

RMS however stated that none of the fits is adequate and for two reasons.

Reason 1: RMS noticed that there was a significant difference in concentration of the test item between the DAT-0 and DAT-0.08 samples, what might have influenced the shape of the kinetic curve in its initial phase, especially in case of bi-phasic models (FOMC and DFOP). Thorough analysis of the data showed that true DAT-0 samples were not processed and analysed. Instead for that time point the 100% level, based on the results of verification of the level and homogeneity of application, was set. on. The concentrations in DAT 0.08 samples are therefore first truly measured concentrations of FOE Sulfonic acid in soil. Elimination of the theoretical DAT 0 values may result in change of the curve's shape in its initial part, eliminating the alleged breakpoint at DAT 0.08.

Reason 2: The concentrations at DAT 30 and DAT 63 time points were unusually high in comparison to preceding time points, indicating problems with sample processing at earlier some points, or some problems with DAT-30 and DAT-63 samples, not necessarily related to sample processing. Evaluating the source study (please refer to the summary of the **Study 9** above) RMS postulated that these two time points may be outliers, not to be used in kinetic analysis.

Reason 3: For the samples recovered at last two sampling points – DAT 80 and DAT 100, a substantial difference between the concentrations of FOE Sulfonic acid in replicates was observed, what also possibly influenced the results of the fitting. In this case however the situation seems not to be as clear as it was for the samples collected on DAT-30 and DAT-63, and it may be difficult to indicate which values are outliers.

As a result RMS decided to repeat the kinetic analysis with modified data set: DAT-0, DAT-30 and DAT-63 samples were removed from it. The results are presented further down the report, under the point 8).

- 4) The results of the kinetic analysis of the data obtained for FOE Sulfonic acid in Laacherhof AXXa soil (study by [Hellpointner; 2003]):

The results of the kinetic analysis performed by the Applicant are presented below, in graphical form on figure B.8.1.1.2.1.1._CA-93 and in numerical form in the table B.8.1.1.2.1.1._CA-188. Additionally the table B.8.1.1.2.1.1._CA-189 provides the kinetic endpoints obtained with each of the kinetic models tested.

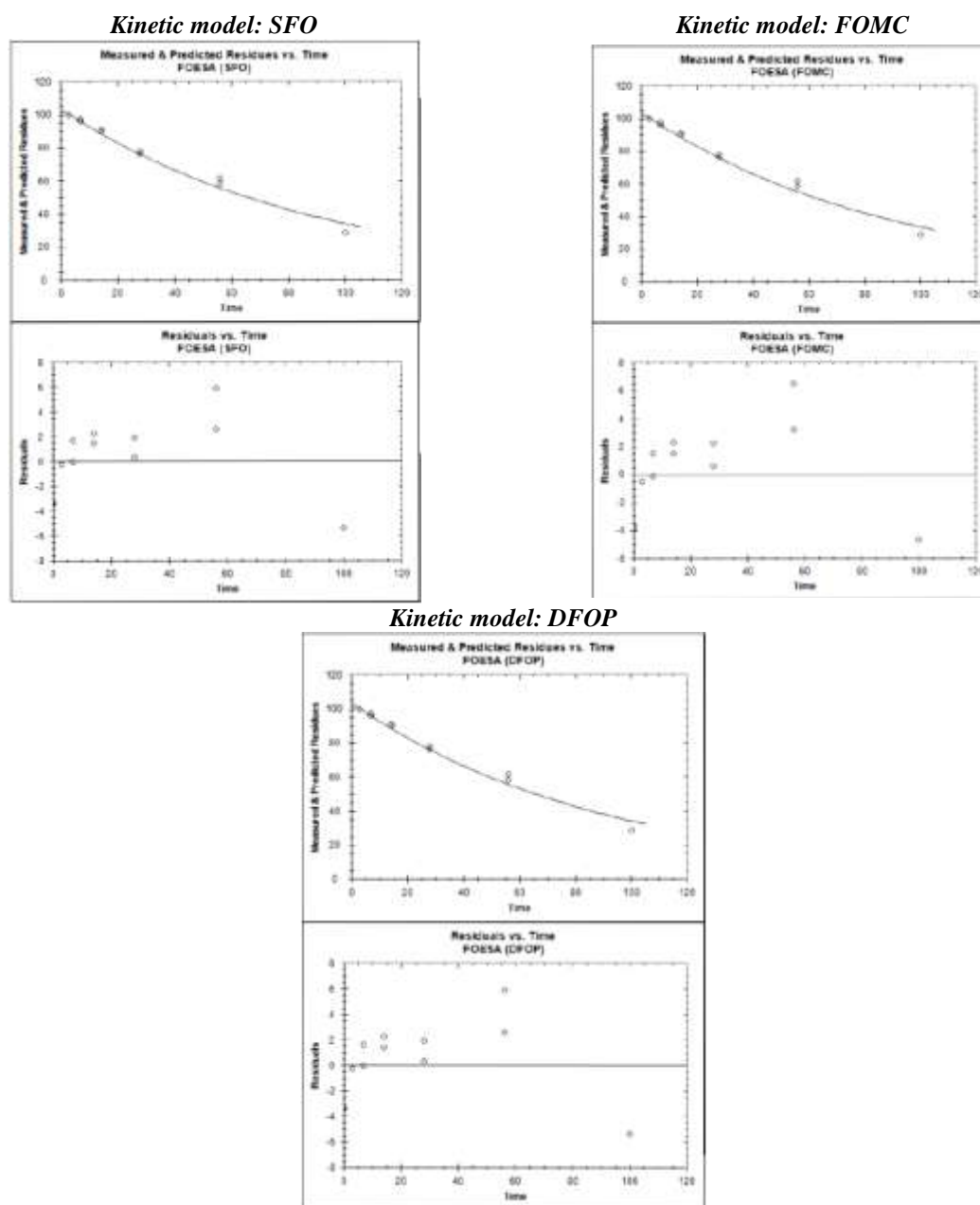


Figure B.8.1.1.2.1.1._CA-93: The graphical results of the kinetic analysis (copied from the study report).

Table B.8.1.1.2.1.1._CA-188: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment ¹⁾
				Lower	Upper			
SFO	M ₀	103.4	1.357	100.7	106.071	< 2 E-16	3.046	0.98; Good fit
	k	0.01112	5.343 E-4	0.01008	0.012	4.36 E-11		
FOMC	M ₀	103.7	1.424	101.0	106.5	< 2 E-16	3.327	0.98; Good fit
	α	451.4	818.0	-1152	2054.7	0.296		
	β	39660	71980	-101400	180746.4	0.296		
DFOP	M ₀	103.411	5.972	91.707	115.116	4.37 E-9	3.625	0.98; Good fit
	k ₁	0.01113	0.01027	-0.00901	0.031	0.1521		
	k ₂	0.01112	0.00255	0.00612	0.016	7.13 E-4		
	g	0.2489	5.4513	-10.4354	10.933	0.4822		

Footnotes to the table:

1) Visual assessment of the kinetic curve as proposed by the Applicant.

Table B.8.1.1.2.1.1._CA-189: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested		
		SFO	FOMC	DFOP
FOE Sulfonic acid	DT ₅₀ [days]	62.31	60.96	62.31
	DT ₉₀ [days]	206.99	202.86	206.98

Conclusion:

All three models returned visually and statistically good fits. In terms of χ^2 error the best fit was obtained using SFO model, although it shall be pointed out that the value of that parameter was very close for all three models tested. At the same time only SFO model returned fully reliable kinetic parameters. In case of FOMC both α and β were not reliable because CI passed through zero. In case of DFOP not fully reliable were k_2 and g – for those parameters the *prob. > t* was higher than 0.1, being close to the level of 0.5 for g . Therefore the Applicant stated that SFO model shall be considered as returning the best fit for FOE Sulfonic acid in Laacherhof AXXa soil and hence appropriate to derive persistence and modelling endpoints for that compound in that test soil. RMS accepted that proposal.

- 5) The results of the kinetic analysis of the data obtained for FOE Sulfonic acid in Laacherhof AIII soil (study by [Hellpointner; 2003]):

The results of the kinetic analysis performed by the Applicant are presented below, in graphical form on figure B.8.1.1.2.1.1._CA-94 and in numerical form in the table B.8.1.1.2.1.1._CA-190. Additionally the table B.8.1.1.2.1.1._CA-191 provides the kinetic endpoints obtained with each of the kinetic models tested.

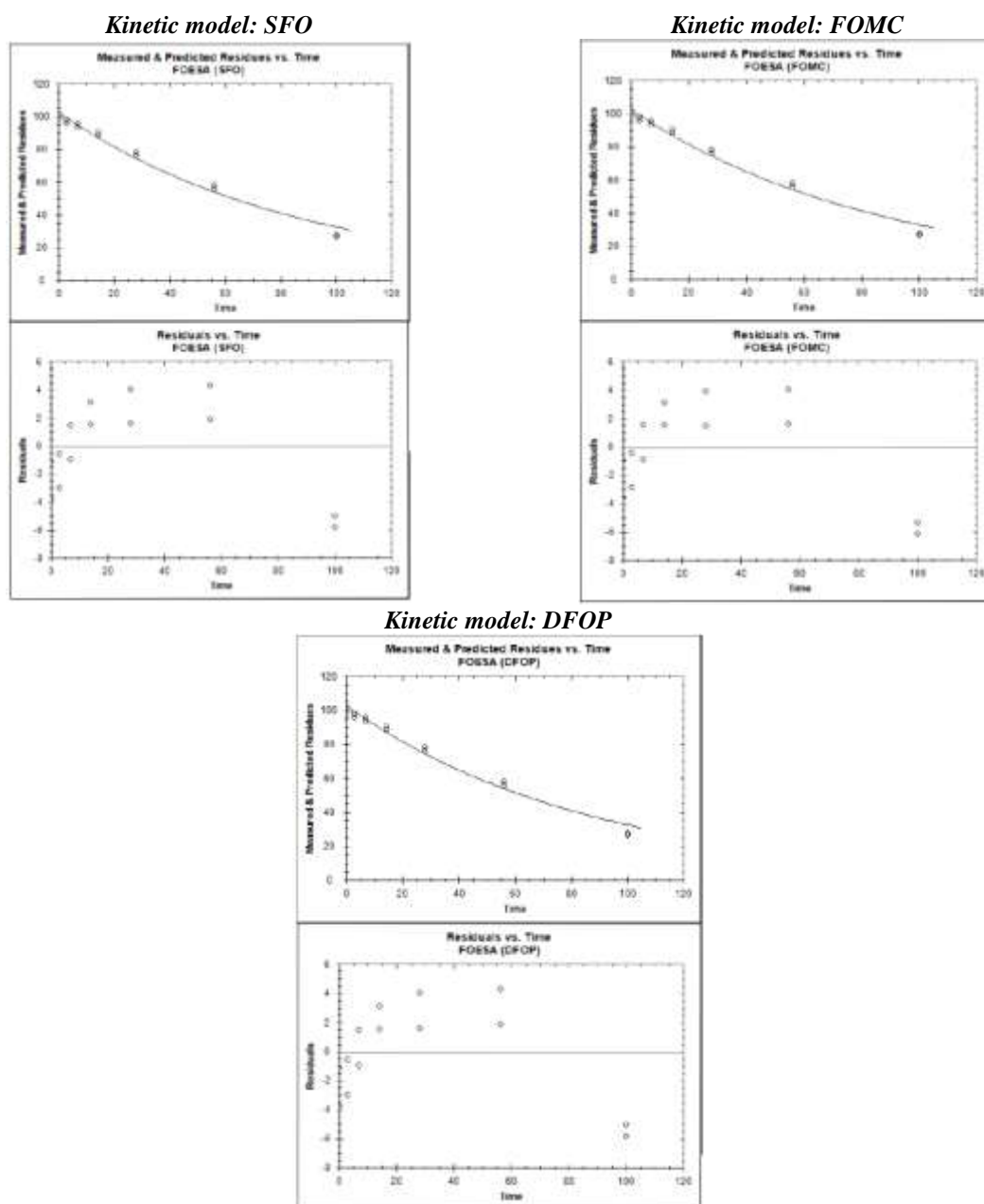


Figure B.8.1.1.2.1.1._CA-94: The graphical results of the kinetic analysis (copied from the study report).

Table B.8.1.1.2.1.1._CA-190: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment ¹⁾
				Lower	Upper			
SFO	M ₀	102.4	1.377	99.73	105.127	< 2 E-16	3.029	0.98; Good fit
	k	0.0115	5.601 E-4	0.01040	0.013	5.12 E-11		
FOMC	M ₀	102.274	1.113	100.092	104.5	< 2 E-16	3.290	0.98; Good fit
	α	345.015	332.316	-306.313	996.3	0.161		
	β	30272.373	29166.272	-26892.470	87437.2	0.161		
DFOP	M ₀	102.428	1.570	99.350	105.505	8.72 E-15	3.605	0.98; Good fit
	k ₁	0.0115	4.848 E-3	2.002 E-3	0.021	0.0195		
	k ₂	0.0115	1.707 E-3	8.156 E-3	0.015	2.56 E-5		
	g	0.2447	2.477	-4.6101	5.100	0.4616		

Footnotes to the table:

1) Visual assessment of the kinetic curve as proposed by the Applicant.

Table B.8.1.1.2.1.1._CA-191: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested		
		SFO	FOMC	DFOP
FOE Sulfonic acid	DT ₅₀ [days]	60.26	60.88	60.26
	DT ₉₀ [days]	200.18	202.71	200.18

Conclusion:

All three models returned visually and statistically good fits. In terms of χ^2 error the best fit was obtained using SFO model, although it shall be pointed out that the value of that parameter was very close for all three models tested. At the same time only SFO model returned fully reliable kinetic parameters. In case of FOMC both α and β were not reliable because CI passed through zero. In case of DFOP not fully reliable was g – for that parameter the $prob. > t$ was significantly higher than 0.1, being close to the level of 0.5. Therefore the Applicant stated that SFO model shall be considered as returning the best fit for FOE Sulfonic acid in Laacherhof AXXa soil and hence appropriate to derive persistence and modelling endpoints for that compound in that test soil. RMS accepted that proposal.

Additional kinetic analysis performed by the RMS

The data used as input in the kinetic examination are presented below in the table B.8.1.1.2.1.1._CA-192. The values not used in the fitting are marked italics.

Table B.8.1.1.2.1.1._CA-192: The processed residue data used in the kinetic analysis.

The data obtained in the study by [Hellpointner; 1999]								
Soil: BBA 2.1			Soil: BBA 2.2			Soil: Laacherhof		
Time Point – DAT [days]	Concentration [%] of FOE Sulfonic acid		Time Point – DAT [days]	Concentration [%] of FOE Sulfonic acid		Time Point – DAT [days]	Concentration [%] of FOE Sulfonic acid	
	Replic. 1	Replic. 2		Replic. 1	Replic. 2		Replic. 1	Replic. 2
0	100.0	100.0	0	100.0	100.0	0	100.0	100.0
0.08	80.6	85.2	0.08	84.2	94.6	0.08	85.6	66.7
3	86.3	87.6	3	83.6	84.6	3	69.6	68.8
7	87.3	88.0	7	82.8	83.0	7	64.9	65.0
14	83.0	81.4	14	77.7	80.6	14	63.2	62.0
30	80.4	81.2	30	78.3	76.6	30	77.7	75.8
63	73.6	74.9	63	70.0	67.2	63	70.0	68.4
80	70.5	71.7	80	64.1	66.9	80	66.9	54.3
100	70.3	70.3	100	64.3	62.1	100	48.0	63.5

The processed data were kinetically examined using CAKE ver. 3.1 modelling tool, developed by Tessella. The optimisation was performed using IRLS (Iteratively Reweighed Nonlinear Least Squares) algorithm. The settings of the optimiser were the defaults of the tool:

- maximum iterations: 100,
- maximum reweighing: 10,
- SANN maximum iterations: 10000,
- convergence tolerance: 1 E-5,
- error variance tolerance: 1 E-5,
- extra solver: yes, if required.

To reproduce as closely as possible the evaluation performed by the Applicant the RMS used all three kinetic models – SFO, FOMC and DFOP. The initial parameters were the same as presented in the study report.

The conceptual metabolic pathway built in the modelling tool was based on the transformation pathway which, in form of simplified scheme, is presented below on figure B.8.1.1.2.1.1._CA-95.

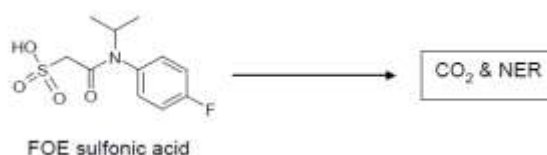


Figure B.8.1.1.2.1.1._CA-95 (-89): The simplified transformation pathway used to create conceptual transformation scheme assumed in the modelling tool (copied from the study report).

The results of the fitting are presented below, individually for each test soil. RMS decided to maintain the consecutive numbering of the fitting experiments.

- 6) The results of the kinetic analysis of the data obtained for FOE Sulfonic acid in BBA 2.1 soil (study by [Hellpointner; 1999]):

The results of the kinetic analysis are presented below, in graphical form on figure B.8.1.1.2.1.1_CA-96 and in numerical form in the table B.8.1.1.2.1.1_CA-193. Additionally the table B.8.1.1.2.1.1_CA-194 provides the kinetic endpoints obtained with each of the kinetic models tested.

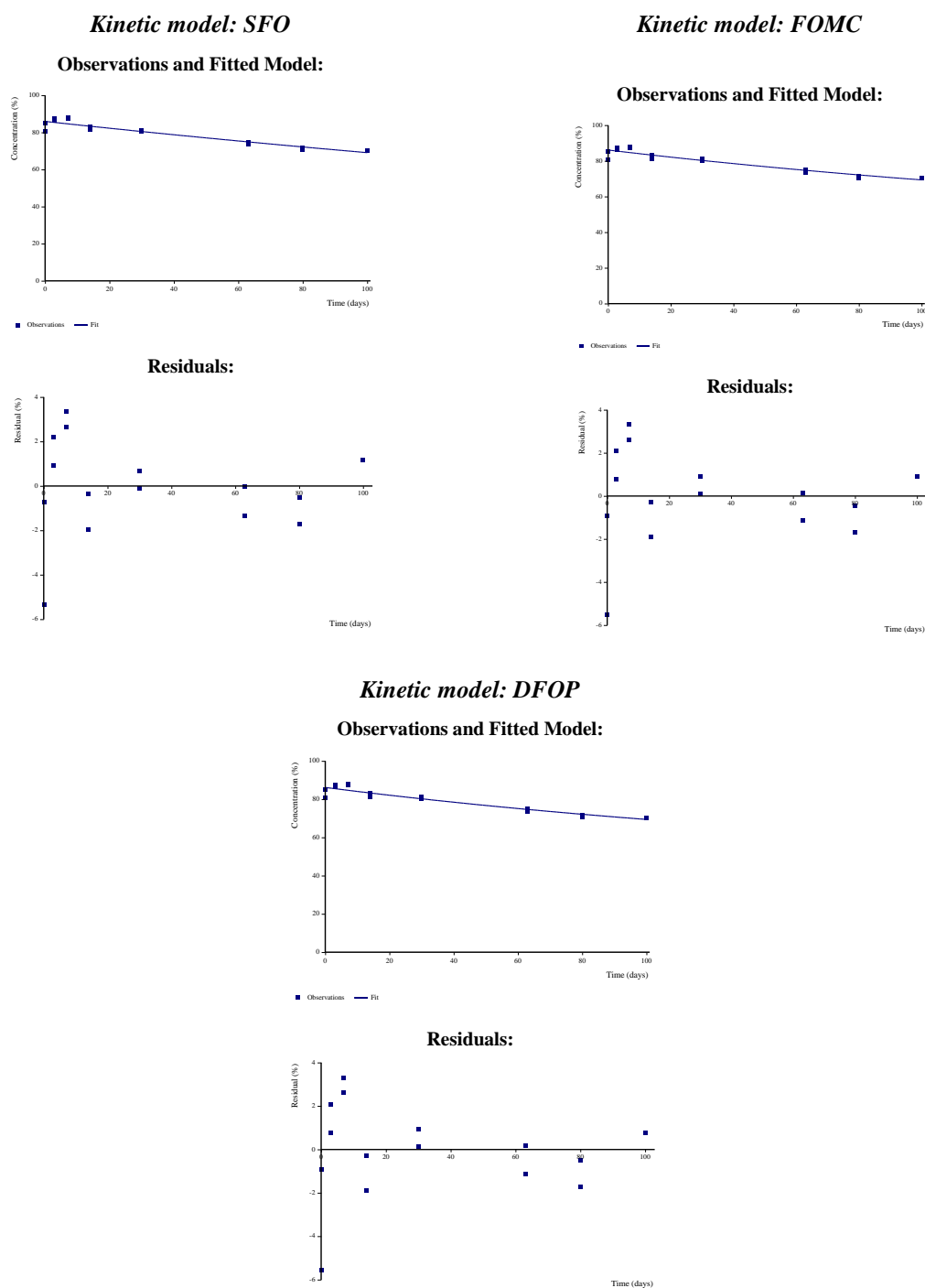


Figure B.8.1.1.2.1.1_CA-96: The graphical results of the kinetic analysis.

Table B.8.1.1.2.1.1._CA-193: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment
				Lower	Upper			
SFO	M_0	85.96	0.791	84.26	87.66	n. c. ¹⁾	1.78	0.902; Good fit
	k	2.179 E-3	1.97 E-4	1.757 E-3	0.003	1.32 E-8		
FOMC	M_0	86.12	1.019	83.92	88.32	n. c. ¹⁾	1.89	0.903; Good fit
	α	0.9652	3.484	-6.561	8.492	n. c. ¹⁾		
	β	398.2	1590	-3041	3840	n. c. ¹⁾		
DFOP	M_0	86.16	0.859	84.28	88.03	n. c. ¹⁾	2.03	0.903; Good fit
	k_1	5.021 E-3	1.917 E-3	8.44 E-4	0.009	0.01121		
	k_2	5.22 E-12	n. d. ²⁾	n. d. ²⁾	n. d. ²⁾	n. d. ²⁾		
	g	0.4913	n. d. ²⁾	n. d. ²⁾	n. d. ²⁾	n. d. ²⁾		

Footnotes to the table:

1) Value not calculated by the modelling tool;

2) Value not determined by the model because the covariance matrix could not be created;

Table B.8.1.1.2.1.1._CA-194: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested		
		SFO	FOMC	DFOP
FOE Sulfonic acid	DT ₅₀ [days]	318	418	> 10000
	DT ₉₀ [days]	1060	3930	> 10000

Conclusion:

All three models returned visually and statistically good fits, with SFO being superior of the three. RMS noticed that the fits visually did not significantly differ, what may indicate that there were problems with the appropriate fitting of the bi-phasic models. At the same time only SFO model returned fully reliable kinetic parameters. In case of FOMC both α and β were not reliable because CI passed through zero. In case of DFOP the model was able to provide statistical analysis only for the parameter k_1 , which therefore can be solely considered reliable. As a result DFOP fit should not be taken into account.

Therefore only the results obtained for SFO fit shall be considered fully reliable and providing persistence and modelling endpoints for FOE Sulfonic acid in BBA 2.1 soil.

RMS noticed also that the results of the fitting improved for SFO kinetic model when the DAT-0 time point was removed from the data set. Therefore, the problems with the fitting, observed in case of the kinetic analysis performed by the Applicant were most probably caused by the inclusion of the artificially set DAT-0 time point.

RMS proposes to include the results of the repeated kinetic analysis into the data set for FOE Sulfonic acid.

- 7) The results of the kinetic analysis of the data obtained for FOE Sulfonic acid in BBA 2.2 soil Study by [Hellpointner; 1999]:

The results of the kinetic analysis are presented below, in graphical form on figure B.8.1.1.2.1.1_CA-97 and in numerical form in the table B.8.1.1.2.1.1_CA-195. Additionally the table B.8.1.1.2.1.1_CA-196 provides the kinetic endpoints obtained with each of the kinetic models tested.

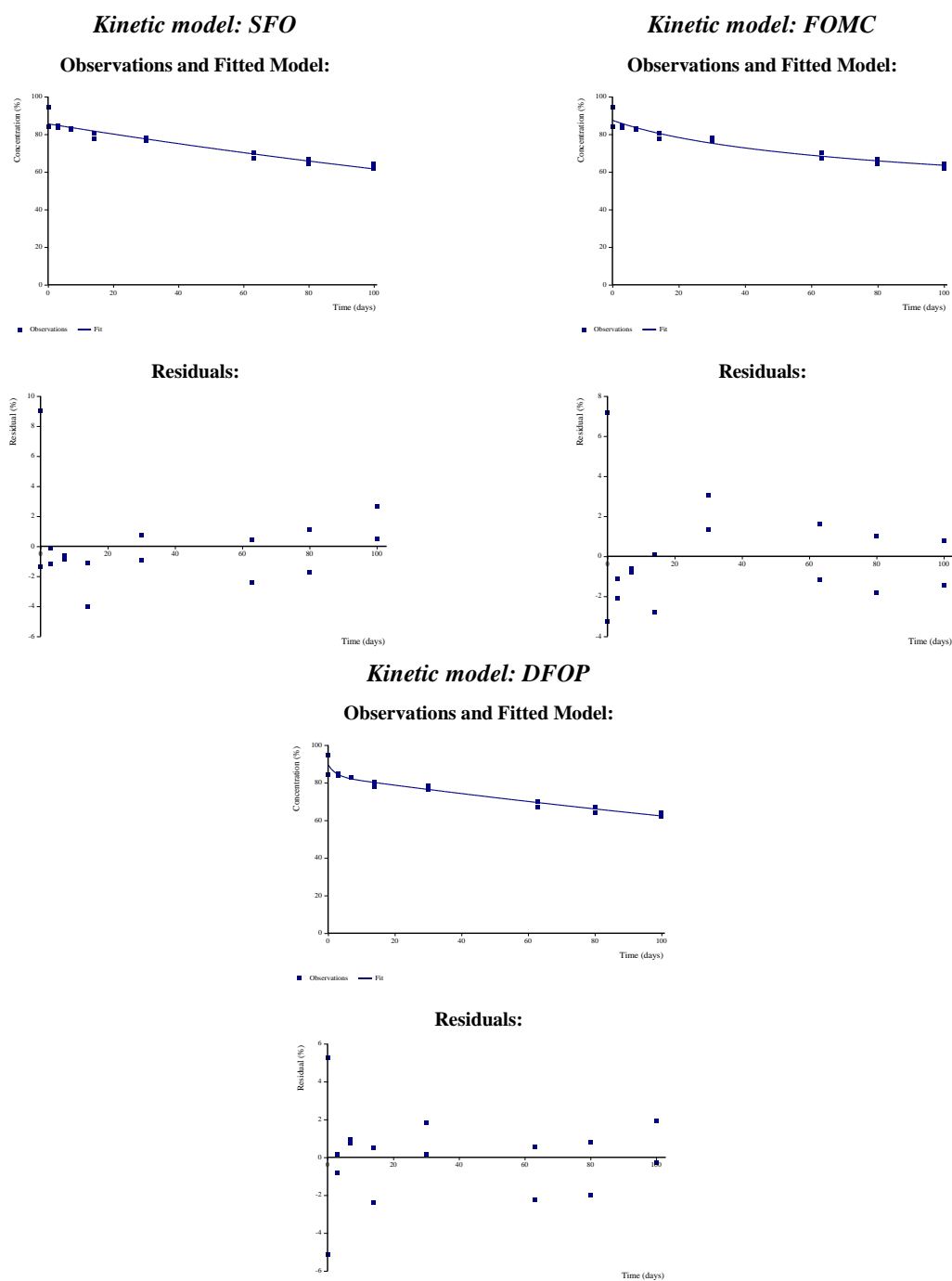


Figure B.8.1.1.2.1.1_CA-97: The graphical results of the kinetic analysis.

Table B.8.1.1.2.1.1._CA-195: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment
				Lower	Upper			
SFO	M_0	85.59	1.098	83.23	87.94	n. c. ¹⁾	1.88	0.908; Good fit
	k	3.285 E-3	2.90 E-4	2.662 E-3	0.004	9.90 E-9		
FOMC	M_0	87.49	1.527	84.19	90.79	n. c. ¹⁾	1.47	0.926; Good fit
	α	0.2201	0.1045	-5.757 E-3	0.446	n. c. ¹⁾		
	β	30.5	26.81	-27.43	88.42	n. c. ¹⁾		
DFOP	M_0	89.57	1.94	85.35	93.8	n. c. ¹⁾	0.905	0.905; Good fit
	k_1	0.4241	0.4574E	-0.5725	1.421	0.186		
	k_2	2.911 E-3	3.45 E-4	2.16 E-3	0.004	1.07 E-6		
	g	0.0686	0.0264	0.0111	0.126	n. c. ¹⁾		

Footnotes to the table:

1) Value not calculated by the modelling tool;

Table B.8.1.1.2.1.1._CA-196: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested		
		SFO	FOMC	DFOP
FOE Sulfonic acid	DT ₅₀ [days]	211	681	214
	DT ₉₀ [days]	701	> 10000	767

Conclusion:

All three models returned visually and statistically good fits, although it shall be stated that the fits returned by bi-phasic models were visually and statistically superior to SFO fit. In terms of χ^2 error the best fit was obtained using DFOP model, although it shall be pointed out that the value of that parameter was very close for all three models tested. At the same time only SFO model returned fully reliable kinetic parameters. In case of FOMC the calculated β was not reliable because CI passed through zero. In case of DFOP not fully reliable was k_1 — for that parameter the *prob. > t* was higher than 0.1. That may indicate that the fast degradation phase may not be relevant for overall degradation kinetics of FOE Sulfonic acid in BBA 2.2 soil.

Therefore the results obtained for SFO fit may be considered as well representing the kinetic behaviour of FOE Sulfonic acid in BBA 2.2 soil and appropriate to derive persistence and modelling endpoints.

RMS noticed also that the results of the fitting improved for SFO kinetic model when the DAT-0 time point was removed from the data set. Therefore, the problems with the fitting, observed in case of the kinetic analysis performed by the Applicant were most probably caused by the inclusion of the artificially set DAT-0 time point.

RMS proposes to include the results of the repeated kinetic analysis into the data set for FOE Sulfonic acid.

- 8) The results of the kinetic analysis of the data obtained for FOE Sulfonic acid in Laacherhof soil (study by [Hellpointner; 1999]):

The results of the kinetic analysis are presented below, in graphical form on figure B.8.1.1.2.1.1_CA-98 and in numerical form in the table B.8.1.1.2.1.1_CA-197. Additionally the table B.8.1.1.2.1.1_CA-198 provides the kinetic endpoints obtained with each of the kinetic models tested.

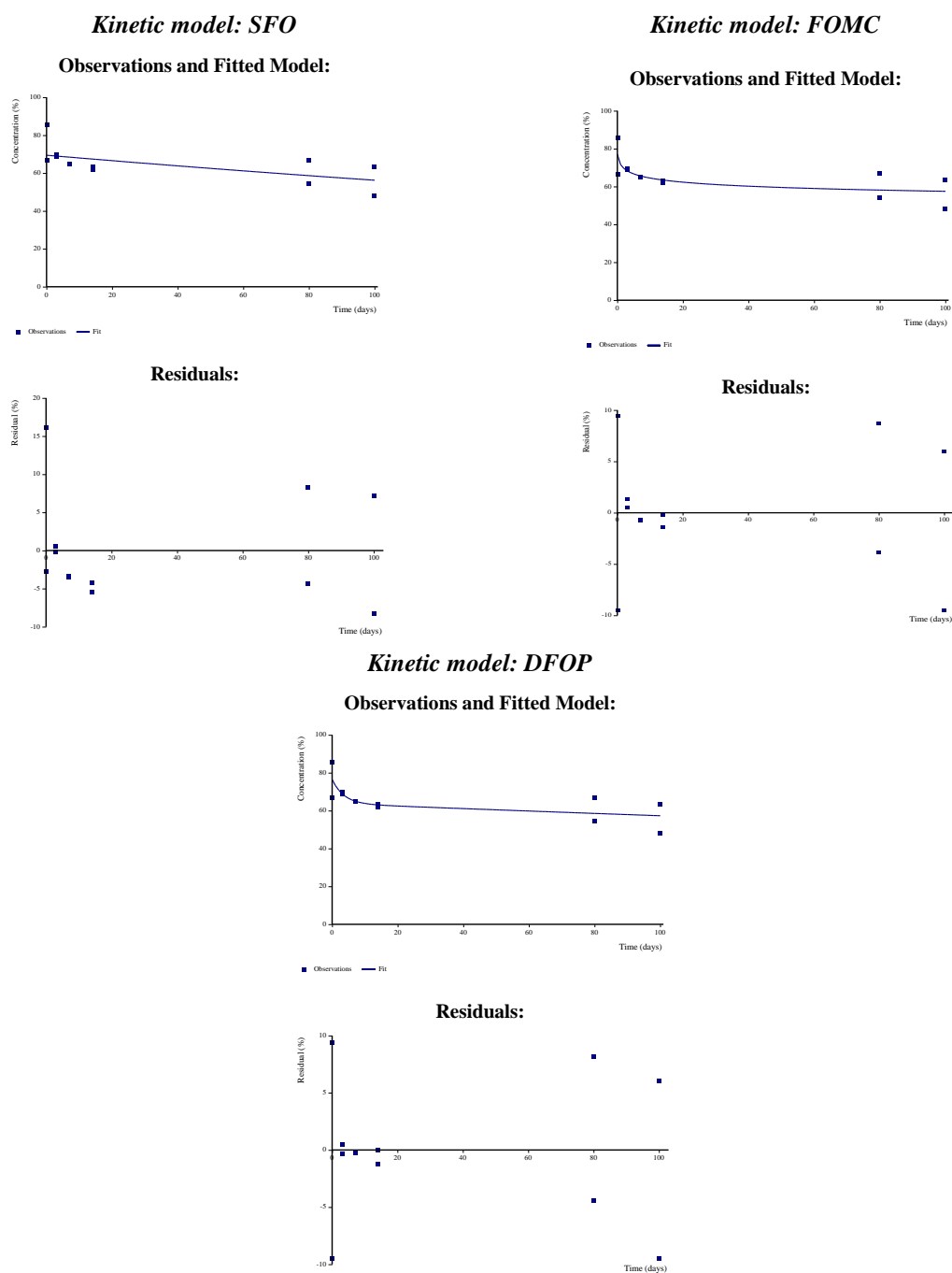


Figure B.8.1.1.2.1.1_CA-98: The graphical results of the kinetic analysis.

Table B.8.1.1.2.1.1_CA-197: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment
				Lower	Upper			
SFO	M_0	69.45	2.838	63.12	75.77	n. c. ¹⁾	4.6	0.380; Poor fit
	k	2.106 E-3	8.80 E-4	1.45 E-4	0.004	0.01888		
FOMC	M_0	77.12	6.571	62.26	91.99	n. c. ¹⁾	3.304	0.546; Acceptable fit
	α	0.05034	0.02882	-0.01486	0.116	n. c. ¹⁾		
	β	0.2956	1.048	-2.075	2.667	n. c. ¹⁾		
DFOP	M_0	76.49	5.114	64.74	88.29	n. c. ¹⁾	1.67	0.556; Acceptable fit
	k_1	0.2822	0.4032	-2.04 E-3	1.212	0.2519		
	k_2	1.062 E-3	1.345 E-3	-2.04 E-3	0.004	0.2263		
	g	0.1664	0.09631	-0.05565	0.389	n. c. ¹⁾		

Footnotes to the table:

1) Value not calculated by the modelling tool;

Table B.8.1.1.2.1.1_CA-198: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested		
		SFO	FOMC	DFOP
FOE Sulfonic acid	DT ₅₀ [days]	329	> 10000	481
	DT ₉₀ [days]	1090	> 10000	2000

Conclusion:

The modification of the data set by removal of the alleged outlier did not significantly improve the results of the fitting. The fits, although statistically acceptable, were visually either poor – SFO fit, or only acceptable – FOMC and DFOP. Additionally, neither FOMC nor DFOP returned reliable kinetic parameters. It shall be noted that the concentrations at the end of experiment were well above 10% of the assumed initial concentration, therefore FOMC fit, even if reliable, should not be used to derive kinetic modelling endpoints.

As a result RMS is of the opinion that none of the obtained kinetic fits may be considered acceptable and the results for that soil should not be included into the data set for FOE Sulfonic acid.

As it was not possible to obtain the reliable kinetic fit for FOE Sulfonic acid in Laacherhof soil using the data set with replicates the RMS, having analysed the available data, decided to repeat the fitting for that soil using the average values for each time point. The analysis was performed for modified data-set, from which the DAT-30 and DAT-63 time points were removed as outliers. The resulting data set used in the fitting is presented below in the table B.8.1.1.2.1.1_CA-199.

Table B.8.1.1.2.1.1_CA-199: The data set used in the kinetic examination.

Time Point – DAT [days]	0.08	3	7	14	80	100
Average concentration [%] of FOE Sulfonic acid	76.2	69.2	64.9	62.6	60.6	55.7

The processed data were kinetically examined using CAKE ver. 3.1 modelling tool, developed by Tessella. The optimisation was performed using IRLS (Iteratively Reweighed Nonlinear Least Squares) algorithm. The settings of the optimiser were the defaults of the tool:

- maximum iterations: 100,
- maximum reweighing: 10,
- SANN maximum iterations: 10000,
- convergence tolerance: 1 E-5,
- error variance tolerance: 1 E-5,
- extra solver: yes, if required.

To reproduce as closely as possible the evaluation performed by the Applicant the RMS used all three kinetic models – SFO, FOMC and DFOP. The initial parameters were the same as presented in the study report.

The results of the kinetic analysis are presented below, in graphical form on figure B.8.1.1.2.1.1_CA-99 and in numerical form in the table B.8.1.1.2.1.1_CA-200.

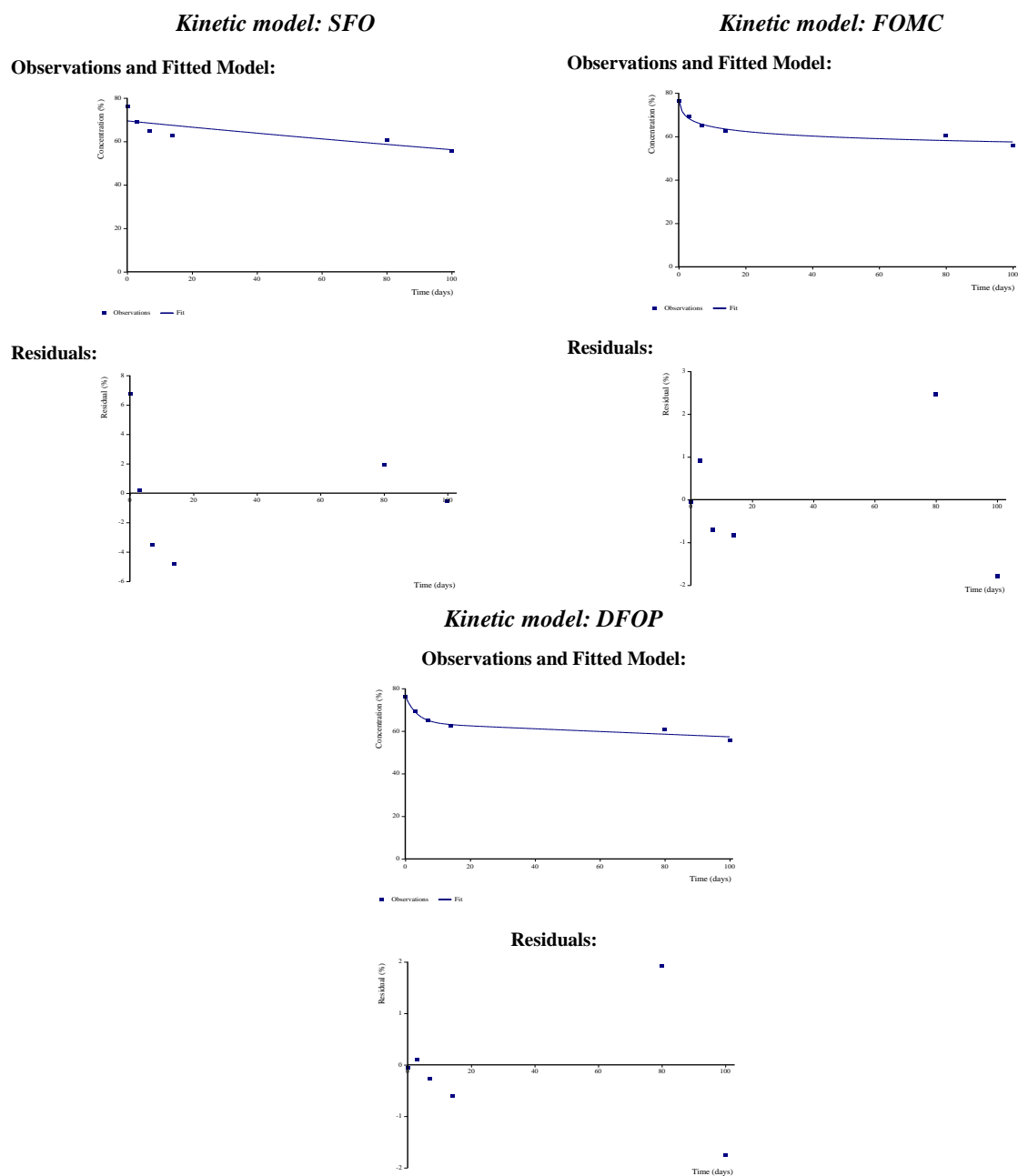


Figure B.8.1.1.2.1.1_CA-99: The graphical results of the kinetic analysis.

Table B.8.1.1.2.1.1._CA-200: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment
				Lower	Upper			
SFO	M_0	69.45	2.508	62.49	76.41	n. c. ¹⁾	4.63	0.664; Acceptable fit
	k	2.112 E-3	7.78 E-4	-4.705 E-5	0.004	0.0266		
FOMC	M_0	77.19	2.715	68.55	85.83	n. c. ¹⁾	1.85	0.956; Good fit
	α	0.0504	0.01181	0.0128	0.088	n. c. ¹⁾		
	β	0.2899	0.4233	-1.057	1.637	n. c. ¹⁾		
DFOP	M_0	76.55	1.942	68.2	84.91	n. c. ¹⁾	1.69	0.972; Good fit
	k_1	0.2846	0.1531	-0.3741	0.943	0.102		
	k_2	1.068 E-3	5.08 E-4	-1.118 E-3	0.003	0.0852		
	g	0.1671	0.03636	0.0106	0.324	n. c. ¹⁾		

Footnotes to the table:

1) Value not calculated by the modelling tool;

Conclusion:

The use of the average concentrations instead of replicates for each time points resulted in improvement of all visual fits – SFO fit became acceptable, while both bi-phasic fits – FOMC and DFOP can be classified as good fits. All three fits are statistically reliable, with DFOP being superior of all three. However, none of bi-phasic fits may be considered acceptable due to the lack of reliability of the kinetic parameters. In case of DFOP fit not reliable was k_1 , for which $prob. > t$ was slightly above 0.1, while in case of FOMC in was β , for which CI passed through zero. Additionally it was noticed that FOMC could not be used because the concentration of the test compound at the end of the experiment – on DAT 100, was well above 10% of the initial (FOCUS Kinetics recommendation). As a result, the statement made previously by the RMS, none of the obtained kinetic fits may be considered acceptable and the results for Laacherhof soil from the study by [Hellpointner; 1999] should not be included into the data set for FOE Sulfonic acid.

Final conclusion of the study:

On the basis of the results of the kinetic analysis presented above was determined the definitive set of the reliable kinetic parameters, presented below in the table B.8.1.1.2.1.1._CA-201. The results for Laacherhof were not presented as it was not possible to obtain fully reliable fit for FOE Sulfonic acid in that soil.

Table B.8.1.1.2.1.1._CA-201: The definitive set of the kinetic endpoints determined in the study.

Soil		Soil properties		Incubation conditions	Selected best-fit model	Evaluation of the fit		Kinetic parameters		Kinetic endpoints	
Soil name	Soil type (USDA)	OC [%]	pH ¹⁾			χ^2 error	Visual fit ²⁾	Par.	Value	DT ₅₀ [days]	DT ₉₀ [days]
BBA 2.1	Sand	0.57	5.3	20 ± 2°C; 75% of 1/3 bar	SFO	1.78	G	k	2.18 E-3	318	1060
BBA 2.2	Loamy sand	2.48	6.3	20 ± 2°C; 75% of 1/3 bar	SFO	1.88	G	k	3.28 E-3	211	701
Laacherhof AXXa	Sandy loam	1.47	6.3	20 ± 2°C; 40% MWHC	SFO	3.046	G	k	0.1112	62.31	206.99
Laacherhof AIII	Silt loam	0.88	6.8	20 ± 2°C; 40% MWHC	SFO	3.029	G	k	0.0115	60.26	200.18

Footnotes to the table:1) Measured in 0.01M CaCl₂.

2) The abbreviations used to describe the visual fit: G. – good, A. – acceptable, P. – poor;

Study 14:

Report: Traub M., (2012): “FOE methylsulfone: Aerobic Degradation in Four European Soils.”; Eurofins Agrosience Services EcoChem GmbH, Eutinger Str. 24, 75223 Niefern-Öschelbronn, Germany, for Bayer Crop Science AG, 40789 Monheim, Germany; unpublished study No. S11-03808; 2012. 10.18; study reference number: M-443658-01-1;

Guidelines: The study was declared to be performed in line with the provisions of the OECD Guideline for the Testing of Chemicals No. 307 – Aerobic and Anaerobic Transformation in Soil. The Applicant stated that no deviations from that Guideline were found. Additionally, because the results of the study were kinetically evaluated and the results presented in the study report, it was declared that the following Guideline was used:

- FOCUS (2006): “Guidance Document on Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration.” Report of the FOCUS Work Group on Degradation Kinetics, EC Document Reference SANCO/10058/2005 version 2.0, 434 pp.;

In this case also no deviations from the Guideline referred to were stated.

GLP: Yes;

RMS comments: This is a new study submitted specifically for purpose of this assessment. It was verified by the RMS and found acceptable. No deviations from the declared Guidelines were stated. The study is summarised below.

Summary:

The aim of the study was to determine the rate of degradation of FOE Methylsulfone in aerobic soil under laboratory conditions. The experiment was performed on four test soils taken from the agriculturally used areas, representing different geographical origin and different soil properties, in line with the requirement of the relevant Guideline. The characteristic of the test soils is provided below in the table B.8.1.1.2.1.1._CA-202.

Table B.8.1.2.1.1.CA-202: The characteristic of soils used in the study.

Parameter		Soil			
		<i>Laacherhof AXx</i> (AX)	<i>Dollendorf II</i> (DD)	<i>Höfchen am Hohenseh 4a</i> (HH)	<i>Wurmwiese</i> (WW)
Soil origin		Monheim/ North Rhine-Westphalia /Germany	Blankenheim/ North Rhine-Westphalia /Germany	Burscheid/ North Rhine-Westphalia /Germany	Monheim/ North Rhine-Westphalia /Germany
Soil type (USDA)		Loamy sand	Loam	Silt loam	Sandy loam
Particle size distribution	Sand [%]	84	48	22	60
	Silt [%]	10	28	62	26
	Clay [%]	6	24	16	14
pH value	in 0.01M CaCl ₂ (1:2)	6.2	7.0	6.1	5.0
	in H ₂ O (1:1)	6.3	7.1	6.3	5.2
	in 1M KCl (1:1)	6.0	6.7	5.8	4.7
Organic Carbon content (OC) [%]		1.7	4.6	2.0	1.8
Organic Matter content (OM) [%] ¹⁾		2.9	7.9	3.4	3.1
Cation Exchange Capacity – CEC [mEq/100g]		9.2	19.5	11.1	10.4
Water holding capacity	MWHC [g H ₂ O/ 100 g soil d. w.]	48.5	79.1	54.8	56.3
	at ½ bar [%]	10.8	35.1	20.9	15.6
Soil bulk density (disturbed) [g/cm ³]		1.19	1.03	1.09	1.17
Soil biomass [mg microbial C/ 100g soil] ²⁾	<i>DAT-0</i>	BIO- ⁴⁾ 204.4	447.4	229.9	196.3
	<i>DAT-58</i>	BIO- ⁴⁾ 182.0	447.4	186.5	131.0
		BIO+ ⁵⁾ 175.6	446.9	198.8	153.4
	<i>DAT-120</i>	BIO- ⁴⁾ 138.6	421.7	141.4	100.8
		BIO+ ⁵⁾ 123.2	405.2	166.9	103.9
Soil biomass [% OC] ³⁾	<i>DAT-0</i>	BIO- ⁴⁾ 7.05	9.73	11.50	10.91
	<i>DAT-58</i>	BIO- ⁴⁾ 6.28	9.73	9.33	7.28
		BIO+ ⁵⁾ 6.05	9.71	9.94	8.52
	<i>DAT-120</i>	BIO- ⁴⁾ 4.78	9.17	7.07	5.60
		BIO+ ⁵⁾ 4.25	8.81	8.35	5.77

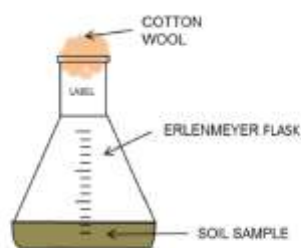
Footnotes to the table:

- 1) Value calculated from experimentally determined OC content, using the following equation: OM = 1.724 OC;
- 2) Determined using the SIR method developed by Anderson & Domsch [1978];
- 3) Values recalculated by the RMS using the OC content reported in the table for each test soil;
- 4) Determined in samples not treated with blank application solution – 0.4 mL of 1:1 MeOH/H₂O;
- 5) Determined in samples treated with blank application solution – 0.4 mL of 1:1 CH₃OH/H₂O;

The test soils were sampled shortly before being used (20 days before the experiment began) with shovel from 0-20 cm layer of grassland plot. No Plant Protection Products were used on the sampling field for 5 years preceding sampling. The samples of the test soils were transported to the test facility in plastic bags. There they were stored at $T = 6^{\circ}\text{C}$ until being used. Prior to their use test soils were sieved through 2-mm sieve. The whole soil sampling-and-handling procedure was declared to be performed in accordance with ISO 10381-6.

The experiment was performed using 300-mL Erlenmeyer flasks for kinetic samples and concurrent recovery samples, and in 250-mL Erlenmeyer flasks for the determination of soil biomass. 100-g (d. w.) portions of sieved test soils were weighed into each flask. Next the soil moisture of each sample was adjusted to $55 \pm 5\%$ MWHC by addition of the appropriate amount of deionised water. So prepared incubation flask were stoppered with cotton-wool plugs to allow free exchange of air. The example incubation vessel is presented below on figure B.8.1.1.2.1.1._CA-100. In total 32 incubation vessels were prepared – 22 as kinetic samples and 10 for the determination of soil biomass. Additionally there were prepared 47 flasks containing Laacherhof AXXa soi, used as concurrent recovery samples.

After adjustment of the soil moisture the incubation vessels were pre-conditioned for 5 days in the dark, in a temperature-controlled walk-in climatic chamber at $T = 20 \pm 2^{\circ}\text{C}$, until being treated with the test compound. The number of incubation vessels prepared for each test soils was such to grant at least to have duplicate treated samples at each sampling point and those for the determination of soil biomass in soil samples not treated and treated with blank application solution.



The treated soils were incubated in 300 mL Erlenmeyer glass flasks. The untreated soil samples for the biomass determination were incubated in 250 mL glass flasks with a screw thread. Each flask was closed by cotton wool.

Figure B.8.1.1.2.1.1._CA-100: The example incubation vessel (copied from the study report).

The test compound was a non-radiolabelled FOE Methylsulfone, having the chemical purity of 97.2%. Its structural formula is shown below on figure B.8.1.1.2.1.1._CA-101.

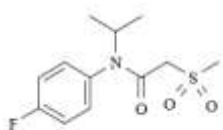


Figure B.8.1.1.2.1.1._CA-101: The structural formula of the test compound used in the experiment (copied from the study report).

It was delivered as a solid sample, in form of a light-yellow powder. That sample was used entirely to prepare firstly a **Stock solution** and then **Application solutions**.

The **Stock solution** was prepared by dissolving the whole delivered sample of FOE Methylsulfone in appropriate amount of $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ (1:1 v/v), to obtain a solution having a nominal concentration 100 mg FOE Methylsulfone. From it, by dilution with the appropriate amounts of $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ 1:1 (v/v), three following **Application solutions** were prepared:

- **Application solution S40**, having a concentration 40 mg FOE Methylsulfone/L, used to treat all kinetic samples and to prepare the **Application solution S2**, characterised below;
- **Application solution S44**, having a concentration 44 mg FOE Methylsulfone/L, used to treat the recovery samples at fortification level of 22 LOQ;

- Additionally, by diluting **Application solution S40**, was prepared the **Application solution S2**, having a concentration 2.0 mg FOE Methylsulfone/L and used to treat the concurrent recovery samples at LOQ level.

All application solutions were prepared in the same solvent as used for the **Stock solution** – CH₃OH/H₂O 1:1 (v/v).

The **Application solution S40** was used to treat degradation samples. To do that 0.198 mL of it was applied dropwise onto soil surface in each incubation vessel to obtain the application dose of 7.94 µg FOE Methylsulfone/100 g soil (d. w.). That application dose – equal to 0.0794 mg/kg soil, was determined using the following assumptions:

- field application rate of Flufenacet (parent compound, precursor of FOE Methylsulfone): 600 g/ha;
- maximum occurrence of FOE Methylsulfone in aerobic soil (determined in the laboratory studies): 6.6%;
- molar weight of Flufenacet $M = 363.3$ g/mol;
- molar weight of FOE Methylsulfone $M' = 273.3$ g/mol;
- soil bulk density: 1.5 g/cm³;
- thickness of the soil layer: 2.5 cm.

RMS analysing the calculations noticed that the assumed soil layer was ½ of that routinely used to calculate field application rate (in [g/ha]) Therefore the would-be application rate for Methylsulfone was recalculated using the standard assumptions:

- soil bulk density: 1.5 g/cm³;
- thickness of the soil layer: 5 cm.

The so calculated field application rate **A = 59.55 g FOE Methylsulfone/ha**.

Using the measured soil bulk density of each test soil used in the experiment that value would be:

- for Laacherhof AXXa soil: **A = 47.24 g/ha**;
- for Dollendorf II soil: **A = 40.89 g/ha**;
- for Höfchen am Hohenseh 4a soil: **A = 43.27 g/ha**;
- for Wurmwiese soil: **A = 46.45 g/ha**

The verification of application rate and homogeneity of application of kinetic samples was performed using **Application solution S40** (100% application level), in duplicate, at the beginning and at the end of application. That was done by transferring 0.198-mL portions of the application solution into volumetric flask The solution was brought to the volume with 4:1 (v/v) CH₃CN/H₂O and analysed using HPLC-MS/MS.

In the same manner, using the appropriate application solutions, was performed the verification of application rate and homogeneity of application of concurrent recovery samples, fortified at 110% application level and at LOQ level.

Immediately after treatment the incubation vessels designated as degradation samples were stoppered with cotton wool plugs, placed in the darkness in temperature-controlled walk-in climatic chamber and incubated for up to 120 days under aerobic conditions at $T = 20 \pm 2^\circ\text{C}$. Duplicate samples were removed from incubation chamber at following time-points (DAT stands for “Days After Treatment”):

- for Laacherhof AXXa soil: DAT 0, DAT 1, DAT 2, DAT 6, DAT 13, DAT 27, DAT 61, DAT 92 and DAT 120;
- for Dollendorf II soil: DAT 0, DAT 1, DAT 2, DAT 6, DAT 13, DAT 27, DAT 61, DAT 92 and DAT 120;
- for Höfchen am Hohenseh 4a soil: DAT 0, DAT 1, DAT 2, DAT 6, DAT 13, DAT 27, DAT 61, DAT 92 and DAT 120;
- for Wurmwiese soil: DAT 0, DAT 1, DAT 2, DAT 6, DAT 13, DAT 27, DAT 61, DAT 70, DAT 92 and DAT 120.

The soil moisture content in incubation vessels was controlled by weighing them twice a week during incubation and adjusting water content, if necessary, to the designated level by adding the appropriate amount of distilled water.

Samples removed from the incubation chamber were processed and analysed immediately after sampling. That was done for the entire portions of the test soil recovered at each sampling point, using the procedure presented below on figure B.8.1.1.2.1.1._CA-102. The same procedure was applied to Concurrent Recovery Samples.

Flow Chart of the Procedure for Sample Analysis

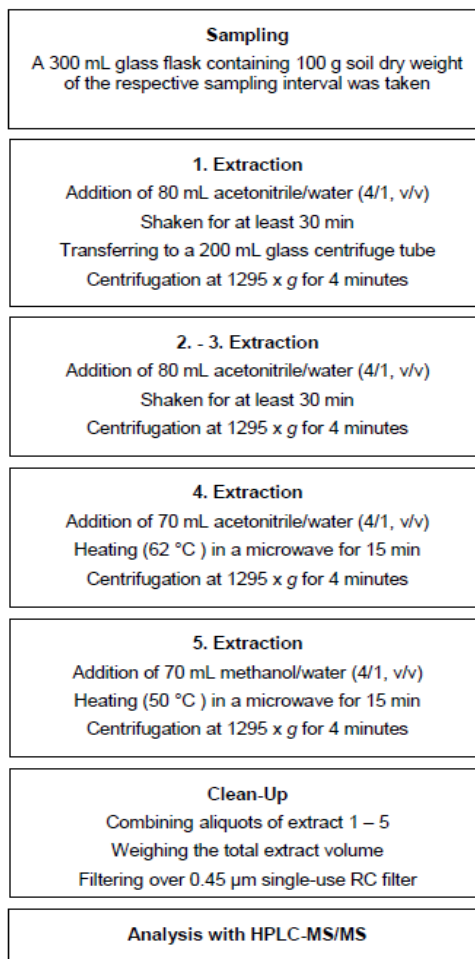


Figure B.8.1.1.2.1.1._CA-102: The sample-processing procedure used in the experiment (scheme copied from the study report).

The samples for the determination of soil biomass were set alongside the degradation samples. The soil biomass was determined in pre-conditioned test soil samples sampled on DAT 0 (beginning of the incubation period), DAT 58 (middle of the incubation period) and DAT 120 (end of incubation period). The experiment was performed in two variants:

- “BIO-” samples, not treated with blank application solution; these samples were taken for the analysis on DAT 0, DAT 58 and DAT 120;
- “BIO+” samples, treated with 0.198 mL of blank application solution (CH₃OH/H₂O 1:1 v/v); these samples were taken for the analysis on DAT 58 and DAT 120.

The quantitative and qualitative analysis of combined soil extracts and other liquid samples was performed by means of HPLC-MS/MS. The analysis was performed using Agilent LC-system equipped with autosampler and Sciex API5000 detector. The chromatographic separation was performed on Phenomenex Synergi Fusion-RP 80-A 50*2 mm chromatographic column, preceded by 4-mm guard column of the same type, working in a gradient mode. The column was maintained at constant temperature T = 20°C. The gradient elution programme is presented below in the table B.8.1.1.2.1.1._CA-203.

Table B.8.1.1.2.1.1._CA-203: The HPLC gradient modes used in the study.

Time [min]	Solvent ratio	
	<i>Solvent A – Water + 0.1% CH₃COOH</i>	<i>Solvent B – CH₃OH + + 0.1% CH₃COOH</i>
0.00	80	20
0.50	80	20
2.00	10	90
3.50	10	90
3.51	80	20
4.00	80	20

The elution lasted for 6 minutes and the flow rate of the mobile phase was 0.5 mL/min.

The identification of the test compound was performed by means of MS analysis. Its parameters were following:

- ionization mode: ESI;
- source polarity: positive;
- Ion spray voltage: 5500V;
- Temperature: 450⁰C;
- Collision gas: 5V;
- Entrance potential: 10V;
- Declustering potential: 116V.

The analysis was performed using the following fragment ions:

- m/z = 231.8 as quantifier;
- m/z = 111.9 as qualifier.

Additional identification parameter for FOE Methylsulfone was the retention time $R_t = 2.1$ min. (approx.).

The quantitative analysis was performed using the external 10-point calibration curve ranging from 0.2 ng/mL to 40 ng/mL. It was prepared from the stock solution of the test compound in CH₃OH/H₂O 1:1 (v/v). The concentration of the stock solution was 100 mg/L. The calibration curve was prepared for each test soil in blank soil matrix obtained by processing 100-g test soil samples in a manner identical to that presented on figure B.8.1.1.2.1.1._CA-102 for kinetic samples. The solutions used to construct the calibration curves had following nominal concentrations of FOE Methylsulfone: 0.2 ng/mL, 0.3 ng/mL, 0.5 ng/mL, 1.0 ng/mL, 5.0 ng/mL, 8.0 ng/mL, 10.0 ng/mL, 20.0 ng/mL, 30 ng/mL and 40 ng/mL.

The accuracy and repeatability was assessed for each test soil. That was done using recovery samples prepared at each sampling point and fortified with the test compound at LOQ- and 22-fold LOQ- levels.

The obtained results – concentrations of FOE Methylsulfone in each test soil at each time point, were subjected to the kinetic analysis in order to identify the best-fit kinetic model and determine persistence kinetic endpoints for FOE Methylsulfone in each test soil.

The kinetic analysis was performed in line with the recommendations of the FOCUS Kinetics Guidance Document [FOCUS; 2006], using KinGUI 2 modelling tool. It followed the procedure used in several already summarised studies, in particular **Study 4** and **Study 5** models. Three kinetic models were used in the assessment – SFO, FOMC and DFOP. The obtained fit were evaluated using the same principles as presented in the summaries of **Studies 2 – 8**.

The results of the study are presented below.

Results and their discussion:

The results of the determination of soil physicochemical properties and soil microbial activity in each test soil are presented in the table B.8.1.1.2.1.1._CA-202 at the beginning of this summary. On their basis it can be stated that the soils were appropriately selected, in line with the recommendations of OECD 307 Guideline, and were biologically viable throughout the experiment.

The results of the monitoring of the incubation temperature are presented below on figure B.8.1.1.2.1.1._CA-103. In the study report it was stated that the mean incubation temperature was 19.7⁰C and it ranged from 17.7⁰C to 22.3⁰C. It was indicated however, that that highest temperature was measured sporadically – on three occasions during incubation period, and it lasted for no longer than 1 hour, therefore it had no impact on the study results.

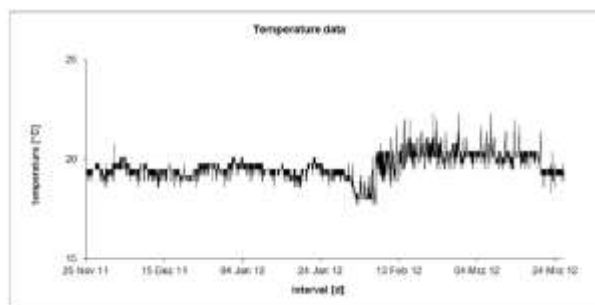


Figure B.8.1.1.2.1.1_CA-103: The temperature recorded during soil pre-conditioning and samples incubation period (copied from the study report).

The results of the monitoring of soil moisture during the experiment demonstrated that that parameter was maintained at the designated level of $55 \pm 5^{\circ}\text{C}$ throughout the study duration.

The results of the determination of application rate and the homogeneity of application are presented below, in the table B.8.1.1.2.1.1_CA-204. On their basis it was stated that the actual application rate was $8.17 \mu\text{g}$ FOE Methylsulfone/100 g soil (d.w.) – 0.0817 mg FOE Methylsulfone/kg soil (d. w.). That value was set as 100% applied – a reference value for expressing the concentration of FOE Methylsulfone as [% Applied].

Table B.8.1.1.2.1.1_CA-204: The results of the verification of application rate and homogeneity of application.

Sample	Replicate	Chromatographic peak area [counts]	Amount of FOE Methylsulfone [μg]	% of theoretically applied
100% before application	1	127895.4	8.81	107.8
	2	94395.4	7.79	95.4
100% after application	1	82948.8	7.34	89.8
	2	126418.8	8.75	107.1

The LOQ – limit of quantification, was defined as 1.0 ng/mL . The corresponding LOD was set to 0.2 ng/mL – 1% of applied.

The results of the determination of linearity of analytical method is presented below, in numerical and graphical form, individually for each calibration curve constructed using each test soil blank matrix.

The linearity of the calibration curve constructed using blank matrix of Laacherhof AXXa soil is presented below in table B.8.1.1.2.1.1_CA-205 and on figure B.8.1.1.2.1.1_CA-104.

Table B.8.1.1.2.1.1_CA-205: The numerical results of the determination of the linearity of the response of MS/MS detector for calibration curve constructed on soil blank matrix from Laacherhof AXXa soil.

Calibration sample No.	Nominal concentration [ng/mL]	Peak area [a.u.]			Accuracy [%]
		Replicate 1	Replicate 2	Mean	
1	40.0	1872627	1675204	1773916	96.6
2	30.0	1318121	1369969	1344045	97.5
3	20.0	980525	868744	924635	100.4
4	10.0	539060	487968	5135114	110.9
5	8.0	402750	378465	390608	105.0
6	5.0	290128	237516	263822	112.6
7	1.0	54469	42937	48703	92.7
8	0.5	29521	27840	28681	97.9
9	0.3	20105	19266	19686	97.5
10	0.2	12658	16183	14421	88.7

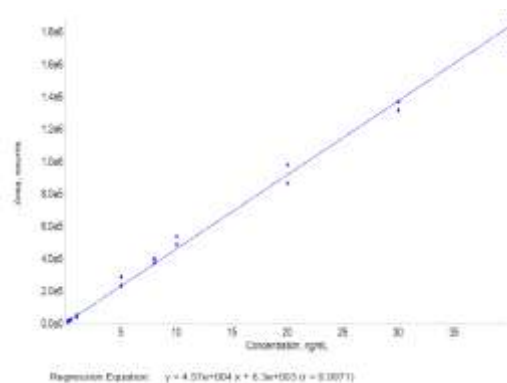


Table B.8.1.1.2.1.1._CA-104: The graphical results of the determination of the linearity of the response of MS/MS detector for calibration curve constructed on soil blank matrix from Laacherhof AXXa soil (copied from the study report).

The linearity of the calibration curve constructed using blank matrix of Dollendorf II soil is presented below in table B.8.1.1.2.1.1._CA-206 and on figure B.8.1.1..2.1.1._CA-105.

Table B.8.1.1.2.1.1._CA-206: The numerical results of the determination of the linearity of the response of MS/MS detector for calibration curve constructed on soil blank matrix from Dollendorf II soil.

Calibration sample No.	Nominal concentration [ng/mL]	Peak area [a.u.]			Accuracy [%]
		Replicate 1	Replicate 2	Mean	
1	40.0	1464255	1457619	1460937	100.5
2	30.0	1085545	1127829	1106687	101.4
3	20.0	722609	692033	707321	97.1
4	10.0	382956	365479	374218	102.2
5	8.0	295801	288733	292267	99.5
6	5.0	174419	180440	177430	95.7
7	1.0	40566	39361	39964	99.3
8	0.5	21760	20320	21040	94.2
9	0.3	14213	16159	15186	103.1
10	0.2	11181	12281	11731	107.0

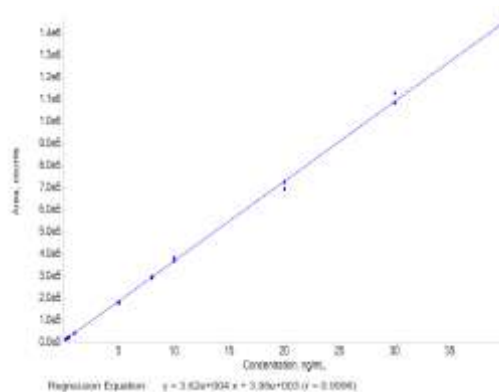


Table B.8.1.1.2.1.1._CA-105: The graphical results of the determination of the linearity of the response of MS/MS detector for calibration curve constructed on soil blank matrix from Dollendorf II soil (copied from the study report).

The linearity of the calibration curve constructed using blank matrix of Höfchen am Hohenseh 4a soil is presented below in table B.8.1.1.2.1.1._CA-207 and on figure B.8.1.1.2.1.1._CA-106.

Table B.8.1.1.2.1.1._CA-207: The numerical results of the determination of the linearity of the response of MS/MS detector for calibration curve constructed on soil blank matrix from Höfchen am Hohenseh 4a soil.

Calibration sample No.	Nominal concentration [ng/mL]	Peak area [a.u.]			Accuracy [%]
		Replicate 1	Replicate 2	Mean	
1	40.0	1653199	1671085	1662142	99.8
2	30.0	1282754	1305851	1294302	103.0
3	20.0	768398	819760	794079	95.1
4	10.0	441218	407984	424601	101.2
5	8.0	319267	337747	328507	97.5
6	5.0	208784	215745	212264	100.0
7	1.0	47878	54334	51106	111.7
8	0.5	25615	23637	24626	95.8
9	0.3	15161	15520	15341	85.0
10	0.2	14728	13104	13916	110.4

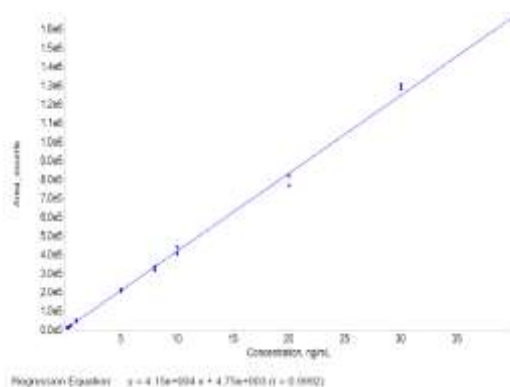


Table B.8.1.1.2.1.1._CA-106: The graphical results of the determination of the linearity of the response of MS/MS detector for calibration curve constructed on soil blank matrix from Höfchen am Hohenseh 4a soil (copied from the study report).

The linearity of the calibration curve constructed using blank matrix of Wurmwiese soil is presented below in table B.8.1.1.2.1.1._CA-208 and on figure B.8.1.1.2.1.1._CA-107.

Table B.8.1.1.2.1.1._CA-208: The numerical results of the determination of the linearity of the response of MS/MS detector for calibration curve constructed on soil blank matrix from Wurmwiese soil.

Calibration sample No.	Nominal concentration [ng/mL]	Peak area [a.u.]			Accuracy [%]
		Replicate 1	Replicate 2	Mean	
1	40.0	2397534	2555369	2476452	99.2
2	30.0	1874955	1911743	1893349	101.1
3	20.0	128432	1242508	685470	99.7
4	10.0	630790	630523	630657	100.8
5	8.0	488968	489744	489356	97.6
6	5.0	323586	326314	324950	103.4
7	1.0	62242	62804	62523	95.9
8	0.5	35453	33716	34585	102.0
9	0.3	18891	22471	20681	95.7
10	0.2	17009	14633	15821	104.5

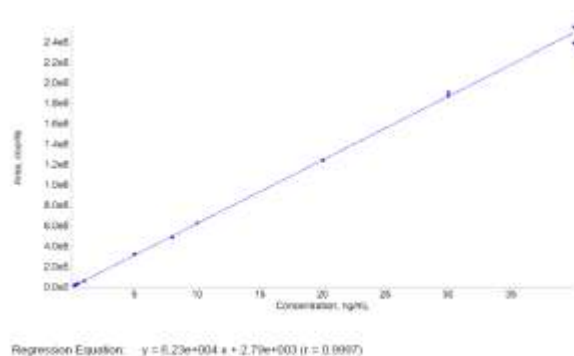


Table B.8.1.1.2.1.1._CA-107: The graphical results of the determination of the linearity of the response of MS/MS detector for calibration curve constructed on soil blank matrix from Wurmwiese soil (copied from the study report).

The results of the validation of the method on the basis of recovery, accuracy and precision, were following:

- for Laacherhof AXXa soil recovery at fortification level of 0.004 mg/kg (mean of five) was $91.1 \pm 2.0\%$, recovery at fortification level 0.101 mg/kg (mean of five) was $93.4 \pm 1.8\%$ and the overall mean recovery was $92.3 \pm 2.2\%$;
- for Dollendorf II soil recovery at fortification level of 0.004 mg/kg (mean of five) was $103.8 \pm 1.7\%$, recovery at fortification level 0.101 mg/kg (mean of five) was $90.7 \pm 2.0\%$ and the overall mean recovery was $97.2 \pm 7.3\%$;
- for Höfchen am Hohenseh 4a soil recovery at fortification level of 0.004 mg/kg (mean of five) was $96.5 \pm 2.8\%$, recovery at fortification level 0.101 mg/kg (mean of five) was $104.6 \pm 3.3\%$ and the overall mean recovery was $100.5 \pm 5.1\%$;
- for Wurmwiese soil recovery at fortification level of 0.004 mg/kg (mean of five) was $96.2 \pm 2.3\%$, recovery at fortification level 0.101 mg/kg (mean of five) was $100.3 \pm 2.9\%$ and the overall mean recovery was $98.3 \pm 3.3\%$.

On that basis it was stated that the accuracy and precision of analytical method was acceptable, with mean recoveries in range 70-110% and RSD < 20%.

The results of the concurrent recoveries, determined using Laacherhof AXXa soil, are presented below in the table B.8.1.1.2.1.1._CA-209. On their basis, as well as on the basis of the recoveries for each test soil, it was stated that the applied soil processing method was appropriate.

Table B.8.1.1.2.1.1._CA-209: The results of the determination of the recovery in concurrent recovery samples.

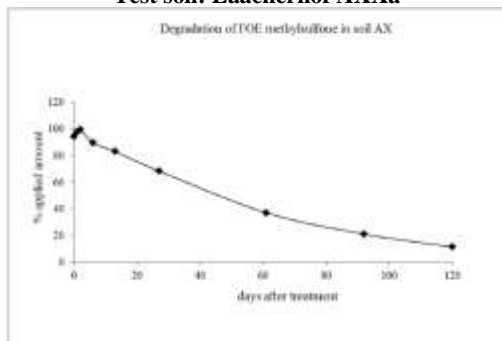
Time point – DAT [days]	Recovery in concurrent samples treated at LOQ level (0.004 mg/kg)				Recovery in concurrent samples treated at 22-fold LOQ level (0.0899 mg/kg)			
	Recovery [% applied]:			RSD [%]	Recovery [% applied]:			RSD [%]
	Replicate 1	Replicate 2	Mean		Replicate 1	Replicate 2	Mean	
0	154.3	104.3	104.3	n. d.	96.6	112.9	104.8	11.0
1	103.6	116.4	110.0	8.2	110.1	106.6	108.4	2.3
2	96.8	97.8	97.3	0.7	95.1	92.2	93.7	2.2
6	108.0	109.4	108.7	0.9	100.2	91.1	95.7	6.7
13	103.8	102.5	103.2	0.9	98.0	100.6	99.3	1.9
27	99.5	101.3	100.4	1.3	97.9	98.9	98.4	0.7
61	100.9	107.1	104.0	4.2	107.6	98.7	103.2	6.1
70	107.5	n. d.	107.5	n. d.	96.0	n. d.	96.0	n. d.
92	99.3	99.2	99.3	0.1	90.3	101.6	96.0	8.3
120	96.8	97.3	97.1	0.4	97.1	100.7	98.9	2.6

The results of the experiment – concentrations of FOE Methylsulfone in soil in function of time, are presented below in the table B.8.1.1.2.1.1._CA-210. For each test soil the concentrations of the test compound are reported as % of applied amount – [% AA] and in [µg/kg soil]. The values expressed as [% AA] were calculated using the determined experimentally application rate – 0.0817 mg FOE Methylsulfone/kg soil, as 100% level. The graphic presentation of the results is given on figure B.8.1.1.2.1.1._CA-108.

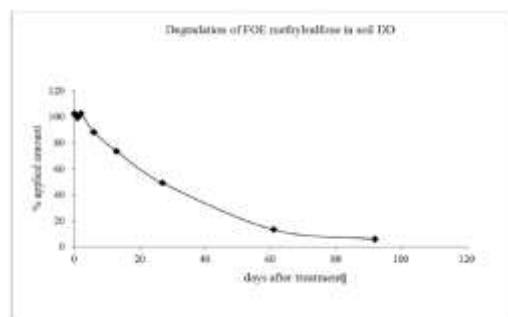
Table B.8.1.1.2.1.1._CA-210: Concentration of FOE Methylsulfone in test soils in function of time.

Results obtained in Laacherhof AXXa soil							Results obtained in Dollendorf II soil						
DAT [days]	Concentration of FOE Methylsulfone						DAT [days]	Concentration of FOE Methylsulfone					
	[% AA]			[µg/kg soil]				[% AA]			[µg/kg soil]		
	Rep. 1	Rep. 2	Mean	Rep. 1	Rep. 2	Mean		Rep. 1	Rep. 2	Mean	Rep. 1	Rep. 2	Mean
0	92.7	95.3	94.0	75.7	77.9	76.8	0	107.6	97.4	102.5	87.9	79.6	83.8
1	95.8	99.0	97.4	78.3	80.9	79.6	1	100.1	98.5	99.3	81.8	80.5	81.2
2	94.7	103.7	99.2	77.4	84.7	81.1	2	105.8	99.0	102.4	86.4	80.9	83.7
6	90.3	88.5	89.4	73.8	72.3	73.1	6	88.6	87.8	88.2	72.4	71.7	72.1
13	83.6	82.3	82.9	68.2	67.2	67.8	13	73.7	73.1	73.4	60.2	59.7	60.0
27	69.5	67.1	68.3	56.8	54.8	55.8	27	48.1	49.9	49.0	39.3	40.8	40.1
61	35.6	38.4	37.0	29.1	31.4	30.3	61	12.2	13.7	13.8	10.0	11.2	10.6
92	21.3	20.7	21.0	17.4	16.9	17.2	92	4.5	7.0	5.8	3.7	5.7	4.7
120	12.5	10.3	11.4	10.2	8.4	9.3							
Results obtained in Höfchen am Hohenseh 4a soil							Results obtained in Wurmwiese soil						
DAT [days]	Concentration of FOE Methylsulfone						DAT [days]	Concentration of FOE Methylsulfone					
	[% AA]			[µg/kg soil]				[% AA]			[µg/kg soil]		
	Rep. 1	Rep. 2	Mean	Rep. 1	Rep. 2	Mean		Rep. 1	Rep. 2	Mean	Rep. 1	Rep. 2	Mean
0	101.3	111.5	106.4	82.8	91.1	87.0	0	102.6	102.7	102.7	83.9	83.9	83.9
1	103.3	109.4	106.4	84.4	89.4	86.9	1	100.4	105.9	103.1	82.0	86.5	84.3
2	96.1	94.1	95.1	78.5	76.9	77.7	2	95.8	102.2	99.0	78.3	83.5	80.9
6	93.9	89.0	91.4	76.7	72.7	74.7	6	102.6	95.8	99.2	83.8	78.3	81.1
13	77.7	81.6	79.7	63.5	66.7	65.1	13	89.4	89.2	89.3	73.0	72.9	73.0
27	66.0	70.4	68.2	53.9	57.5	55.7	27	79.7	76.1	77.9	65.1	62.2	63.7
61	40.9	41.0	41.0	33.5	33.5	33.5	61	72.2	71.5	71.8	59.0	58.4	58.7
92	29.5	20.8	25.2	24.1	17.0	20.6	70	68.2	54.3	61.3	55.7	44.4	50.1
120	13.0	15.4	14.2	10.6	12.6	11.6	92	55.9	51.7	53.8	45.7	42.2	44.0
							120	37.5	41.4	39.4	30.6	33.8	32.2

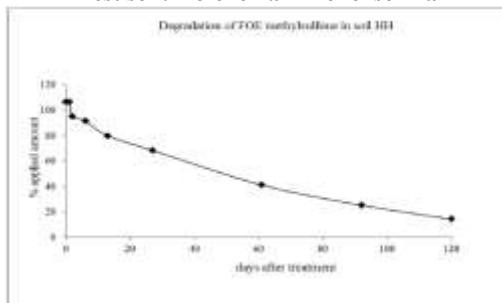
Test soil: Laacherhof AXXa



Test soil: Dollendorf II



Test soil: Höfchen am Hohenseh 4a



Test soil: Wurmwiese

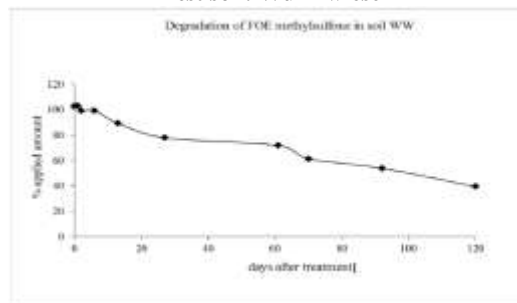


Figure B.8.1.1.2.1.1._CA-108: The graphic presentation of the results obtained in test soils (copied from the study report).

The data presented in the table B.8.1.1.2.1.1._CA-210 were subjected to the kinetic analysis aimed on the determination of the best kinetic fit and derivation of the kinetic endpoints representing persistence of the test compound. For that purpose the values obtained for replicates, expressed as [%AA], were used. The values were inserted to the model as they are presented in the table evoked above. RMS noticed that the same data set was analysed in a separate study, aimed on the identification of the appropriate fit and derivation of the kinetic endpoints representing persistence of FOE Methylsulfone in soil and suitable for modelling – study by [Reinken and Partsch; 2014] summarised below as **Study 15**. The methodology of the kinetic analysis and its results presented in both studies were compared by the RMS. It was stated that while the methodology was very similar, taking into account somewhat different goals of the kinetic analysis, the results obtained in both studies were generally the same. The differences resulted from the different aims of the kinetic analysis – in case of the currently summarised study it was to identify the best-fit kinetic model and determine the persistence endpoints for FOE Methylsulfone in the test soils. In case of the summarised below study by [Reinken and Partsch; 2014], the major goal was to kinetically examine the data set in order to derive kinetic endpoints suitable for modelling. It was stated that, due to the fact that the study was specifically aimed on the kinetic analysis of the data, the procedure of kinetic fitting was characterised in a more detailed way, e.g. the optimisation method was reported.

As a results, in order not to duplicate the identical results and by that overburden the Assessment Report, RMS decided not to present the results of the kinetic analysis provided in the currently summarised study by [Traub; 2012], focusing instead on the study by [Reinken and Partsch; 2014] summarised below as **Study 15**.

Study 15:

Report: Reinken G., Partsch S., (2014): “Kinetic Evaluation of the Degradation of Flufenacet Degradation Product FOE methylsulfone under Aerobic Soil conditions in Laboratory according to FOCUS Kinetics Using the KinGUI 2 Tool. FOE methylsulfone acid.”; Bayer CropScience AG, Environmental Safety, Alfred-Nobel-Strasse 50, 40789 Monheim, Germany; unpublished Study Report No. EnSa-12-0578; 2014. 02. 17; study reference number: M-477839-01-1;

Guidelines: The study was declared to be performed to comply with the following guidelines:

- FOCUS (2006): “Guidance Document on Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration.” Report of the FOCUS Work Group on Degradation Kinetics, EC Document Reference SANCO/10058/2005 version 2.0, 434 pp.;
- FOCUS (2011): “Generic guidance for Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration”, version 1.0 (issued on 23 November 2011).

GLP: No, not applicable – this is a modelling study;

RMS comments: RMS verified the study for its compliance with the provisions of the Guidelines listed above. It was stated that the study generally complied with the two evoked Guidance Documents. The study was aimed on the derivation of the modelling kinetic endpoints for FOE Methylsulfone. It followed modelling approach outlined already in other studies summarised above – **Study 2**, **Study 7** and **Study 8**. The analysis was performed for the results of the summarised above study by [Traub; 2012] (**Study 14**). The study was found to be acceptable and is summarised below.

Summary:

The aim of the study was to kinetically examine the data for FOE Methylsulfone obtained in summarised above as **Study 14** the study by [Traub; 2012], in order to derive the kinetic endpoints suitable for use in modelling exposure assessment.

In the source study the the degradation of FOE Methylsulfone was examined in four soils. Their key properties are presented below in the table B.8.1.1.2.1.1._CA-211. The experimental conditions used in the study are summarised further down, in the table B.8.1.1.2.1.1._CA-212.

Table B.8.1.1.2.1.1._CA-211: The brief characteristic of the test soils.

Soil name	Soil type (USDA classification)	Soil properties			
		pH in CaCl ₂	OC [%]	Soil microbial biomass at the beginning of the study	
				mg microbial C/kg soil	% OC
Laacherhof AXXa	Loamy sand	6.2	1.7	2044	7.05
Dollendorf II	Loam	7.0	4.6	4474	9.73
Höfchen am Hohenseh 4a	Silt loam	6.1	2.0	2299	111.50
Wurmweise	Sandy loam	5.0	1.8	1963	10.91

Table B.8.1.1.2.1.1._CA-212: The experimental conditions used in each experiment.

Test soil		Experimental conditions			
Name	Type (USDA classification)	Incubation temperature T [°C]	Soil moisture		
			In experiment [% MWHC]	Reference value	
				MWHC [g/100g soil d. w.]	% MWHC at 1/3bar
Laacherhof AXXa	Loamy sand	20 ± 2	55 ± 5	48.5	10.8
Dollendorf II	Loam	20 ± 2	55 ± 5	79.1	35.1
Höfchen am Hohenseh 4a	Silt loam	20 ± 2	55 ± 5	54.8	20.9
Wurmweise	Sandy loam	20 ± 2	55 ± 5	56.3	15.6

The not-processed input data used in the kinetic analysis are presented below in the table B.8.1.1.2.1.1._CA-213.

Table B.8.1.1.2.1.1._CA-213: The non-processed data obtained in the test soils, used in kinetic analysis.

Results obtained in Laacherhof AXXa soil			Results obtained in Dollendorf II soil			Results obtained in Höfchen am Hohenseh 4a soil			Results obtained in Wurmweise soil		
DAT [days]	Concentration [%] of FOE Methylsulfone		DAT [days]	Concentration [%] of FOE Methylsulfone		DAT [days]	Concentration [%] of FOE Methylsulfone		DAT [days]	Concentration [%] of FOE Methylsulfone	
	Rep. 1	Rep. 2		Rep. 1	Rep. 2		Rep. 1	Rep. 2		Rep. 1	Rep. 2
0	92.7	95.3	0	107.6	97.4	0	101.3	111.5	0	102.6	102.7
1	95.8	99.0	1	100.1	98.5	1	103.3	109.4	1	100.4	105.9
2	94.7	103.7	2	105.8	99.0	2	96.1	94.1	2	95.8	102.2
6	90.3	88.5	6	88.6	87.8	6	93.9	89.0	6	102.6	95.8
13	83.6	82.3	13	73.7	73.1	13	77.7	81.6	13	89.4	89.2
27	69.5	67.1	27	48.1	49.9	27	66.0	70.4	27	79.7	76.1
61	35.6	38.4	61	12.2	13.7	61	40.9	41.0	61	72.2	71.5
92	21.3	20.7	92	4.5	7.0	92	29.5	20.8	70	68.2	54.3
120	12.5	10.3				120	13.0	15.4	92	55.9	51.7
									120	37.5	41.4

The data presented above were subjected to a multistep evaluation procedure, almost identical to that already presented above in the summary of the **Study 2**, for convenience repeated below. It consisted of the following steps:

- **Step 1:** Processing of the raw input data;
- **Step 2:** Kinetic evaluation of the processed data using the following 1st order kinetic models: SFO, FOMC and DFOP, and KinGUI 2 as a modelling tool, in order to determine the appropriate kinetic model.
- **Step 3:** Evaluation of the results of kinetic examination of the data;
- **Step 4:** Reporting of the obtained results, in particular kinetic parameters recommended for modelling.

The data-processing to obtain the input values for kinetic analysis (**Step 1**) was identical to the procedure described in the summary of the **Study 2**, on page 166. The processed data used as input in the kinetic examination are presented below in the table B.8.1.1.2.1.1._CA-214.

Table B.8.1.1.2.1.1._CA-214: The processed residue data used in the kinetic analysis.

Results obtained in Laacherhof AXXa soil			Results obtained in Dollendorf II soil			Results obtained in Höfchen am Hohenseh 4a soil			Results obtained in Wurmweise soil		
DAT [days]	Concentration [%] of FOE Methylsulfone		DAT [days]	Concentration [%] of FOE Methylsulfone		DAT [days]	Concentration [%] of FOE Methylsulfone		DAT [days]	Concentration [%] of FOE Methylsulfone	
	Rep. 1	Rep. 2		Rep. 1	Rep. 2		Rep. 1	Rep. 2		Rep. 1	Rep. 2
0	92.7	95.3	0	107.6	97.4	0	101.3	111.5	0	102.6	102.7
1	95.8	99.0	1	100.1	98.5	1	103.3	109.4	1	100.4	105.9
2	94.7	103.7	2	105.8	99.0	2	96.1	94.1	2	95.8	102.2
6	90.3	88.5	6	88.6	87.8	6	93.9	89.0	6	102.6	95.8
13	83.6	82.3	13	73.7	73.1	13	77.7	81.6	13	89.4	89.2
27	69.5	67.1	27	48.1	49.9	27	66.0	70.4	27	79.7	76.1
61	35.6	38.4	61	12.2	13.7	61	40.9	41.0	61	72.2	71.5
92	21.3	20.7	92	4.5	7.0	92	29.5	20.8	70	68.2	54.3
120	12.5	10.3				120	13.0	15.4	92	55.9	51.7
									120	37.5	41.4

The processed data were kinetically examined using KinGUI ver. 2 modelling tool, developed by Bayer. The optimisation was performed using IRLS (Iteratively Reweighted Nonlinear Least Squares) algorithm. The fitting procedure consisted on the determination of the appropriate kinetic model for FOE Methylsulfone

The conceptual metabolic pathway built in the modelling tool was based on the transformation pathway which, in form of a simplified scheme, is presented below on figure B.8.1.1.2.1.1._CA-109.

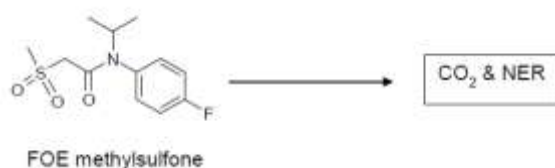


Figure B.8.1.1.2.1.1_CA-109: The simplified transformation pathway used to create conceptual transformation scheme assumed in the modelling tool (copied from the study report).

The obtained results of the kinetic analysis of the data were evaluated by the Applicant. That was done by means of a detailed statistical analysis comprising the following components:

- visual assessment of the fit;
- χ^2 -error statistics;
- t-test significance;
- correlation analysis.

The detailed characteristic of the evaluation procedure was presented in the summary of the **Study 2** on pages 170 – 171. RMS decided not to repeat it here in order to not overburden the Renewal Assessment Report.

On that basis the following multistep assessment procedure was followed:

- **Step 1:** bearing in mind the aim of the kinetic evaluation of the data – determination of the kinetic parameters used in modelling, the SFO kinetic model was tested as first option and if passed the acceptance criteria (visually acceptable, χ^2 -error not exceeding or not significantly exceeding 15%, *prob. > t* value in t-test less than 0.05 for parent and 0.10 for the degradation products), it was considered acceptable;
- **Step 2:** in case the χ^2 -error was significantly greater than 15%, model parameters were fixed and fitting repeated using SFO model;
- **Step 3:** if the **Step-2** fitting failed the χ^2 -error test, bi-phasic models were included. These were FOMC, DFOP and, possibly HS. The model with smaller error was indicated as the most appropriate;
- **Step 4:** if none of the bi-phasic model returned significantly improved fit, SFO model was selected if visually acceptable; that was done in order to avoid of an over-parameterised model based on a marginally better fit.

Analysing the proposed assessment procedure RMS stated that it complied with the procedure for determination of the kinetic endpoints for modelling, presented in FOCUS Kinetics Guidance Document [FOCUS; 2006].

The results of the kinetic analysis are presented below, individually for each test soil.

- 1) The results of the kinetic analysis of the data obtained for FOE Methylsulfone in Laacherhof AXXa soil.

The results of the kinetic analysis performed by the Applicant are presented below, in graphical form on figure B.8.1.1.2.1.1._CA-110 and in numerical form in the table B.8.1.1.2.1.1._CA-215. Additionally the table B.8.1.1.2.1.1._CA-216 provides the kinetic endpoints obtained with each of the kinetic models tested.

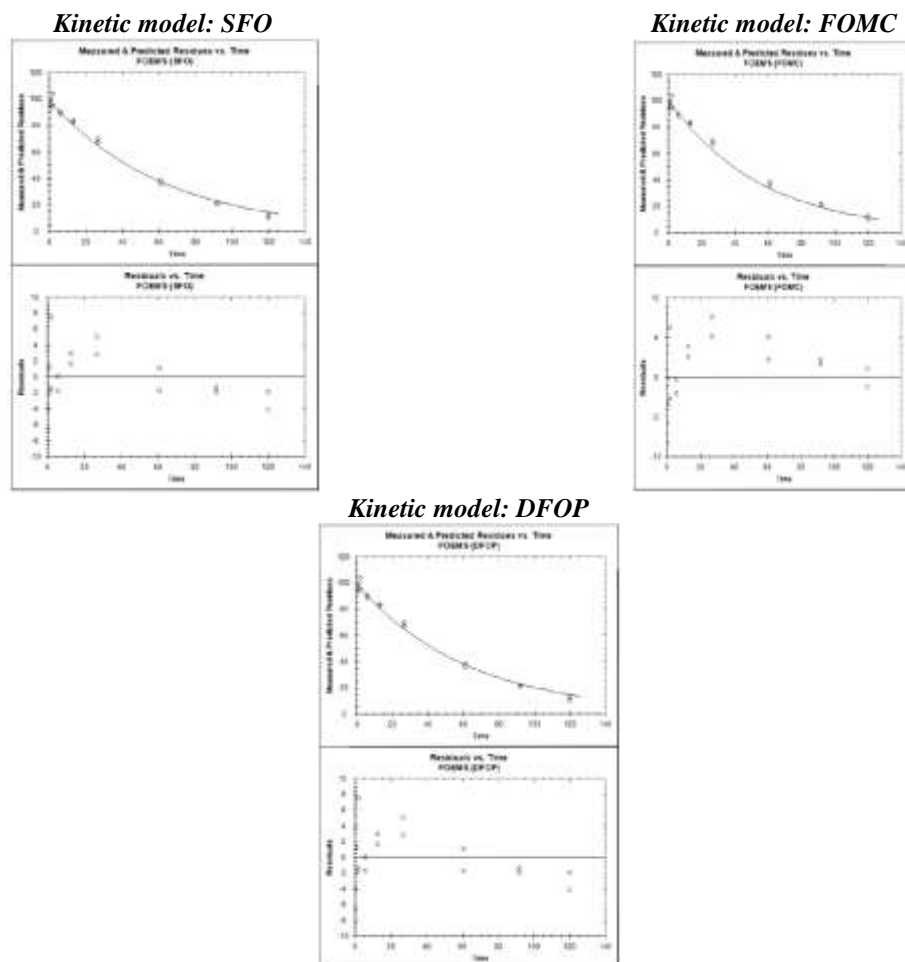


Figure B.8.1.1.2.1.1._CA-110: The graphical results of the kinetic analysis (copied from the study report).

Table B.8.1.1.2.1.1._CA-215: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment ¹⁾
				Lower	Upper			
SFO	M_0	99.34	1.266	96.86	101.82	< 2 E-16	3.373	0.990; Good fit
	k	0.01607	6.741 E-4	0.01474	0.017	3.16 E-14		
FOMC	M_0	101.00	1.522	98.017	104.0	< 2 E-16	4.74	0.986; Good fit
	α	280.479	645.370	-984.423	1545.4	0.335		
	β	15418.321	35539.153	-54237.14	85073.8	0.335		
DFOP	M_0	99.338	1.334	96.724	101.951	< 2 E-16	3.802	0.990; Good fit
	k_1	0.01607	4.268 E-3	7.703 E-3	0.024	1.05 E-3		
	k_2	0.01606	2.243 E-3	0.01167	0.020	2.42 E-6		
	g	0.3365	0.6477	-0.9330	1.606	0.3057		

Footnotes to the table:

- 1) Visual assessment of the kinetic curve as proposed by the Applicant.

Table B.8.1.1.2.1.1._CA-216: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested		
		<i>SFO</i>	<i>FOMC</i>	<i>DFOP</i>
<i>FOE Methylsulfone</i>	DT ₅₀ [days]	43.14	38.15	43.14
	DT ₉₀ [days]	143.32	127.10	143.32

Conclusion:

All three models returned visually and statistically good fits. SFO was superior of the three fits with fully reliable kinetic parameters. Neither FOMC nor DFOP, despite being visually and statistically good fits, can be considered acceptable, because they returned not reliable kinetic parameters. In case of FOMC fit the problem concerned α and β , which were not reliable because CI for them passed through zero. The additional problem was that the concentration of the test compound at the end of the experiment was still, although slightly, above the level of 10%.

For DFOP not fully reliable was g , for which the $prob. > t$ was higher than 0.1. Additionally it was noticed that the model calculated the DT₅₀ and DT₉₀ values for DFOP fit exactly the same as for SFO. Also k_1 and k_2 values were practically identical, indicating that DFOP fit was artificial.

As a result, the Applicant stated that SFO model shall be considered as returning the appropriate fit for FOE Methylsulfone acid in Laacherhof AXXa soil and hence appropriate to derive persistence and modelling endpoints for that compound in that test soil. It shall be noted that also in the preceding study by [Traub; 2012] SFO was identified as returning the best fit with the same kinetic endpoints reported.

RMS accepted the Applicant's proposal.

- 2) The results of the kinetic analysis of the data obtained for FOE Methylsulfone acid in Dollendorf II soil.

The results of the kinetic analysis performed by the Applicant are presented below, in graphical form on figure B.8.1.1.2.1.1._CA-111 and in numerical form in the table B.8.1.1.2.1.1._CA-217. Additionally the table B.8.1.1.2.1.1._CA-218 provides the kinetic endpoints obtained with each of the kinetic models tested.

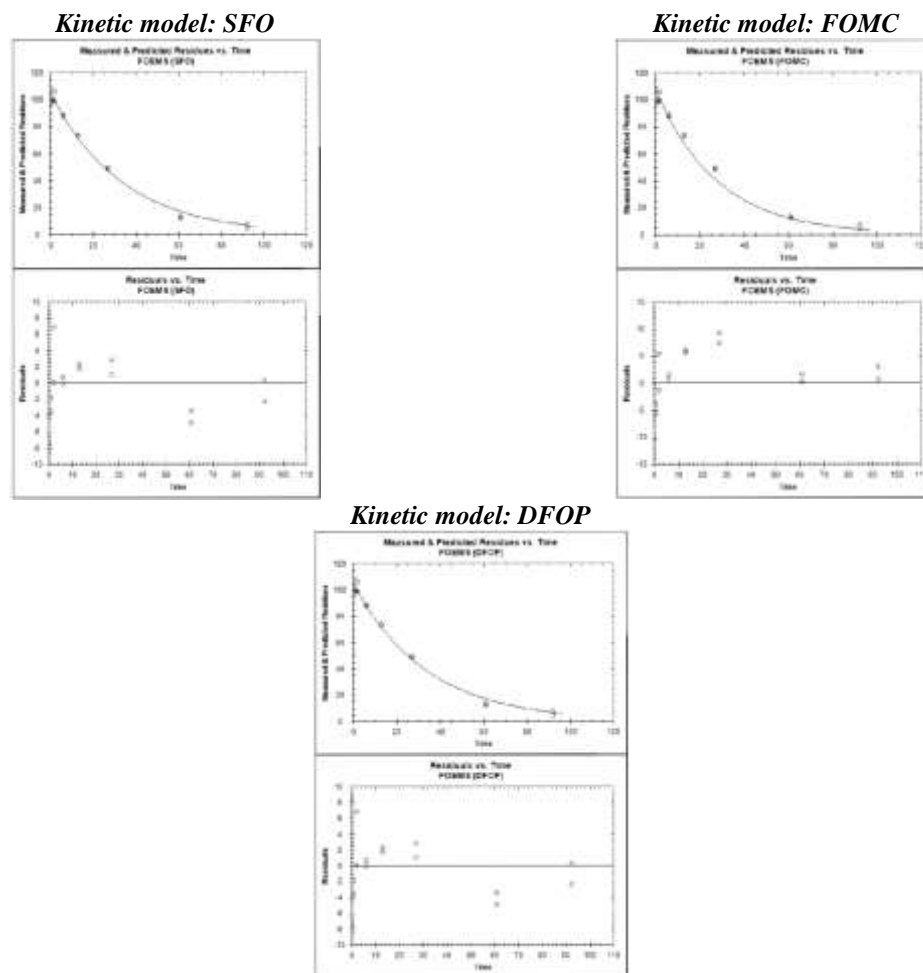


Figure B.8.1.1.2.1.1._CA-111: The graphical results of the kinetic analysis (copied from the study report).

Table B.8.1.1.2.1.1._CA-217: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment ¹⁾
				Lower	Upper			
SFO	M_0	105.0	1.449	102.2	107.856	< 2 E-16	3.042	0.992; Good fit
	k	0.02975	1.399 E-3	0.0270	0.032	2.35 E-12		
FOMC	M_0	107.86	2.12	103.70	112.0	< 2 E-16	5.765	0.986; Acceptable fit
	α	372.39	794.69	-1185.18	1930.0	0.324		
	β	10322.53	22067.69	-32929.35	53574.0	0.324		
DFOP	M_0	105.015	1.568	101.942	108.089	< 2 E-16	3.505	0.992; Good fit
	k_1	0.02974	5.30 E-3	0.01936	0.040	5.96 E-5		
	k_2	0.02975	6.897 E-3	0.01623	0.043	5.04 E-4		
	g	0.5527	2.5975	-4.5382	5.644	0.4175		

Footnotes to the table:

- 1) Visual assessment of the kinetic curve as proposed by the Applicant.

Table B.8.1.1.2.1.1_CA-218: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested		
		<i>SFO</i>	<i>FOMC</i>	<i>DFOP</i>
<i>FOE Methylsulfone</i>	DT ₅₀ [days]	23.30	19.23	23.30
	DT ₉₀ [days]	77.41	64.03	77.41

Conclusion:

SFO and DFOP model returned fits that were classified by the Applicant as visually good. The fit returned by FOMC model was classified as acceptable, mainly because of the levels of residuals and their distribution. All three fits were statistically reliable – the χ^2 level for them was well below the threshold value of 15%.

The Applicant indicated the SFO model fit as returning the appropriate fit for determining the kinetic endpoints representing persistence and suitable for modelling. That model was fit was also identified as returning the best fit in the previously summarised study by [Traub; 2012].

RMS analysing the results stated that neither FOMC nor DFOP fits can be considered acceptable, because they returned not reliable kinetic parameters.

In case of FOMC fit the problem concerned α and β , which were not reliable because CI for them passed through zero.

For DFOP not fully reliable was g , for which the $prob. > t$ was higher than 0.1. Additionally it was noticed that the model calculated the DT₅₀ and DT₉₀ values for DFOP fit exactly the same as for SFO. Also k_1 and k_2 values were practically identical, indicating that DFOP fit was artificial.

The final conclusion drawn by the Applicant was that SFO model shall be considered as returning the appropriate fit for FOE Methylsulfone acid in Dollendorf II soil and hence appropriate to derive persistence and modelling endpoints for that compound in that test soil. It was in line with the conclusion drawn in the study by [Traub; 2012], with the identical set of kinetic endpoints determined.

RMS accepted the Applicant's proposal.

- 3) The results of the kinetic analysis of the data obtained for FOE Methylsulfone in Höfchen am Hohenseh 4a soil.

The results of the kinetic analysis performed by the Applicant are presented below, in graphical form on figure B.8.1.1.2.1.1._CA-112 and in numerical form in the table B.8.1.1.2.1.1._CA-219. Additionally the table B.8.1.1.2.1.1._CA-220 provides the kinetic endpoints obtained with each of the kinetic models tested.

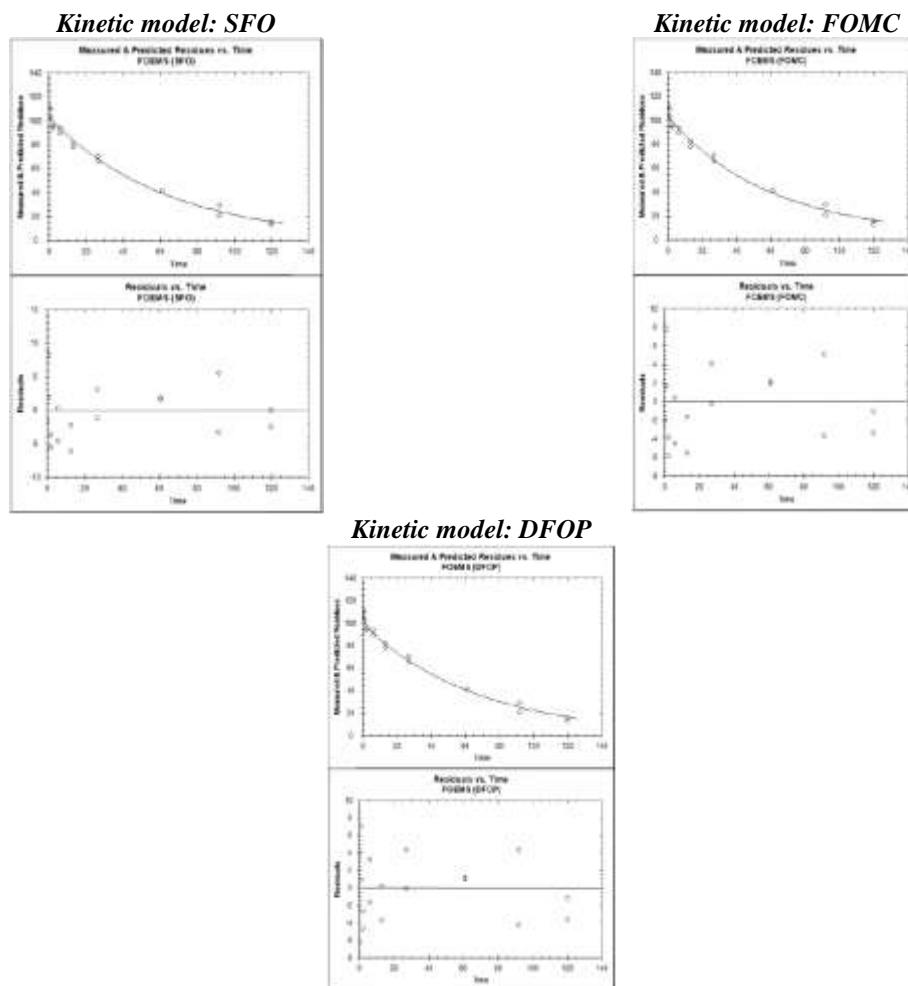


Figure B.8.1.1.2.1.1._CA-112: The graphical results of the kinetic analysis (copied from the study report).

Table B.8.1.1.2.1.1._CA-219: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment ¹⁾
				Lower	Upper			
SFO	M_0	102.9	1.588	99.82	106.041	< 2 E-16	3.578	0.984; Good fit
	k	0.01581	8.267 E-4	0.01419	0.017	9.54 E-13		
FOMC	M_0	103.384	1.912	99.636	107.13	< 2 E-16	3.732	0.984; Acceptable fit
	α	9.996	22.411	-33.928	53.92	0.331		
	β	593.503	1415.817	-2181.448	3368.45	0.341		
DFOP	M_0	107.5	2.558	102.5	112.516	< 2 E-16	2.915	0.988; Acceptable fit
	k_1	0.5465	0.4315	-0.2992	1.392	0.1130		
	k_2	0.01487	8.423 E-4	0.01322	0.017	2.89 E-11		
	g	0.08144	0.03370	0.01539	0.147	0.0150		

Footnotes to the table:

- 1) Visual assessment of the kinetic curve as proposed by the Applicant.

Table B.8.1.1.2.1.1_ CA-220: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested		
		<i>SFO</i>	<i>FOMC</i>	<i>DFOP</i>
<i>FOE Methylsulfone</i>	DT ₅₀ [days]	43.84	42.62	40.90
	DT ₉₀ [days]	145.64	153.74	149.11

Conclusion:

All three models returned first that were statistically reliable – the χ^2 error for them was well below 15%, however the applicant classified only SFO fit as good in terms of visual assessment, while both FOMC and DFOP were classified as acceptable. As a result the Applicant proposed to consider SFO fit appropriate for deriving the persistence and kinetic endpoints.

That assessment differed from the presented in the study by [Traub; 2012] in the following points:

- in the study by [Traub; 2012] all three fits were considered good in terms of the visual assessment, and that classification in RMS's opinion better reflects the results;
- in the study by [Traub; 2012] DFOP was proposed as returning the best fit.

It shall be pointed out however that neither DFOP nor FOMC fits can be considered acceptable, as they returned not reliable kinetic endpoints. In case of FOMC fit the problem concerned α and β , which were not reliable because CI for them passed through zero. The additional problem was that the concentration of the test compound at the end of the experiment was still above the level of 10%.

For DFOP fit not fully reliable was k_1 , for which the *prob.* > *t* was higher than 0.1. Also the *g* value, although statistically reliable, made the fit problematic, being low – 0.081. That indicated that DFOP fit was probably artificial. Similar problems were identified in the kinetic analysis presented in the study by [Traub; 2012].

As a result it may be stated that the Applicant's proposal to consider SFO fit as appropriately representing persistence of FOE Methylsulfone in Höfchen am Hohenseh 4a soil and appropriate for deriving modelling endpoints is correct. As such it was found acceptable by the RMS.

- 4) The results of the kinetic analysis of the data obtained for FOE Methylsulfone in Wurmwiese soil.

The results of the kinetic analysis performed by the Applicant are presented below, in graphical form on figure B.8.1.1.2.1.1_CA-113 and in numerical form in the table B.8.1.1.2.1.1_CA-221. Additionally the table B.8.1.1.2.1.1_CA-222 provides the kinetic endpoints obtained with each of the kinetic models tested.

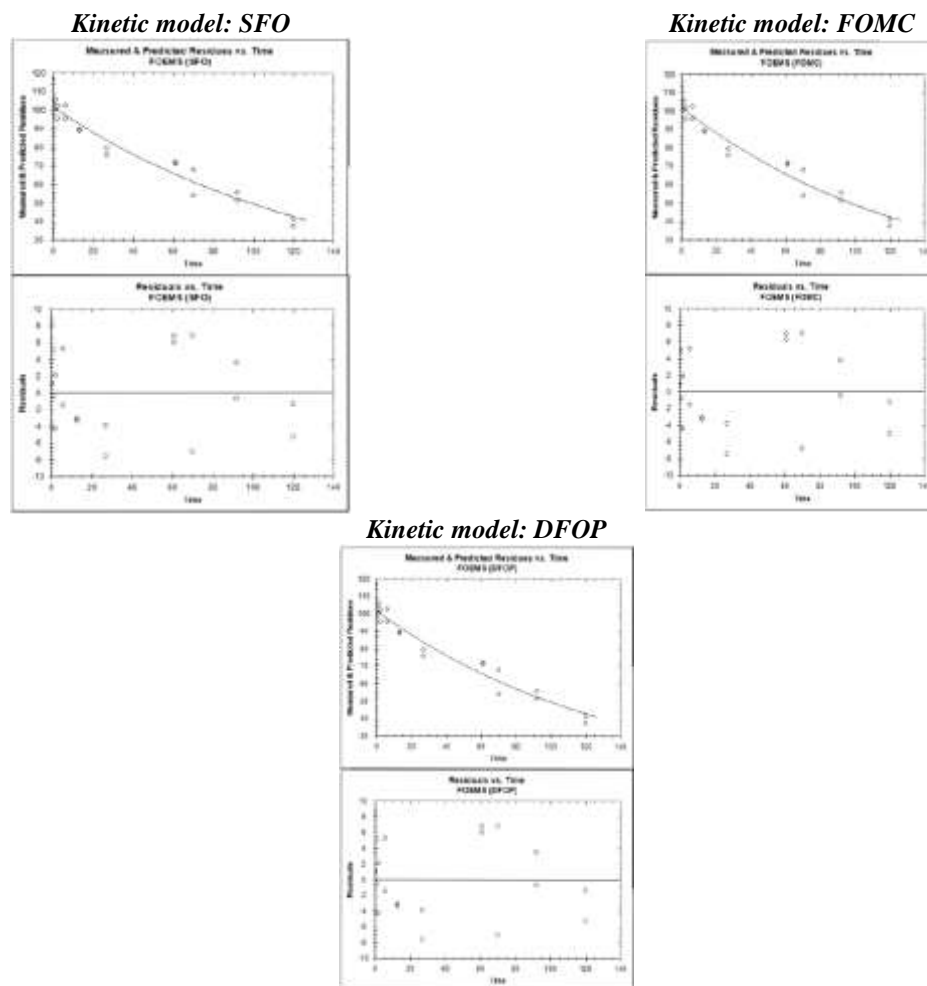


Figure B.8.1.1.2.1.1_CA-113: The graphical results of the kinetic analysis (copied from the study report).

Table B.8.1.1.2.1.1_CA-221: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment ¹⁾
				Lower	Upper			
SFO	M_0	101.6	1.551	98.53	104.612	< 2 E-16	3.317	0.958; Good fit
	k	7.211 E-3	4.179 E-4	6.392 E-3	0.008	6.05 E-13		
FOMC	M_0	101.71	1.42	98.93	104.5	< 2 E-16	3.488	0.958; Good fit
	α	89.45	111.88	-129.84	308.7	0.218		
	β	12253.25	15384.63	-17900.08	42406.6	0.218		
DFOP	M_0	101.565	39.740	23.676	179.45	0.0106	3.681	0.958; Good fit
	k_1	7.307 E-3	0.2615	-0.5053	0.52	0.4890		
	k_2	7.176 E-3	0.07785	-0.1454	0.16	0.4639		
	g	0.2495	8.0076	-15.4451	15.94	0.4878		

Footnotes to the table:

- 1) Visual assessment of the kinetic curve as proposed by the Applicant.

Table B.8.1.1.2.1.1._CA-222: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested		
		<i>SFO</i>	<i>FOMC</i>	<i>DFOP</i>
<i>FOE Methylsulfone</i>	DT ₅₀ [days]	96.13	95.32	96.16
	DT ₉₀ [days]	319.32	319.52	319.46

Conclusion:

All three models returned visually and statistically good fits. SFO was superior of the three fits with fully reliable kinetic parameters. Neither FOMC nor DFOP, despite being visually and statistically good fits, can be considered acceptable, because they returned not reliable kinetic parameters.

In case of FOMC fit the problem concerned α and β , which were not reliable because CI for them passed through zero. The additional problem was that the concentration of the test compound at the end of the experiment was still, although slightly, above the level of 10%.

For DFOP none of the three determined kinetic parameters – k_1 , k_2 or g , may be considered reliable, because for calculated for them $prob. > t$ was significantly higher than 0.1, being close to 0.5. Additionally it was noticed that the model calculated the DT₅₀ and DT₉₀ values for DFOP fit very similar to those determined for SFO kinetic fit. Finally, the k_1 and k_2 values were almost identical, what may indicate that DFOP fit was artificial.

As a result, the Applicant stated that SFO model shall be considered as returning the appropriate fit for FOE Methylsulfone acid in Wurmwiese soil and hence appropriate to derive persistence and modelling endpoints for that compound in that test soil. It shall be noted that also in the preceding study by [Traub; 2012] SFO was identified as returning the best fit with the same kinetic endpoints reported.

RMS accepted the Applicant's proposal.

Final conclusion of the study:

On the basis of the results of the kinetic analysis presented above was determined the definitive set of the reliable kinetic parameters, presented below in the table B.8.1.1.2.1.1._CA-223.

Table B.8.1.1.2.1.1._CA-223: The definitive set of the kinetic endpoints determined in the study.

Soil		Soil properties		Incubation conditions	Selected best-fit model	Evaluation of the fit		Kinetic parameters		Kinetic endpoints	
Soil name	Soil type (USDA)	OC [%]	pH ¹⁾			χ^2 error	Visual fit ²⁾	Par.	Value	DT ₅₀ [days]	DT ₉₀ [days]
<i>Laacherhof AXXa</i>	Loamy sand	1.7	6.2	19.7°C/ 55% MWHC	SFO	3.373	G	k	1.607 E-2	43.14	143.3
<i>Dollendorf II</i>	Loam	4.6	7.0	19.7°C/ 55% MWHC	SFO	3.042	G	k	2.975 E-2	23.30	77.41
<i>Hoefchen Am Hohenseh 4a;</i>	Silt loam	2.0	6.1	19.7°C/ 55% MWHC	SFO	3.578	G	k	1.581 E-2	43.84	145.6
<i>Wurmwiese</i>	Sandy loam	1.8	5.0	19.7°C/ 55% MWHC	SFO	3.317	G	k	7.211 E-3	96.13	319.3

Footnotes to the table:

1) Measured in 0.01M CaCl₂.

2) The abbreviations used to describe the visual fit: G. – good, A. – acceptable, P. – poor;

Study 16: Ströch K., Junge T., (2013): „FOE methylsulfone: Degradation in Four Aerobic Soils.”; Bayer CropScience AG, BCS-D-EnSa-Testing, 40789 Monheim, Germany; unpublished Study Report No. EnSa-13-0617; 2013. 10. 24; study reference number: M-467858-01-1;

Guidelines: The study was declared to be performed in line with the provisions of the OECD Guideline for the Testing of Chemicals No. 307 – Aerobic and Anaerobic Transformation in Soil. The Applicant declared that no deviations from that Guideline were found. Additionally, as the data obtained in the study were kinetically evaluated and the results presented in the study report, it was declared that the following Guideline was used:

- FOCUS (2006): “Guidance Document on Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration.” Report of the FOCUS Work Group on Degradation Kinetics, EC Document Reference SANCO/10058/2005 version 2.0, 434 pp.;

In this case also no deviations from the Guideline referred to were stated.

GLP: Yes;

RMS comments: This is a new study submitted specifically for purpose of this assessment. It was verified by the RMS and found acceptable. No deviations from the declared Guidelines were stated. The study is summarised below.

Summary:

The aim of the study was to determine the kinetic degradation rate of FOE Methylsulfone in aerobic soil under laboratory conditions. The experiment was performed on four test soils taken from the agriculturally used areas, representing different geographical origin and different soil properties, in line with the requirement of the relevant Guideline. The characteristic of the test soils is provided below in the table B.8.1.1.2.1.1_CA-224.

Table B.8.1.2.1.1.CA-224: The characteristic of soils used in the study.

Parameter		Soil			
		<i>Hanscheider Hof</i>	<i>Frankenforst</i>	<i>LUFA 2.3</i>	<i>LUFA 6S</i>
Soil origin		Burscheid/ North Rhine-Westphalia/ Germany	Vinxel/ North Rhine-Westphalia/ Germany	Offenbach/ Rheinland-Palatinate/ Germany	Siebelingen/ Rheinland-Palatinate/ Germany
Soil type (USDA)		Loam	Silt loam	Sandy loam	Clay
Particle size distribution	Sand [%]	42	30	63	35
	Silt [%]	45	51	27	23
	Clay [%]	13	19	10	42
pH value	in 0.01M CaCl ₂ (1:2)	5.6	6.8	6.8	7.0
	in H ₂ O (1:1)	5.8	7.0	7.1	7.2
	in 1M KCl (1:1)	5.3	6.3	6.7	6.6
Organic Carbon content (OC) [%]		2.8	1.8	1.1	1.9
Organic Matter content (OM) [%]¹⁾		4.8	3.1	1.9	3.3
Cation Exchange Capacity – CEC [mEq/100g]		10.8	15.4	8.9	21.5
Water holding capacity	MWHC [g H ₂ O/ 100 g soil d. w.]	64.4	56.7	39.3	48.3
	at pF 2.0 (0.1 bar) [%]	30.1	30.5	17.8	32.8
Soil bulk density (disturbed) [g/cm³]		1.04	1.15	1.28	1.22
Soil biomass [mg microbial C/ kg soil d. w.]²⁾	<i>DAT-0</i>	BIO- ⁴⁾	764	1055	269
		BIO- ⁴⁾	659	827	270
	<i>DAT-59</i>	BIO- ⁴⁾	679 ⁶⁾	627	276
		BIO+ ⁵⁾	679 ⁶⁾	627	276
	<i>DAT-120</i>	BIO- ⁴⁾	621	790	268
		BIO+ ⁵⁾	575	761	245
Soil biomass [% OC]³⁾	<i>DAT-0</i>	BIO- ⁴⁾	2.73	5.86	2.44
		BIO- ⁴⁾	2.35	4.59	2.45
	<i>DAT-59</i>	BIO- ⁴⁾	2.43	3.48	2.51
		BIO+ ⁵⁾	2.43	3.48	2.51
	<i>DAT-120</i>	BIO- ⁴⁾	2.22	4.39	2.44
		BIO+ ⁵⁾	2.05	4.23	2.23

Footnotes to the table:

- 1) Value calculated from experimentally determined OC content, using the following equation: OM = 1.724 OC;
- 2) Determined using the SIR method developed by Anderson & Domsch [1978];
- 3) Values recalculated by the RMS using the OC content reported in the table for each test soil;
- 4) Determined in samples not treated with blank application solution – 0.4 mL of 1:1 CH₃OH/H₂O; instead 0.2 mL of distilled water was added;
- 5) Determined in samples treated with blank application solution – 0.4 mL of 1:1 CH₃OH/H₂O;
- 6) Due to deviation during measurement that sample was reanalysed on DAT 63.

The test soils were sampled shortly before being used (19 or 22 days before the experiment began) with shovel from 0-20 cm layer of grassland plot. No Plant Protection Products were used on the sampling field for 5 years preceding sampling. The samples of the test soils were transported to the test facility in plastic bags. There they were sieved through 2-mm sieve and stored in the darkness at either $T < 8^{\circ}\text{C}$ or $T = 20^{\circ}\text{C}$ until being used. The whole soil sampling-and-handling procedure was declared to be performed in accordance with ISO 10381-6.

The experiment was performed using 300-mL Erlenmeyer flasks into which 100-g (d. w.) portions of sieved test soils were weighed. Next, the soil moisture of each sample was adjusted to $55 \pm 5\%$ MWHC by addition of the appropriate amount of deionised water. So prepared incubation flask were then capped with PU plugs to allow free exchange of air. The example incubation vessel is presented below on figure B.8.1.1.2.1.1._CA-114. After adjustment of the soil moisture the incubation vessels were pre-conditioned for 3 days in the dark, in a temperature-controlled walk-in climatic chamber at $T = 20 \pm 2^{\circ}\text{C}$, until being treated with the test compound. The number of incubation vessels prepared for each test soils was such to grant at least to have duplicate treated samples at each sampling point and those for the determination of soil biomass in soil samples not treated and treated with blank application solution.

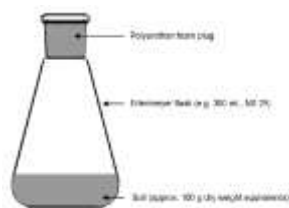


Figure B.8.1.1.2.1.1._CA-114: The example incubation vessel (copied from the study report).

The test compound was not radiolabelled FOE Methylsulfone, having the chemical purity of 97.2%. Its structural formula is shown below on figure B.8.1.1.2.1.1._CA-115.

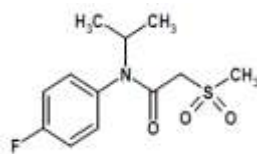


Figure B.8.1.1.2.1.1._CA-115: The structural formula of the test compound used in the experiment (copied from the study report).

It was delivered as a solid sample, in form of a light-yellow powder. The whole delivered amount of the test compound was used to prepare first a **Stock solution** and then **Application solutions**.

The **Stock solution** was prepared by dissolving the whole delivered sample of FOE Methylsulfone in 1.0 mL of CH_3CN , followed by 10-minutes lasting sonication, to obtain a solution having a nominal concentration 9.7 mg FOE Methylsulfone/mL. The so prepared **Stock solution**, labelled **TM108_SS**, was stored in the darkness at $T \leq -18^{\circ}\text{C}$ until being used.

The **Stock solution TM108_SS** was subsequently used to prepare the **Application solution of Test Item at Application Rate Level**, labelled **TM108_AS_AR**, further called **Application solution TM 108_AS_AR**. The **Application solution TM 108_AS_AR** was in turn used to prepare the **Application solution of Test Item at LOQ Level**, labelled **TM108_AS_LOQ**, further called **Application solution TM 108_AS_LOQ**.

The **Application solution TM 108_AS_AR** was used to treat degradation samples and method validation samples, and to create the calibration curve used in quantitative HPLC-MS/MS analysis. The **Application solution TM 108_AS_LOQ** was used for treatment of concurrent recovery samples at LOQ and for method validation.

The **Application solution TM 108_AS_AR** was prepared by transferring 0.205 mL of the **Stock solution TM108_SS** into 100-mL volumetric flask and evaporating it to dryness under the constant gentle stream of N_2 . The residue was redissolved in appropriate amount of $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ 1:1 (v/v) solution and sonicated for 10 minutes. The obtained solution had a nominal concentration 19.9 $\mu\text{g}/\text{mL}$. The identity of the test compound in so prepared solution was conformed by HPLC-MS/MS. The **Application solution TM 108_AS_AR** was stored in the dark at $T \leq 8^{\circ}\text{C}$.

The **Application solution TM 108_AS_LOQ** was prepared from **Application solution TM 108_AS_AR** by diluting the latter. That was done in the following way: 2.5 mL of the **Application solution TM 108_AS_AR** was transferred to the 50-mL volumetric flask, brought to volume with the adequate amount of CH₃OH/H₂O 1:1 (v/v) solution and sonicated for 10 minutes. The obtained solution had a nominal concentration 1.0 µg/mL. That solution was also stored in the dark at $T \leq 8^{\circ}\text{C}$.

Additionally the stable-labelled test compound was used in the experiment. The labelling was performed in isopropyl group and consisted on replacing ¹H (*protium*) atoms with ²H (*deuterium*, marked with symbol D) atoms. Its structural formula is presented below on figure B.8.1.1.2.1.1._CA-116. The compound's chemical purity was > 98%. It was used as an internal standard in quantitative analysis of FOE Methylsulfone performed using HPLC-MS/MS method.

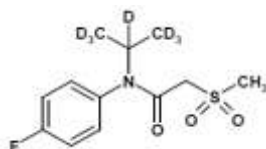


Figure B.8.1.1.2.1.1._CA-116: The structural formula of the deuterised test compound (internal standard) used in the experiment (copied from the study report).

It was delivered as a solid sample, in form of a light-yellow powder. The whole delivered amount of the test compound was used to prepare first a **Stock solution** and then a set of **Internal standard solutions**.

The **Stock solution** was prepared by dissolving the whole delivered sample of ²H-FOE Methylsulfone in 5.0 mL of CH₃CN and sonicating it for 10 minutes, to obtain a solution having a nominal concentration 0.980 mg ²H-FOE Methylsulfone/mL. The so prepared **Stock solution**, labelled **TM108IS_SS**, was stored in the dark at $T \leq -18^{\circ}\text{C}$ until being used.

The prepared from **TM108IS_SS** solution **Internal standard solutions** were following:

- **Internal standard solution TM108IS_AR**, prepared by transferring 0.406 mL of the **Stock solution TM108IS_SS** into 50-mL volumetric flask, bringing it to the volume with the appropriate amount of CH₃CN/H₂O 4:1 (v/v) and sonicating it for 10 minutes; the nominal concentration of so prepared solution was 0.0079 mg/mL;
- **Internal standard solution TM108IS_D1**, prepared by transferring 0.041 mL of the **Stock solution TM108IS_SS** into 20-mL volumetric flask, bringing it to the volume with the appropriate amount of CH₃CN/H₂O 4:1 (v/v) and sonicating it for 10 minutes; the nominal concentration of so prepared solution was 0.0020 mg/mL;
- **Internal standard solution TM108IS_D2**, prepared by transferring 5 mL of the **Internal standard solution TM108IS_D1** into 20-mL volumetric flask, bringing it to the volume with the appropriate amount of CH₃CN/H₂O 4:1 (v/v) and sonicating it for 10 minutes; the nominal concentration of so prepared solution was 0.0005 mg/mL;

All listed above **Internal standard solutions** were stored in the darkness at $T \leq -18^{\circ}\text{C}$. **Internal standard solution TM108IS_AR** was added to soil extracts and was used in the verification of application rate and homogeneity of application. The **Internal standard solution TM108IS_D2** was added to the standard solutions used to construct the calibration curve.

The **Application solution TM 108_AS_AR** was used to treat degradation samples. To do that its 0.4-mL aliquots were applied dropwise onto soil surface in each incubation vessel to obtain the target application dose of 7.9 µg FOE Methylsulfone/100 g soil (d. w.). That application dose – equal to 0.079 mg/kg soil, was determined using the following assumptions:

- field application rate of Flufenacet (parent compound, precursor of FOE Methylsulfone): 600 g/ha;
- maximum occurrence of FOE Methylsulfone in aerobic soil (determined in the laboratory studies): 6.6%;
- molar weight of Flufenacet $M = 363.3 \text{ g/mol}$;
- molar weight of FOE Methylsulfone $M' = 273.3 \text{ g/mol}$;
- soil bulk density: 1.5 g/cm^3 ;
- thickness of the soil layer: 2.5 cm.

RMS analysing the calculations noticed that the assumed soil layer was $\frac{1}{2}$ of that routinely used to calculate field application rate (in [g/ha]) from that expressed in mg/kg soil. Therefore the RMS back calculated the would-be field application rate for FOE Methylsulfone using the standard assumptions:

- soil bulk density: 1.5 g/cm³;
- thickness of the soil layer: 5 cm.

The so calculated would-be field application rate **A = 59.55 g FOE Methylsulfone/ha**.

Using the measured soil bulk density of each test soil used in the experiment that value would be:

- for Hanscheider Hof soil: **A = 41.08 g/ha**;
- for Frankforst soil: **A = 45.43 g/ha**;
- for LUFA 2.3 soil: **A = 50.56 g/ha**;
- for LUFA 6S soil: **A = 48.19 g/ha**

The verification of application rate and homogeneity of application was performed using **Application solution TM 108_AS_AR**, at the beginning of application procedure and after treatment of each test soil. That was done by transferring of 0.4-mL portions of the application solution into 250-mL volumetric flasks, to which 0.1-mL portions of the **Internal standard solution TM108IS_AR** were added next. The solutions were then brought to volume with the appropriate amount of CH₃CN/H₂O 4:1 (v/v) and mixed thoroughly.

The same **Application solution** and the **Application solution TM 108_AS_LOQ** were used to treat the Concurrent Recovery Samples. The dosing of each **Application solution** was the same as for degradation samples – 0.4 mL/100 g soil. That resulted in fortification level of 0.079 mg/kg soil for samples treated with **Application solution TM 108_AS_AR** and 0.395 µg/100 g/soil (0.00395 mg/kg soil) – 5% of the nominal application rate for samples treated with **Application solution TM 109_AS_LOQ**. The samples were freshly prepared at each sampling point using LUFA 2.3 soil.

The verification of application rate and homogeneity of application was performed in the same manner as for degradation samples.

Immediately after treatment the incubation vessels designated as degradation samples were closed with PU plugs to grant free access of air, placed in the darkness in temperature-controlled walk-in climatic chamber and incubated for up to 120 days under aerobic conditions at $T = 20 \pm 2^{\circ}\text{C}$. Duplicate samples were removed from incubation chamber at following time-points (DAT stands for “Days After Treatment”): DAT 0, DAT 3, DAT 7, DAT 14, DAT 30, DAT 59, DAT 93 and DAT 120.

The soil moisture content in incubation vessels was controlled by weighing them at designated time points: DAT 0, DAT 3, DAT 7, DAT 9, DAT 14, DAT 22, DAT 30, DAT 37, DAT 44, DAT 59, DAT 71, DAT 93, DAT 99 and DAT 120. Soil moisture in the test vessels was adjusted to the designated level, by addition of appropriate amount of deionised water, at following time-points: DAT 3, DAT 9, DAT 22, DAT 37, DAT 44, DAT 59, DAT 71, DAT 93 and DAT 99.

The samples for the determination of soil biomass were set alongside the degradation samples. The soil biomass was determined in pre-conditioned test soil samples sampled on DAT 0 (beginning of the incubation period), DAT 59 (middle of the incubation period) and DAT 120 (end of incubation period). The experiment was performed in two variants:

- “BIO-” samples, not treated with blank application solution (instead 0.2 mL of distilled water was added to each test vessel) ; these samples were taken for the analysis on DAT 0, DAT 59 and DAT 120;
- “BIO+” samples, treated with 0.4 mL of blank application solution (CH₃OH/H₂O 1:1 v/v); these samples were taken for the analysis on DAT 59 and DAT 120.

Samples removed from the incubation chamber were processed and analysed immediately after sampling. That was done for the entire portions of the test soil recovered at each sampling point, using the procedure presented below on figure B.8.1.1.2.1.1._CA-117. The same procedure was applied to Concurrent Recovery Samples.

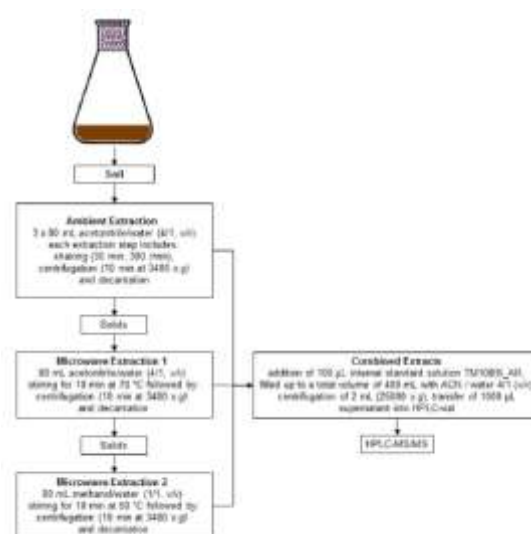


Figure B.8.1.1.2.1.1._CA-117: The sample-processing procedure used in the experiment (scheme copied from the study report).

The quantitative and qualitative analysis of combined soil extracts and other liquid samples was performed by means of HPLC-MS/MS. The analysis was performed using Agilent HP1200 chromatography workstation equipped with Finnigan TSQ Vantage (Thermo Electron Corporation, San Jose, CA, USA) MS detector. The chromatographic separation was done on Nucleodur Gravity C8 50*2 mm * 5 µm chromatographic column working in a gradient mode. The column was maintained at constant temperature $T = 40^{\circ}\text{C}$. The gradient elution programme is presented below in the table B.8.1.1.2.1.1._CA-225.

Table B.8.1.1.2.1.1._CA-225: The HPLC gradient modes used in the study.

Time [min]	Solvent ratio	
	<i>Solvent A – Water + 0.1% HCOOH</i>	<i>Solvent B – Acetonitrile + 0.1% HCOOH</i>
0	80	20
1	80	20
2	60	40
5	40	60
6	5	95

The elution lasted for 6 minutes and the flow rate of the mobile phase was 0.3 mL/min.

The identification of the test compound was performed by means of MS analysis using the following MS signals:

- for non-labelled test item: $m/z = 274.1$ as parent ion and $m/z = 232.1$ as product ion (quantifier);
- for ^2H -labelled internal standard: $m/z = 281.1$ as parent ion and $m/z = 233.1$ as product ion (quantifier).

Additional identification parameter for FOE Methylsulfone was the retention time $R_t = 3.5$ min. (approx.).

The quantitative analysis was performed using the external calibration curve constructed using the calibration solutions having concentration 1% SAR (0.198 µg FOE Methylsulfone/L), 5% SAR (0.988 µg FOE Methylsulfone/L), 10% SAR (1.975 µg FOE Methylsulfone/L), 50% SAR (9.875 µg FOE Methylsulfone/L), 100% SAR (19.750 µg FOE Methylsulfone/L) and 150% SAR (29.625 µg FOE Methylsulfone/L), where SAR stands for Standard Application Rate, defined as 7.9 µg test compound in 400 mL of extract. The calibration curve was constructed using $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ 4:1 (v/v) as a solvent.

The procedure of the preparation of calibration curve is described below.

Firstly the **Standard solution TM108_SS_D1** was prepared by transferring 2 mL of the **Application solution TM 108_AS_AR** to 20-mL volumetric flask, filling it to the volume with the appropriate amount of $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ 4:1 (v/v) and sonicating for 10 minutes. The nominal concentration of so obtained solution was 2.0 µg/mL. That solution was used to prepare next dilute – **Standard solution TM108_SS_D2**. That was done by

transferring 2 mL of the **Standard solution TM108_SS_D1** to 20-mL volumetric flask, filling it to the volume with the appropriate amount of CH₃CN/H₂O 4:1 (v/v) and sonicating for 10 minutes. The nominal concentration of so obtained solution was 0.2 µg/mL. These two **Standard solutions** were stored in the dark at T ≤ -18°C until being used.

The solutions used to build calibration curve were freshly prepare on the day of measurements in the following way:

- 0.375 mL of the **Standard solution TM108_SS_D1** and 0.1 mL of the **Internal standard solution TM108IS_D2** were transferred into 25-mL volumetric flask, the resulting solution was brought up to the volume with the appropriate amount of CH₃CN/H₂O 4:1 (v/v) and sonicated for 10 minutes to obtain 150% SAR calibration solution,
- 0.25 mL of the **Standard solution TM108_SS_D1** and 0.1 mL of the **Internal standard solution TM108IS_D2** were transferred into 25-mL volumetric flask, the resulting solution was brought up to the volume with the appropriate amount of CH₃CN/H₂O 4:1 (v/v) and sonicated for 10 minutes to obtain 100% SAR calibration solution,
- 0.125 mL of the **Standard solution TM108_SS_D1** and 0.1 mL of the **Internal standard solution TM108IS_D2** were transferred into 25-mL volumetric flask, the resulting solution was brought up to the volume with the appropriate amount of CH₃CN/H₂O 4:1 (v/v) and sonicated for 10 minutes to obtain 50% SAR calibration solution,
- 0.25 mL of the **Standard solution TM108_SS_D2** and 0.1 mL of the **Internal standard solution TM108IS_D2** were transferred into 25-mL volumetric flask, the resulting solution was brought up to the volume with the appropriate amount of CH₃CN/H₂O 4:1 (v/v) and sonicated for 10 minutes to obtain 10% SAR calibration solution
- 0.125 mL of the **Standard solution TM108_SS_D2** and 0.1 mL of the **Internal standard solution TM108IS_D2** were transferred into 25-mL volumetric flask, the resulting solution was brought up to the volume with the appropriate amount of CH₃CN/H₂O 1:1 (v/v) and sonicated for 10 minutes to obtain 5% SAR calibration solution,
- 0.025 mL of the **Standard solution TM108_SS_D2** and 0.1 mL of the **Internal standard solution TM108IS_D2** were transferred into 25-mL volumetric flask, the resulting solution was brought up to the volume with the appropriate amount of CH₃CN/H₂O 1:1 (v/v) and sonicated for 10 minutes to obtain 1% SAR calibration solution.

The obtained results – concentrations of FOE Methylsulfone in each test soil at each time point, were subjected to the kinetic analysis in order to identify the best-fit kinetic model and determine persistence and modelling kinetic endpoints for FOE Methylsulfone in each test soil.

The kinetic analysis was performed in line with the recommendations of the FOCUS Kinetics Guidance Document [FOCUS; 2006], using KinGUI 2 modelling tool. It followed the procedure used in several already summarised studies, in particular **Study 4** and **Study 5**. Two kinetic models were used in the assessment – SFO and FOMC. The obtained fits were evaluated using the same principles as presented in the summaries of **Studies 2 – 8**.

The results of the study are presented below.

Results and their discussion:

The results of the determination of soil physicochemical properties and soil microbial activity in each test soil are presented in the table B.8.1.1.2.1.1._CA-224 at the beginning of this summary. On their basis it can be stated that the soils were appropriately selected, in line with the recommendations of OECD 307 Guideline, and were biologically viable throughout the experiment.

The results of the monitoring of the incubation temperature are presented below on figure B.8.1.1.2.1.1._CA-118. In the study report it was stated that the main incubation temperature was 19.9°C and it ranged from 19.4°C to 20.7°C.

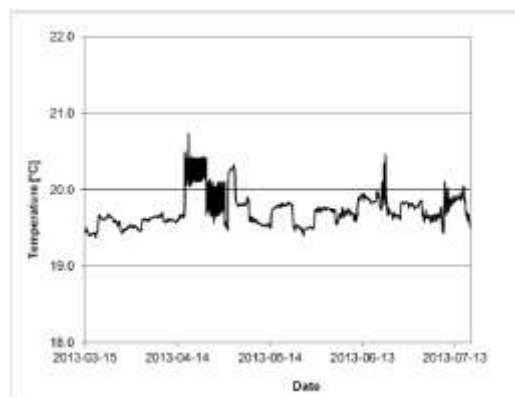


Figure B.8.1.2.1.1_CA-118: The temperature recorded during soil pre-conditioning and samples incubation period (copied from the study report).

The results of the monitoring of soil moisture during the experiment are presented below, in the table B.8.1.2.1.1_CA-226. On their basis it may be stated that this parameter was maintained on the assumed level during the whole experiment.

Table B.8.1.2.1.1_CA-226: The results of the determination of soil moisture content.

Test soil	Soil moisture content [g H ₂ O/100 g soil]			Soil moisture during incubation [% MWHC]		
	MWHC	55% MWHC	Actual – in sieved soil	mean	min.	max.
Hanscheider Hof	64.4	35.4	27.6	55.1	52.4	58.0
Frankenforst	56.7	31.2	17.1	54.7	51.4	58.1
LUFA 2.3	39.3	21.6	8.0	53.6	50.2	58.2
LUFA 6S	48.3	26.6	8.5	54.0	50.2	58.1

The results of the determination of application rate and the homogeneity of application for DAT 0 – DAT 120 samples were following:

- the application rate at the beginning of the process was determined to be 78.1 µg/kg;
- the application rate at the end of the 1st series was determined to be 80.7 µg/kg;
- the application rate at the end of the 2nd series was determined to be 77.2 µg/kg;
- the application rate at the end of the 3rd series was determined to be 78.3 µg/kg;
- the application rate at the end of the 4th series was determined to be 78.8 µg/kg;
- the mean application rate was determined to be 78.6 µg/kg with RSD = 1.5%.

On that basis it was stated that the application was homogenous and in good agreement with assumed theoretical application rate.

The LOQ – limit of quantification, was defined as 5% of nominal study application rate – 4.0 µg/kg soil. The corresponding LOD was set to $\frac{1}{5}$ LOQ – 1% of the nominal study application rate, and was equal to 0.8 µg/kg soil. The values were determined experimentally by examining the linearity of the response of MS/MS detector to the calibration curve. The numerical results of this examination presented below in the table B.8.1.2.1.1_CA-227 and in the graphical form on figure B.8.1.2.1.1_CA-119. They conform the good linearity of the detector's response and hence the correctness of the determined LOQ and LOD values.

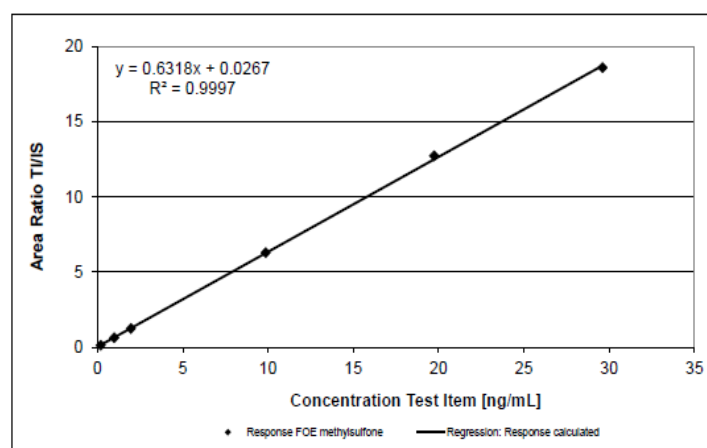
Table B.8.1.1.2.1.1._CA-227: The numerical results of the determination of the linearity of the response of MS/MS detector.

Calibration sample No.	Nominal concentration		Peak area ratio TI ¹⁾ /IS ²⁾				RSD [%]
	[% AA]	[ng/mL]	Replicate 1	Replicate 2	Replicate 3	Mean	
1	1	0.198	0.1193	0.1123	0.1262	0.1193	4.8
2	5	0.988	0.6147	0.6338	0.6223	0.6236	1.3
3	10	1.975	1.2156	1.3208	1.1915	1.2426	4.5
4	50	9.875	6.1497	6.5333	6.1817	6.2882	2.8
5	100	19.750	12.5513	12.7374	12.8824	12.7237	1.1
6	150	29.625	18.0628	19.3203	18.3995	18.5942	2.9

Footnotes to the table:

1) TI – Test Item;

2) IS – Internal standard; its amount is always 10% of the nominal study's application rate.

**Table B.8.1.1.2.1.1._CA-119:** The graphical results of the determination of the linearity of the response of MS/MS detector – calibration curve (copied from the study report).

The determination of the accuracy and precision of the method, assessed on the basis of the recovery rates at LOQ level (5% SAR) and application level (100% SAR), looked as follows:

- for Hanscheider Hof soil mean recovery at LOQ and application levels was 98.8% (91.4 – 103.5%) with RSD = 3.5%;
- for Frankenforst soil mean recovery at LOQ and application levels was 97.3% (93.0 – 100.8%) with RSD = 2.1%;
- for LUFA 2.3 soil mean recovery at LOQ and application levels was 102.3% (96.9 – 106.8%) with RSD = 2.7%;
- for LUFA 6S soil mean recovery at LOQ and application levels was 101.2% (95.7 – 107.0%) with RSD = 3.6%;
- the mean recovery at LOQ and application levels was 99.9% (91.4 – 107.0%) with RSD = 3.5%.

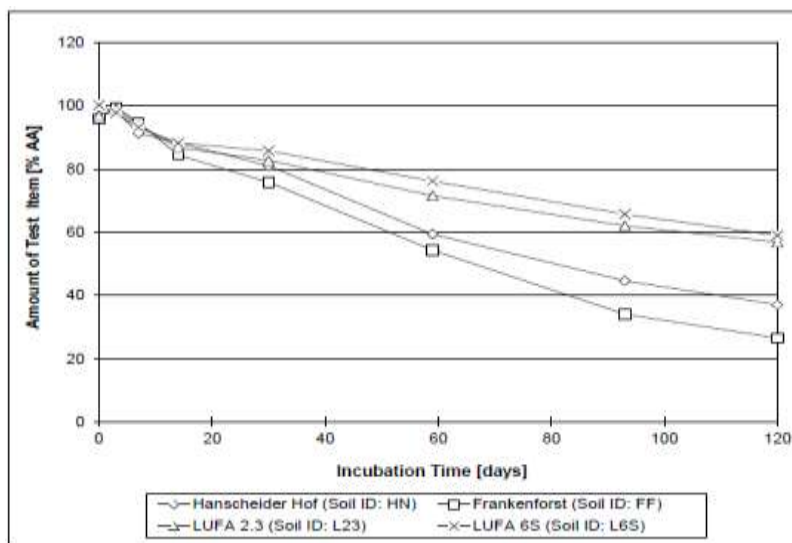
The results of the experiment – concentrations of FOE Methylsulfone in soil in function of time, are presented below in the table B.8.1.1.2.1.1._CA-228. For each test soil the concentrations of the test compound are reported as % of applied amount – [% AA] and in [µg/kg soil]. The values expressed as [%AA] were calculated using the following assumptions:

- for all samples the application rate was determined to be 7.9 µg/ test system, corresponding to 79 µg/kg soil, and that value was set to 100% AA (Applied Amount);

The graphic presentation of the results is given on figure B.8.1.1.2.1.1._CA-120.

Table B.8.1.1.2.1.1._CA-228: Concentration of FOE Sulfonic acid in tets soils in function of time.

Results obtained in Hanscheider Hof soil							Results obtained in Frankenforst soil						
DAT [days]	Concentration of FOE Methylsulfone						DAT [days]	Concentration of FOE Methylsulfone					
	[% AA]			[µg/kg soil]				[% AA]			[µg/kg soil]		
	Rep. 1	Rep. 2	Mean	Rep. 1	Rep. 2	Mean		Rep. 1	Rep. 2	Mean	Rep. 1	Rep. 2	Mean
0	94.5	98.2	96.8	75.0	77.2	76.1	0	98.8	92.9	95.8	77.7	73.1	75.3
3	101.9	95.0	98.3	80.1	74.6	77.3	3	100.0	99.1	99.5	78.6	77.9	78.2
7	91.9	90.6	91.3	72.2	71.2	71.7	7	95.7	93.6	94.6	75.2	73.5	74.4
14	88.9	87.6	88.3	69.9	68.9	69.4	14	84.2	84.6	84.4	66.2	66.5	66.3
30	80.7	81.2	81.0	63.5	63.8	63.6	30	75.2	76.4	75.8	59.1	60.0	59.6
59	59.3	59.4	59.4	46.6	46.7	46.6	59	52.7	55.9	54.3	41.4	43.9	42.7
93	43.3	45.5	44.6	34.1	35.7	34.9	93	33.4	34.7	34.1	26.3	27.3	26.8
120	34.4	37.1	37.0	27.0	29.2	28.1	120	26.3	26.8	26.6	20.7	21.0	20.9
Results obtained in LUFA 2.3 soil							Results obtained in LUFA 6S soil						
DAT [days]	Concentration of FOE Methylsulfone						DAT [days]	Concentration of FOE Methylsulfone					
	[% AA]			[µg/kg soil]				[% AA]			[µg/kg soil]		
	Rep. 1	Rep. 2	Mean	Rep. 1	Rep. 2	Mean		Rep. 1	Rep. 2	Mean	Rep. 1	Rep. 2	Mean
0	95.6	97.9	96.7	75.1	76.9	76.0	0	100.7	99.6	100.2	79.1	78.3	78.7
3	99.1	99.0	99.0	77.9	77.8	77.8	3	95.8	99.6	97.7	75.3	78.2	76.8
7	94.2	93.1	93.7	74.1	73.2	73.6	7	92.5	93.7	93.1	72.7	73.6	73.2
14	85.6	87.8	86.7	67.3	69.0	68.2	14	87.8	88.6	88.2	69.0	69.6	69.3
30	84.9	80.6	82.7	66.7	63.4	65.0	30	86.5	84.9	85.7	68.0	66.7	67.4
59	72.6	70.4	71.5	57.0	55.4	56.2	59	74.9	77.3	76.1	58.9	60.8	59.8
93	62.0	61.9	62.0	48.8	48.7	48.7	93	66.4	65.0	65.7	52.2	51.1	51.6
120	56.8	56.9	56.9	44.7	44.7	44.7	120	58.9	59.0	58.9	46.3	46.3	46.3

**Figure B.8.1.1.2.1.1._CA-120:** The graphic presentation of the obtained results (copied from the study report).

The data presented in the table B.8.1.1.2.1.1._CA-228 were subjected to the kinetic analysis aimed on the determination of the best kinetic fit and derivation of the kinetic endpoints representing persistence of the test compound and suitable for modelling. For that purpose the values obtained for replicates, expressed as [%AA], were used. The values were inserted to the model as they are presented in the table above. The results of the kinetic analysis are presented below, separately for each test soil. The results are provided only for two kinetic models – SFO and FOMC. That was due to the fact that the kinetic evaluation using FOMC model was demonstrated to be statistically not reliable. Additionally the χ^2 error was demonstrated to be not significantly different between SFO and FOMC, therefore it was decided not to test DFOP model.

- 1) The results of the kinetic analysis of the data obtained for FOE Methylsulfone in Hanscheider Hof soil.

The results of the kinetic analysis performed by the Applicant are presented below, in graphical form on figure B.8.1.1.2.1.1._CA-121 and in numerical form in the table B.8.1.1.2.1.1._CA-229. Additionally the table B.8.1.1.2.1.1._CA-230 provides the kinetic endpoints obtained with each of the kinetic models tested.

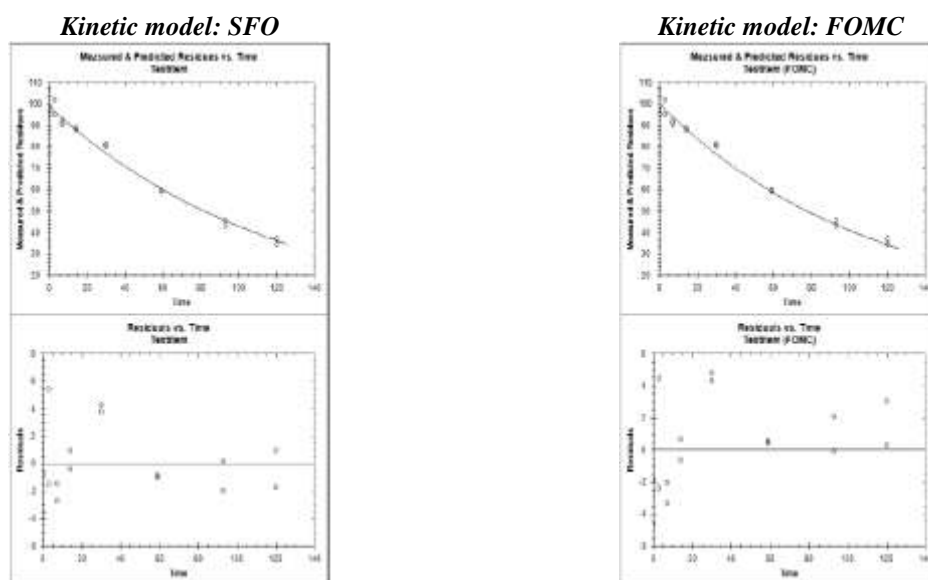


Figure B.8.1.1.2.1.1._CA-121: The graphical results of the kinetic analysis (copied from the study report).

Table B.8.1.1.2.1.1._CA-229: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	Visual assessment ¹⁾
				Lower	Upper			
SFO	M ₀	98.97	1.013	96.98	100.956	< 2 E-16	2.106	Good fit
	k	8.399 E-3	2.989 E-4	7.813 E-3	0.009	5.15 E-14		
FOMC	M ₀	100.053	1.135	97.830	102.3	< 2 E-16	2.666	Good fit
	α	293.917	271.037	-237.306	825.1	0.149		
	β	32692.219	30199.389	-26497.495	91881.9	0.149		

Footnotes to the table:

- 1) Visual assessment of the kinetic curve as proposed by the Applicant.

Table B.8.1.1.2.1.1._CA-230: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested	
		SFO	FOMC
FOE Methylsulfone	DT ₅₀ [days]	82.53	77.19
	DT ₉₀ [days]	274.14	257.12

Conclusion:

Both models returned visually and statistically good fits. In terms of χ^2 error better fit was obtained using SFO model, although it shall be pointed out that the value of that parameter was very similar for both models tested. At the same time only SFO model returned fully reliable kinetic parameters. In case of FOMC the calculated α and β were not reliable because CI for them passed through zero. Therefore the Applicant stated that SFO model shall be considered as returning the best fit for FOE Methylsulfone in Hanscheider Hof soil and hence appropriate to derive persistence and modelling endpoints for that compound in that test soil. RMS accepted that proposal.

- 2) The results of the kinetic analysis of the data obtained for FOE Methylsulfone in Frankenforst soil.

The results of the kinetic analysis performed by the Applicant are presented below, in graphical form on figure B.8.1.1.2.1.1._CA-122 and in numerical form in the table B.8.1.1.2.1.1._CA-231. Additionally the table B.8.1.1.2.1.1._CA-232 provides the kinetic endpoints obtained with each of the kinetic models tested.

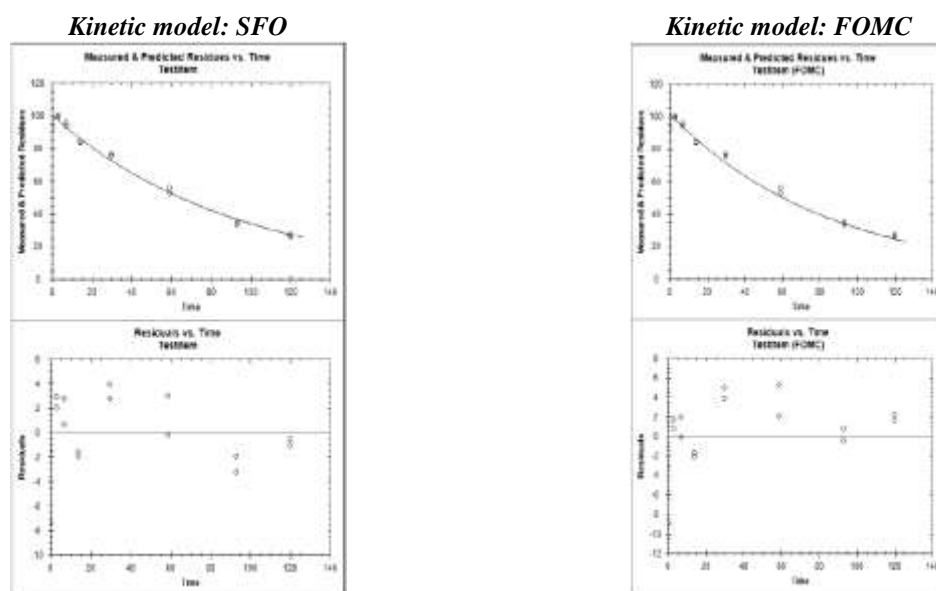


Figure B.8.1.1.2.1.1._CA-122: The graphical results of the kinetic analysis (copied from the study report).

Table B.8.1.1.2.1.1._CA-231: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	Visual assessment ¹⁾
				Lower	Upper			
SFO	M ₀	100.3	1.207	97.92	102.651	< 2 E-16	2.878	Good fit
	k	0.01083	4.096 E-4	0.01003	0.012	1.18 E-13		
FOMC	M ₀	101.821	1.353	99.170	104.5	<2 E-16	3.772	Good fit
	α	493.459	794.8135	-1064.345	2051.3	0.273		
	β	41635.283	67127.354	-89931.913	173202.5	0.273		

Footnotes to the table:

- 1) Visual assessment of the kinetic curve as proposed by the Applicant.

Table B.8.1.1.2.1.1._CA-232: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested	
		SFO	FOMC
FOE Methylsulfone	DT ₅₀ [days]	63.98	58.53
	DT ₉₀ [days]	212.53	194.73

Conclusion:

Both models returned visually and statistically good fits. In terms of χ^2 error better fit was obtained using SFO model, although it shall be pointed out that the value of that parameter was similar for both models tested. At the same time only SFO model returned fully reliable kinetic parameters. In case of FOMC the calculated α and β were not reliable because CI for them passed through zero. Therefore the Applicant stated that SFO model shall be considered as returning the best fit for FOE Methylsulfone in Frankenforst soil and hence appropriate to derive persistence and modelling endpoints for that compound in that test soil. RMS accepted that proposal.

- 3) The results of the kinetic analysis of the data obtained for FOE Methylsulfone in LUFA 2.3 soil.

The results of the kinetic analysis performed by the Applicant are presented below, in graphical form on figure B.8.1.1.2.1.1._CA-123 and in numerical form in the table B.8.1.1.2.1.1._CA-233. Additionally the table B.8.1.1.2.1.1._CA-234 provides the kinetic endpoints obtained with each of the kinetic models tested.

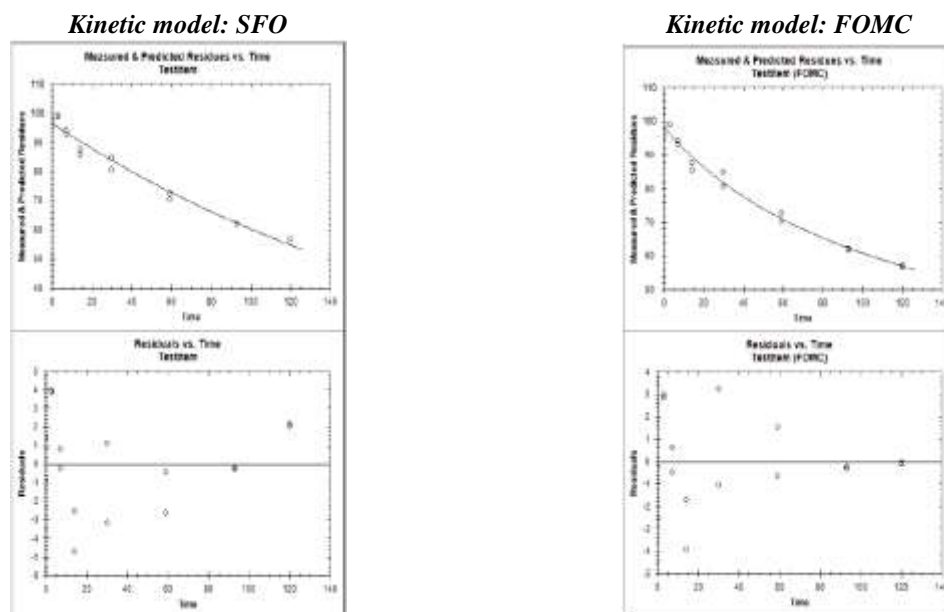


Figure B.8.1.1.2.1.1._CA-123: The graphical results of the kinetic analysis (copied from the study report).

Table B.8.1.1.2.1.1._CA-233: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	Visual assessment ¹⁾
				Lower	Upper			
SFO	M ₀	96.50	0.939	94.66	98.337	< 2 E-16	2.095	Good fit
	k	4.722 E-3	2.241 E-4	4.238 E-3	0.005	2.65 E-12		
FOMC	M ₀	98.154	1.048	96.100	100.208	<2 E-16	1.65	Good fit
	α	0.6659	0.2507	0.1645	1.147	0.0107		
	β	92.6605	49.9191	-5.1792	190.500	0.0431		

Footnotes to the table:

- 1) Visual assessment of the kinetic curve as proposed by the Applicant.

Table B.8.1.1.2.1.1._CA-234: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested	
		SFO	FOMC
FOE Methylsulfone	DT ₅₀ [days]	146.78	173.92
	DT ₉₀ [days]	487.60	3008.1

Conclusion:

Both models returned visually and statistically good fits. In terms of χ^2 error better fit was obtained using FOMC model, although it shall be pointed out that the value of that parameter was very close for both models tested. At the same time only SFO model returned fully reliable kinetic parameters. In case of FOMC the calculated β was not reliable because CI for it passed through zero. Therefore the Applicant stated that SFO model shall be considered as returning the best fit for FOE Methylsulfone in in LUFA 2.3 soil, hence appropriate to derive persistence and modelling endpoints for that compound in that test soil. RMS accepted that proposal.

- 4) The results of the kinetic analysis of the data obtained for FOE Methylsulfone in LUFA 6S soil.

The results of the kinetic analysis performed by the Applicant are presented below, in graphical form on figure B.8.1.1.2.1.1._CA-124 and in numerical form in the table B.8.1.1.2.1.1._CA-235. Additionally the table B.8.1.1.2.1.1._CA-236 provides the kinetic endpoints obtained with each of the kinetic models tested.

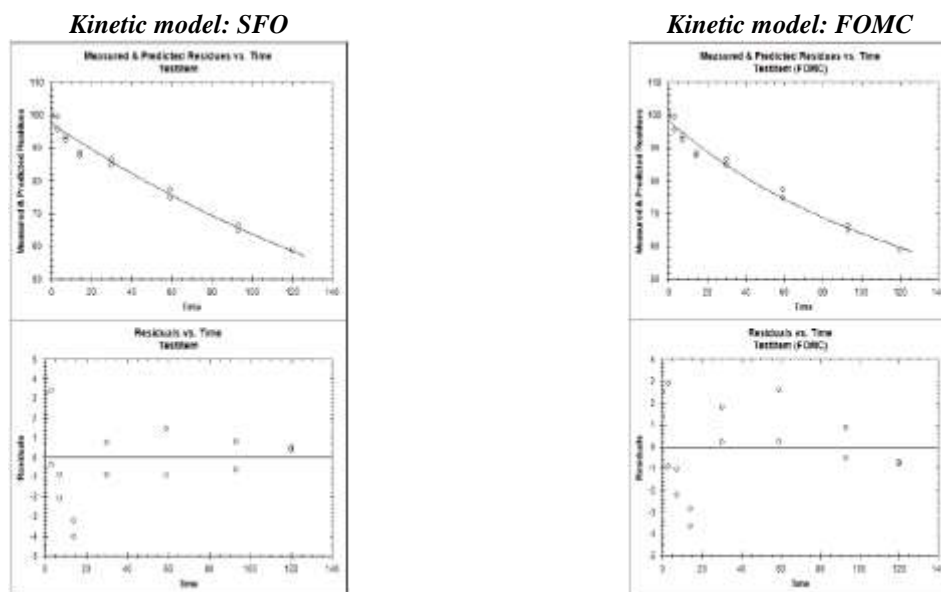


Figure B.8.1.1.2.1.1._CA-124: The graphical results of the kinetic analysis (copied from the study report).

Table B.8.1.1.2.1.1._CA-235: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	Visual assessment ¹⁾
				Lower	Upper			
SFO	M_0	97.41	0.7858	95.872	98.949	< 2 E-16	1.697	Good fit
	k	4.251 E-3	1.796 E-4	3.899 E-3	0.005	5.42 E-13		
FOMC	M_0	98.228	1.099	96.075	100.382	< 2 E-16	1.668	Good fit
	α	1.0587	0.8623	-0.6314	2.749	0.121		
	β	199.5828	199.4171	-191.2675	590.433	0.168		

Footnotes to the table:

- 1) Visual assessment of the kinetic curve as proposed by the Applicant.

Table B.8.1.1.2.1.1._CA-236: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested	
		SFO	FOMC
FOE Methylsulfone	DT ₅₀ [days]	163.06	184.54
	DT ₉₀ [days]	541.68	1557.1

Conclusion:

Both models returned visually and statistically good fits. In terms of χ^2 error better fit was obtained using FOMC model, although it shall be pointed out that the value of that parameter was very close for both models tested. At the same time only SFO model returned fully reliable kinetic parameters. In case of FOMC the calculated α and β were not reliable because CI for them passed through zero. Therefore the Applicant stated that SFO model shall be considered as returning the best fit for FOE Methylsulfone in LUFA 6S soil and hence appropriate to derive persistence and modelling endpoints for that compound in that test soil. RMS accepted that proposal.

Final conclusion of the study:

On the basis of the results of the kinetic analysis presented above was determined the definitive set of the reliable kinetic parameters, presented below in the table B.8.1.1.2.1.1._CA-237.

Table B.8.1.1.2.1.1._CA-237: The definitive set of the kinetic endpoints determined in the study.

Soil		Soil properties		Incubation conditions	Selected best-fit model	Evaluation of the fit		Kinetic parameters		Kinetic endpoints	
Soil name	Soil type (USDA)	OC [%]	pH ¹⁾			χ^2 error	Visual fit ²⁾	Par.	Value	DT ₅₀ [days]	DT ₉₀ [days]
<i>Hanscheider Hof</i>	Loam	2.8	5.6	19.9°C/ 55% MWHC	SFO	2.106	G	<i>k</i>	8.40 E-3	82.53	274.14
<i>Frankenforst</i>	Silt loam	1.8	6.8	19.9°C/ 55% MWHC	SFO	2.878	G	<i>k</i>	0.01083	63.98	212.53
<i>LUFA 2.3</i>	Sandy loam	1.1	6.8	19.9°C/ 55% MWHC	SFO	2.095	G	<i>k</i>	4.72 E-3	146.78	487.60
<i>LUFA 6S</i>	Clay	1.9	7.0	19.9°C/ 55% MWHC	SFO	1.697	G	<i>k</i>	4.25 E-3	163.06	541.68

Footnotes to the table:

1) Measured in 0.01M CaCl₂.

2) The abbreviations used to describe the visual fit: G. – good, A. – acceptable, P. – poor;

Study 17:

Report: Lentz N. R., Bloomberg A. M., (1999): “Rate of Aerobic Soil Degradation for Thiadone (A Metabolite of FOE 5043).”; Ricerca LLC, Department of Environmental and Metabolic Fate, 7528 Auburn Road, Painesville, Ohio 44077, USA (performing laboratory) for Bayer Corporation, Agriculture Division, P. O. Box 4913, Kansas City, MO 64120, USA; Ricerca document No. 7410-0055-EF-001, study No. F3082103 (Bayer); Bayer Report No. 108722; 16 February 1999, amended on 24 March 1999; study reference number: M-009828-01-1;

Guidelines: The study was performed to comply with the following Guidelines:

- US. Environmental Protection Agency Assessment Guidelines, Subdivision N Chemistry: Environmental Fate, Section 162-1

No deviations from the Guidelines were stated.

Several deviations were stated from the study protocol, however none of them indicated as adversely affecting the results or conclusions of the study. The stated protocol deviations were:

- 1) Additional soil samples were analysed for Iowa test soil on DAT 0.25 (6 hours) and on DAT 2 for Indiana and Nebraska test soils;
- 2) Additional analysis of 1N NaOH traps for volatile compounds was performed on DAT 0.25 and DAT 4 for Iowa test soil, on DAT 0.25, DAT 2 and DAT 4 for Indiana test soil, and on DAT 2 and DAT 4 for Nebraska test soil;
- 3) Additional analysis of the carbotraps for VOC was performed on DAT 4 for Iowa and Indiana test soils, and on DAT 3, DAT 7 and DAT 10 for Nebraska test soil;
- 4) Temperature in the incubation chamber was for a short time 22.1⁰C (short period during the morning of one of incubation days).

GLP: Yes;

RMS comments: This is a newly submitted study, the aim of which was to further examine the rate of degradation of FOE Thiadone in aerobic soil. It was evaluated for its compliance with the following guidelines:

- OECD Guideline 307 – Aerobic and Anaerobic transformation in Soil;
- US EPA Guidelines for Pesticide Registration, Subdivision N, Section 162-1 - Aerobic Soil Metabolism (indicated as reference Guideline in the study report).

RMS stated that the study was compliant with the provisions of the Guidelines listed above, therefore it was found acceptable and is summarised below.

Summary:

The aim of the study was to examine the rate of degradation of FOE Thiadone – the major soil metabolite of Flufenacet, in aerobic soils and to identify major degradation products of that process. The experiment was performed on three soils, obtained from maize growing areas in the USA – Janesville in Iowa, Howe in Indiana and Minden in Nebraska. Justifying the selection of the test soils the authors stated that Iowa and Nebraska soils originated from the sites where GW monitoring studies for Flufenacet were carried out, while Indiana soil was used in other experiments examining fate and behaviour of Flufenacet in soil. Their characteristic is provided below in the table B.8.1.1.2.1.1._CA-238. Iowa and Nebraska soils were declared to come from the field not being treated with any pesticide during the period 1995 – 1998. No such information was provided for Indiana soil, but the cross-examination of other experiments with that soil conformed that it originated from the field not being treated with any pesticide during the period 1995 – 1998. After being shipped to the test laboratory, the test soils were air-dried and sieved through 2-m sieve to remove all skeletal elements.

Table B.8.1.1.2.1.1._CA-238: The characteristic of soils used in the study.

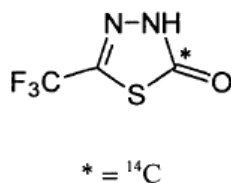
Parameter		Soil		
		<i>Iowa Loamy sand</i>	<i>Indiana sandy loam</i>	<i>Nebraska silt loam</i>
Soil origin		Janesville, Iowa, USA	Howe, Indiana, USA	Minden, Nebraska, USA
Soil type (USDA)		Loamy sand	Sandy loam	Silt loam
Particle size distribution	Sand (50 µm – 2 mm) [%]	79.2	63.6	25.6
	Silt (2 – 50 µm) [%]	12.0	25.6	55.6
	Clay (< 2 µm) [%]	8.8	10.8	18.8
pH value (medium not specified)		7.2	6.5	7.7
Organic carbon content (OC) [%] ¹⁾		1.11	0.74	0.96
Organic matter content (OM) [%] ²⁾		1.91	1.28	1.66
Cation Exchange Capacity – CEC [mEq/100g]		5.64	15.12	6.44
Water holding capacity	at 15 bar [% MWHC]	4.06	3.87	9.16
	at ½ bar [% MWHC]	9.92	13.27	24.19
Bulk density [g/cm ³]		1.34	1.62	1.37
Soil microbial activity expressed as [CFU/g soil] ³⁾ determined on	23/30 march 1998 (beginning of the study)	3.8 E4 – fungi 1.2 E7 – bacteria	4.8 E4 – fungi 9.1 E6 – bacteria	1.0 E5 – fungi 1.0 E7 – bacteria
	2/13 april 1998 (end of the study)	6.0 E4 – fungi 1.1 E7 – bacteria	2.8 E4 – fungi 1.2 E7 – bacteria	1.1 E5 – fungi 6.0 E7 – bacteria

Footnotes to the table:

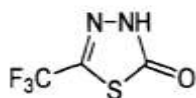
- 1) Value recalculated by the RMS from the OM content given in the study report, using the following equation: OM = 1.724 * OC;
- 2) Value provided in the study report;
- 3) CFU/ g soil = Colony Forming Units/gram of test soil (determined using *plate count agar* method).

50-g portions of test soils, 20 for each test soil, were weighed into 250-mL Nalgene PPCO centrifuge bottles (further called soil sample containers) and adjusted to the target moisture content – 75% of ½ bar, with appropriate amount of distilled water. So prepared individual kinetic samples, samples for the determination of soil microbial activity and spare samples, were randomized and placed in incubation vessels – transparent Nalgene™ dessicators equipped with inlet and outlet tubes. Then they were preincubated for 1 week in the darkness at constant temperature $T = 20 \pm 1^\circ\text{C}$, before being treated with the test compound. The incubation system used in the experiment for both pre-incubation phase and main experiment is presented further down this summary.

The test compound was [2-¹⁴C]-Thiadone, having a specific activity of 50 mCi/mmol, corresponding to 652680 dpm/µg, and radiochemical purity of 97.7%. The structural formula of the test compound, with radiolabelling position indicated by an asterisk, is presented below on figure B.8.1.1.2.1.1._CA-125. The compound was delivered in form of the **Stock solution** in acetone, having a concentration 2.54 µg/mL.

**Figure B.8.1.1.2.1.1._CA-125:** The structural formula of [2-¹⁴C]-FOE Thiadone used in the experiment (copied from the study report).

Additionally the non-radiolabelled FOE Thiadone, having a chemical purity of 99.3% was used as a reference substance. Its structural formula is presented below on figure B.8.1.1.2.1.1._CA-126.

**Figure B.8.1.1.2.1.1._CA-126:** The structural formula of non-radiolabelled FOE Thiadone used in the experiment (copied from the study report).

The reference substance was used in the experiment in form of the **Stock solution**, prepared by dissolving 10.0 mg of it in 10 mL of CH₃CN. The concentration of the so prepared solution, further called **Stock solution 1**, was 1 µg/mL.

Next the **Fortification solution** was prepared by mixing 0.520 mL of the **Stock solution** (containing radiolabelled test substance) with 1.250 mL of the **Stock solution 1** (containing the non-radiolabelled reference substance) and diluting the obtained solution with acetone to the final volume of 10 mL. The so prepared solution had a concentration 0.2571 µg FOE Thiadone/mL and specific activity of 335433 dpm/µg. It was verified for concentration of radiolabelled compound and radiochemical purity by LSC and HPLC-LSC. The prepared **Fortification solution** was stored at T < -5°C until being used.

The kinetic samples were treated with the test compound by applying 0.1 mL of **Fortification solution** onto the soil surface in each sample container. The amount of the **Fortification solution** applied was such to give the nominal fortification level of 0.5 ppm (0.5 mg/kg soil). That level was calculated using the following assumptions:

- the target concentration of Flufenacet in soil (used in the study by [Pangilinan and Smith; 1994], summarised under the point B.8.1.1.1.1. of this Assessment Report as **Study 2**): **1.101 mg/kg**, corresponding to application rate of 0.8 lb a.i./ha (according to RMS that resulted in field application rate 825.75 mg Flufenacet/ha);
- conversion of Flufenacet into FOE Thiadone: **100%**;
- molar weight of Flufenacet: **M = 363 g/mol**;
- molar weight of FOE Thiadone: **M' = 170 g/mol**;

RMS checked the calculations and found them correct.

The samples containing Iowa and Indiana test soils were treated on the same day and those containing Nebraska test soil a week later. After treatment all samples, except DAT-0 samples processed immediately after treatment, were placed in incubation vessel – transparent Nalgene™ dessicators connected to air-supply system (inlet) and the volatile traps-system (outlet), and incubated for up to 14 days in the darkness at T = 20 ± 1°C. The incubation system used in the experiment is presented below on figure B.8.1.1.2.1.1._CA-127.

The sampling regime, set individually for each test soil, looked as follows:

- for Iowa loamy sand soil:
 - soil samples were taken for the analysis on DAT 0, DAT 0.25, DAT 1, DAT 2, DAT 3, DAT 5, DAT 7 and DAT 10; DAT-0, DAT-1, DAT-2, DAT-3 and DAT-5 samples were taken in duplicate;
 - the ¹⁴CO₂ traps were changed and analysed on DAT 0.25, DAT 1, DAT 2, DAT 3, DAT 4, DAT 5, DAT 7 and DAT 10;
 - the VOC traps were changed and analysed on DAT 3, DAT 4 and DAT 10.
- for Indiana sandy loam soil:
 - soil samples were taken for the analysis on DAT 0, DAT 0.5, DAT 1, DAT 2, DAT 3, DAT 5, DAT 7 and DAT 10; DAT-0, DAT-0.5, DAT-1, DAT-3 and DAT-5 samples were taken in duplicate;
 - the ¹⁴CO₂ traps were changed and analysed on DAT 0.25, DAT 0.5, DAT 1, DAT 2, DAT 3, DAT 4, DAT 5, DAT 7 and DAT 10;
 - the VOC traps were changed and analysed on DAT 3, DAT 4 and DAT 10.
- for Nebraska silt loam soil:
 - soil samples were taken for the analysis on DAT 0, DAT 1, DAT 2, DAT 3, DAT 5, DAT 7, DAT 10 and DAT 14; DAT-0, DAT-3, DAT-5 and DAT-7 samples were taken in duplicate;
 - the ¹⁴CO₂ traps were changed and analysed on DAT 1, DAT 2, DAT 3, DAT 4, DAT 5, DAT 7, DAT 10 and DAT 14;
 - the VOC traps were changed and analysed on DAT 3, DAT 5, DAT 7, DAT 10 and DAT 14.

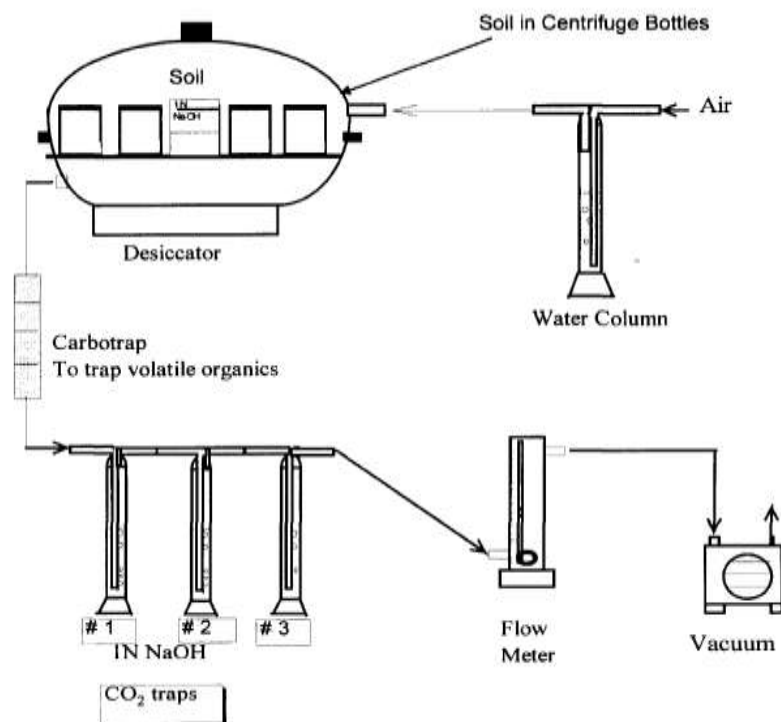


Figure B.8.1.1.2.1.1_CA-127: The schematic presentation of the incubation system used in the experiment (copied from the study report).

Soil from each sample collected at the designated time-points listed above was processed and analysed quantitatively and qualitatively for residues of [¹⁴C]Thiadone using the analytical procedure presented below on figure B.8.1.1.2.1.1_CA-128. Whole samples were used in the analysis which occurred within 24 hours after sampling.

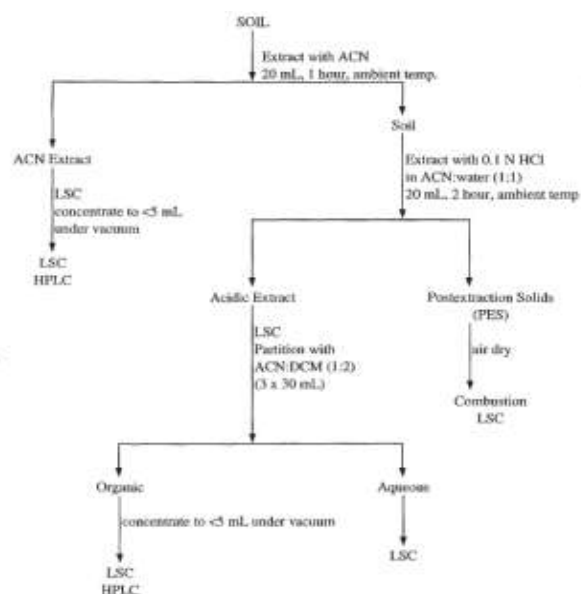


Figure B.8.1.1.2.1.1_CA-128: The sample-processing procedure used in the experiment (copied from the study report).

The extracted soil pellets were air-dried at ambient temperature, ground and their three 500-mg aliquots analysed after combustion for radioactivity content.

The collected VOC-traps (Carbotrap™ 400 tubes) were combusted and the evolved $^{14}\text{CO}_2$ quantified by LSC.

The radioactivity trapped in each alkaline trap for $^{14}\text{CO}_2$ was determined by LSC. That was done in 2-mL aliquots to which 10 mL of liquid scintillation cocktail was added. The conformation of that the trapped radioactivity was $^{14}\text{CO}_2$, was done in a following way:

- the content of alkaline traps for $^{14}\text{CO}_2$ collected at each sampling point was pooled;
- next, to its 2-mL aliquots was added 5 mL of aqueous 5% BaCl_2 /5% NH_4Cl solution;
- sample was then thoroughly mixed and formed solid precipitated by centrifugation;
- finally supernatants were analysed by LSC.

All samples were analysed for the content of radioactivity using LSC method. The LSC (Liquid Scintillation Counting) analysis was performed using either Tractor Mark V Model 5303 LS counter or Beckman LS 6500 counter.

Liquid samples were analysed in duplicate with 5 mL or 10 mL of Ultima Gold liquid scintillation cocktail. The counting of each analysed sample lasted for 2 minutes.

Solid samples (500-mg aliquots) were analysed in triplicate by their combustion in biological oxidiser. The evolved $^{14}\text{CO}_2$ was trapped in 20 mL of Carbon 14 Cocktail and counted by LSC. The results were corrected for oxidiser efficiency.

Sample extracts were analysed using the following techniques:

- HPLC – major identification and quantitation method for parent compound and its degradation products;
- HPLC-MS – conformatory identification method for parent compound and its degradation products;
- GC-MS – conformatory identification method for parent compound and its degradation products.

The HPLC analysis was performed using a Waters™ HPLC system equipped with autosampler, Tunable Absorbance Detector and fraction collector, coupled to one of the following LSC detectors:

- Radiomatic A-500 Radio-chromatography Detector;
- β Radio-Chromatography Detector.

The system was equipped with Phenomenex Luna™, 5 μm C18, 150 x 4.6 mm chromatographic column and Zorbax® RX-C18 10 x 4.6 mm guard column. The chromatographic separation was performed in a gradient mode, using the mobile phase consisting of:

- water + 0.5% CH_3COOH as **Solvent A**, and
- CH_3OH as **Solvent B**.

Gradient elution lasted 70 minutes. Its parameters are shown below in the table B.8.1.1.2.1.1._CA-239. The flow rate was set to 1.5 mL/min. UV detection was performed at $\lambda = 254$ nm.

Table B.8.1.1.2.1.1._CA-239: The HPLC gradient mode used in the study.

Time [min]	Solvent ratio	
	<i>Solvent A – Water + 0.4% CH_3COOH</i>	<i>Solvent B – Methanol</i>
0	100	0
40	30	70
60	30	70
61	100	0
70	100	0

The changes in the gradient of mobile phase were linear.

The minimum detection limit for HPLC method was 300 dpm and its response was demonstrated to be linear within the range 300 – 200000 dpm.

Sample volume injected onto the column was sufficient to detect residues at the level of 1.5% of injected radioactivity for CH_3CN extracts and 8.5% of injected radioactivity for CH_3CN ;0.1N HCl extracts.

The identification of the chromatographic peaks was performed by means of the comparison of their retention times R_t with those of the standards.

The HPLC-MS analysis was performed using Finnigan SSQ710 LC/MS device equipped with Phenomenex Luna 5 μm C8 150 x 2 mm LC column. The chromatographic analysis was carried out in a gradient mode. Its parameters were following:

- **Mobile phase A:** 0.05% HCOOH in Water,
- **Mobile phase B:** CH_3OH ,

- **Gradient mode:** A/B1:1 hold 2 min to A/B 3:7 at 8 min.

The flow rate was set to 0.2 mL/min.

The reported parameters of MS detector were following:

- Ionization mode: (-)ESI;
- Mass range: 115 – 300 amu;
- Scan rate: 1.5 sec/scan;
- Source temperature: 220°C;
- ESI spray voltage: 4.0 kV.

That method was used to direct identification of the test compound – FOE Thiadone, and its degradation product – propionic acid conjugate of FOE Thiadone, in selected extracts. The extracts selected for that analysis were organic partition concentrates of the acid extract obtained from both replicates of DAT-1 Iowa loamy sand sample.

The propionic acid conjugate of FOE Thiadone was further characterised, after hydrolysis or methylation, in selected acid extracts by GC-MS.

Results and their discussion:

The examination of the microbial viability of the test soils showed that they were viable throughout the whole experiment. The detailed results are shown in the table B.8.1.1.2.1.1._CA-238.

The monitoring of incubation temperature showed that the samples were kept in the constant temperature $T = 20 \pm 1^\circ\text{C}$.

The determination of the soil moisture content of air-dried soils showed that that parameter was on the following level:

- in Iowa soil: 1.75%;
- in Indiana soil: 1.98%
- in Nebraska soil: 5.98%.

When adjusted to the designated level – 75% of $\frac{1}{3}$ bar, it became:

- in Iowa soil: 7.44%;
- in Indiana soil: 9.95%
- in Nebraska soil: 18.14%.

The radiochemical purity of the test substance in **Fortification solutions** prepared to treat each test soil, expressed as % [^{14}C]-FOE Thiadone, was following:

- for Iowa soil: 95.4%;
- for Indiana soil: 95.4%
- for Nebraska soil: 95.0%;

The verification of the application rate in each test soil showed that it was in line with the value of nominal application – 0.5 mg/kg. It was performed assuming that the specific activity of the test compound was 335433 dpm/ μg and the amount of the treated soil 50 g (d.w.). The detailed results of that verification are presented below in the table B.8.1.1.2.1.1._CA-240.

Table B.8.1.1.2.1.1._CA-240: The results of the verification of application rate.

Test soil	Applicaton rate of [^{14}C]-FOE Thiadone	
	dpm	ppm
<i>Iowa loamy sand</i>	8654025	0.52
<i>Indiana sandy loam</i>	8654025	0.52
<i>Nebraska silt loam</i>	8535625	0.51

The quantitative analysis of extracts, extracted soil pellets and traps for volatile compounds showed that the recovery of applied radioactivity throughout the study was within the recommended range:

- in Iowa soil: 92.5 – 103.7% AR, mean recovery – 95.75 AR;
- in Indiana soil: 90.7 – 99.9% AR, mean recovery – 96.4% AR ;
- in Nebraska soil: 91.6 – 98.6% AR, mean recovery – 94.9% AR.

The level of radioactivity extracted from soil decreased with time:

- in Iowa soil: from 102.6% AR on Day 0 to 9.6% AR on DAT 10;
- in Indiana soil: from 99.0% AR on Day 0 to 6.2% AR on DAT 10;
- in Nebraska soil: from 97.0% AR on Day 0 to 5.5% AR on DAT 14.

The level of volatile compounds detected at the end of experiment was following:

- in Iowa soil: 63.2% AR as CO₂ and 2.3% AR as VOC (DAT 10);
- in Indiana soil: 82.1% AR as CO₂ and 4.0% AR as VOC (DAT 10);
- in Nebraska soil: 71.8% AR as CO₂ and 3.3% AR as VOC (DAT 14).

The level of NER fraction at the end of incubation period was following:

- in Iowa soil: 19.5% AR (DAT 10);
- in Indiana soil: 7.6% AR (DAT 10);
- in Nebraska soil: 14.7% AR (DAT 14).

Finally, the decrease of the test compound – FOE Thiadone in each test soil looked as follows:

- in Iowa soil: from 98.3% AR on Day 0 to 6.6% AR on DAT 10;
- in Indiana soil: from 94.8% AR on Day 0 to 3.0% AR on DAT 10;
- in Nebraska soil: from 93.5% AR on Day 0 to 3.3% AR on DAT 14.

Apart from FOE Thiadone following compounds were identified in samples:

- propionic acid conjugate of FOE Thiadone,
- Other fraction,
- fortification impurity (1),
- fortification impurity (2),

The structural formula of propionic acid conjugate of FOE Thiadone is presented below on figure B.8.1.1.2.1.1._CA-129.

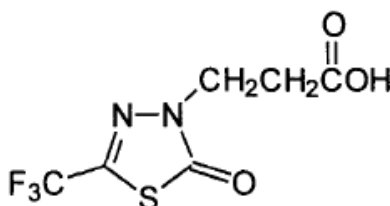


Figure B.8.1.1.2.1.1._CA-129: The postulated structural formula of the propionic acid conjugate of FOE Thiadone (copied from the study report).

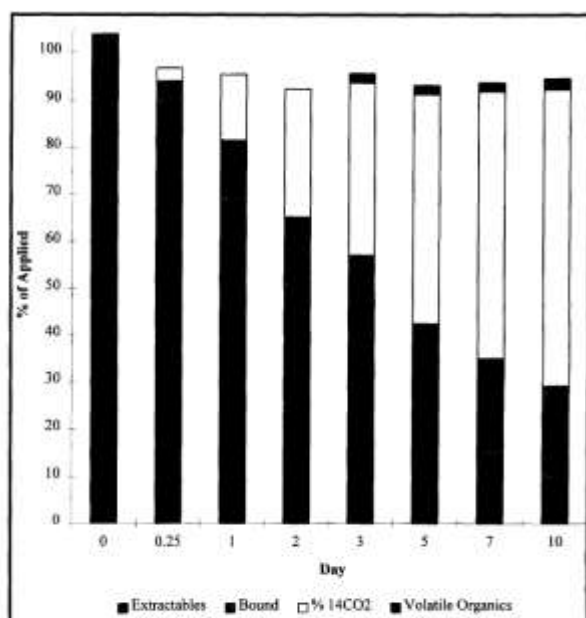
The detailed results of the experiment are presented below, separately for each test soil, in tables B.8.1.1.2.1.1._CA-241 – B.8.1.1.2.1.1._CA-243. Additionally they are presented in graphical form on figures B.8.1.1.2.1.1._CA-130 – B.8.1.1.2.1.1._CA-132 in form of two parallel graphs showing the distribution of radioactivity in the test systems and concentrations of FOE Thiadone and its degradation product – propionic acid conjugate, in function of time.

Table B.8.1.1.2.1.1_CA-241: The detailed results of the experiment obtained in Iowa loamy sand soil.

AR		Results [%AR] obtained for the sampling time point ¹⁾ :							
		DAT 0	DAT 0.25	DAT 1	DAT 2	DAT 3	DAT 5	DAT 7	DAT 10
Extracted	CH ₃ CN extract	96.4	81.3	56.8	34.6	24.1	14.0	8.1	5.4
	CH ₃ CN/HCl extract	6.2	5.5	11.9	15.8	13.3	8.8	6.7	4.2
	Total extracted	102.6	86.8	68.7	50.4	37.4	22.8	14.8	9.6
In extract identified as:	FOE Thiadone	98.3	81.2	57.5	36.6	26.6	16.1	8.9	6.6
	Propionic acid conjugate of FOE Thiadone	n. f. ³⁾	1.3	7.5	10.2	7.5	3.1	1.2	0.1
	Fortification impurity (1) (<i>R_t</i> = 22.5-23.5 min)	0.6	0.7	0.3	n. f. ³⁾	n. f. ³⁾	0.2	n. f. ³⁾	n. f. ³⁾
	Fortification impurity (2) (<i>R_t</i> = 50.0-51.5 min)	0.7	1.3	0.9	1.0	1.8	1.4	1.5	0.9
	Others	3.0	2.3	2.5	2.6	1.5	2.0	3.2	2.0
	Total identified	102.6	86.8	68.7	50.4	37.4	22.8	14.8	9.6
	Bound residues	1.1	7.3	12.9	14.9	19.7	19.7	20.1	19.5
Volatile compounds	CO ₂	n. d. ⁴⁾	2.6	13.9	27.2	36.6	48.9	57.0	63.2
	VOC	n. d. ⁴⁾	n. a. ⁵⁾	n. a. ⁵⁾	n. a. ⁵⁾	1.9	1.9	1.9	2.3
	Total volatiles²⁾	n. d.⁴⁾	2.6	13.9	27.2	38.5	50.8	58.9	65.5
Total recovered		103.7	96.7	95.5	92.5	95.6	93.3	93.8	94.6

Footnotes to the table:

- 1) The values for DAT-0, DAT-1, DAT-2, DAT-3 and DAT-5 time points are the averages of two replicates;
- 2) Sum of all volatiles as given in the study report;
- 3) n. f. – not found; the compound not detected at that time point;
- 4) n. d. – not determined as at that time point no volatile compounds were expected to be formed;
- 5) n. a. – not analysed;

Distribution of radioactivity

The numbers reported are the average of replicates 1 and 2 for sample days 0, 1, 2, 3 and 5.

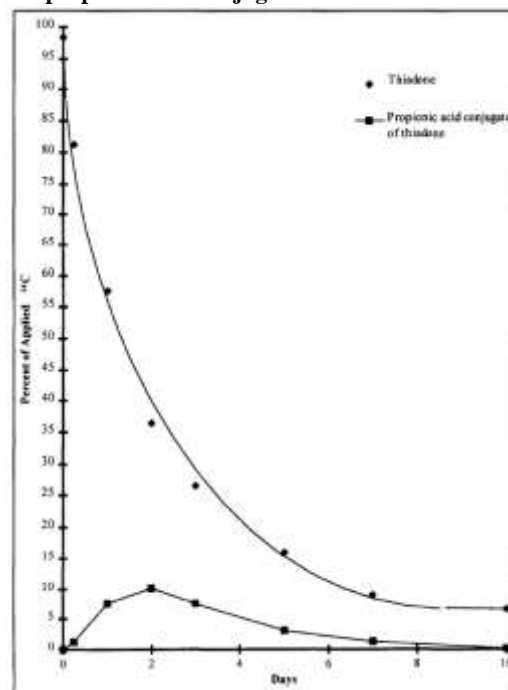
Concentrations of FOE Thiadone and propionic acid conjugate of FOE Thiadone**Figure B.8.1.1.2.1.1_CA-130:** The graphical results of the experiment obtained in Iowa loamy sand soil (copied from the study report).

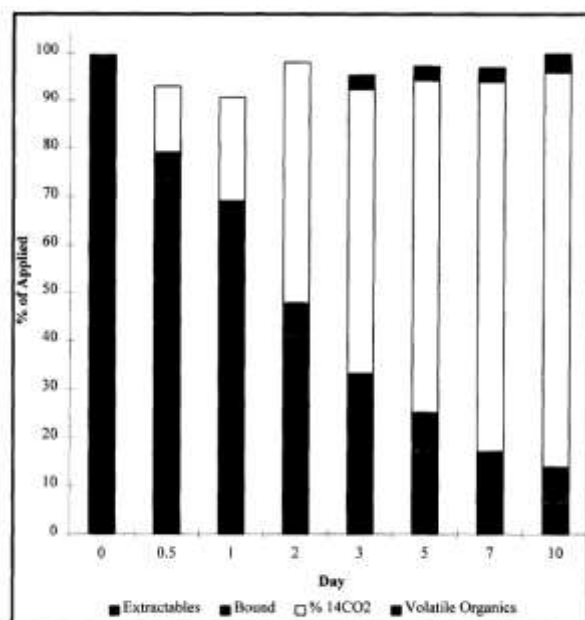
Table B.8.1.2.1.1._CA-242: The detailed results of the experiment obtained in Indiana sandy loam soil.

AR		Results [%AR] obtained for the sampling time point ¹⁾ :							
		DAT 0	DAT 0.5	DAT 1	DAT 2	DAT 3	DAT 5	DAT 7	DAT 10
Extracted	CH ₃ CN extract	95.5	66.9	53.4	30.5	17.4	10.8	7.1	3.7
	CH ₃ CN/HCl extract	3.5	6.4	8.9	9.9	7.7	6.0	2.7	2.5
	Total extracted	99.0	73.3	62.3	40.4	25.1	16.8	9.8	6.2
In extract identified as:	FOE Thiadone	94.8	69.1	54.3	29.0	16.7	8.9	4.6	3.0
	Propionic acid conjugate of FOE Thiadone	n. f. ³⁾	0.8	4.1	7.0	4.9	2.6	n. f. ³⁾	0.1
	Fortification impurity (1) (<i>R_t</i> = 22.5-23.5 min)	0.5	n. f. ³⁾	n. f. ³⁾	n. f. ³⁾	0.3	0.6	0.3	n. f. ³⁾
	Fortification impurity (2) (<i>R_t</i> = 50.0-51.5 min)	1.6	1.3	1.4	1.3	1.8	1.8	1.5	1.8
	Others	2.1	2.1	2.5	3.1	1.4	2.9	3.4	1.3
	Total identified	99.0	73.3	62.3	40.4	25.1	16.8	9.8	6.2
	Bound residues	0.6	5.9	6.9	7.4	8.2	8.4	7.3	7.6
Volatile compounds	CO ₂	n. d. ⁴⁾	13.9	21.5	50.3	59.1	69.1	76.9	82.1
	VOC	n. d. ⁴⁾	n. a. ⁵⁾	n. a. ⁵⁾	n. a. ⁵⁾	3.0	3.0	3.0	4.0
	Total volatiles²⁾	n. d.⁴⁾	13.9	21.5	50.3	62.1	72.1	79.9	86.1
Total recovered		99.6	93.1	90.7	98.1	95.4	97.3	97.0	99.9

Footnotes to the table:

- 1) The values for DAT-0.5, DAT-1, DAT-3 and DAT-5 time points are the averages of two replicates;
- 2) Sum of all volatiles as given in the study report;
- 3) n. f. – not found; the compound not detected at that time point;
- 4) n. d. – not determined as at that time point no volatile compounds were expected to be formed;
- 5) n. a. – not analysed;

Distribution of radioactivity



The numbers reported are the average of replicates 1 and 2 for sample days 0, 0.5, 1, 3 and 5.

Concentrations of FOE Thiadone and propionic acid conjugate of FOE Thiadone

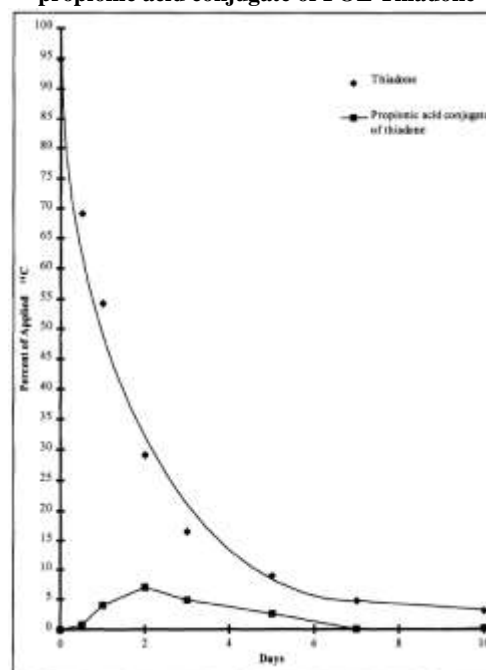


Figure B.8.1.2.1.1._CA-131: The graphical results of the experiment obtained in Indiana sandy loam soil (copied from the study report).

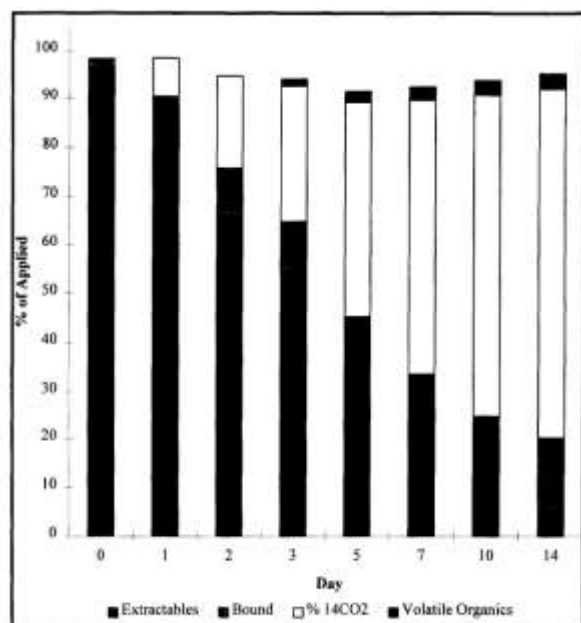
Table B.8.1.2.1.1._CA-243: The detailed results of the experiment obtained in Nebraska silt loam soil.

AR		Results [%AR] obtained for the sampling time point ¹⁾ :							
		DAT 0	DAT 1	DAT 2	DAT 3	DAT 5	DAT 7	DAT 10	DAT 14
Extracted	CH ₃ CN extract	90.1	74.8	59.1	47.7	27.0	15.3	7.8	3.6
	CH ₃ CN/HCl extract	6.9	9.2	7.3	7.2	4.5	3.6	2.3	1.9
	Total extracted	97.0	84.0	66.4	54.9	31.5	18.9	10.1	5.5
In extract identified as:	FOE Thiadone	93.5	79.2	62.7	52.2	28.9	16.2	7.7	3.3
	Propionic acid conjugate of FOE Thiadone	0.2	1.3	1.1	1.0	0.7	0.2	n. f. ³⁾	n. f. ³⁾
	Fortification impurity (1) (<i>R_t</i> = 22.5-23.5 min)	0.7	0.5	n. f. ³⁾	n. f. ³⁾	n. f. ³⁾	n. f. ³⁾	0.1	n. f. ³⁾
	Fortification impurity (2) (<i>R_t</i> = 50.0-51.5 min)	1.9	1.4	1.2	0.6	0.5	0.7	0.6	0.3
	Others	0.7	1.6	1.4	1.1	1.4	1.8	1.7	1.9
	Total identified	97.0	84.0	66.4	54.9	31.5	18.9	10.1	5.5
	Bound residues	1.4	6.5	9.4	10.0	13.8	14.7	14.7	14.7
Volatile compounds	CO ₂	n. d. ⁴⁾	8.1	18.9	27.7	43.9	56.1	66.0	71.8
	VOC	n. d. ⁴⁾	n. a. ⁵⁾	n. a. ⁵⁾	1.5	2.4	2.8	3.1	3.3
	Total volatiles²⁾	n. d.⁴⁾	8.1	18.9	29.2	46.3	58.9	69.1	75.1
Total recovered		98.4	98.6	94.7	94.1	91.6	92.5	93.9	95.3

Footnotes to the table:

- 1) The values for DAT-0, DAT-1, DAT-3 DAT-5 and DAT-7 time points are the averages of two replicates;
- 2) Sum of all volatiles as given in the study report;
- 3) n. f. – not found; the compound not detected at that time point;
- 4) n. d. – not determined as at that time point no volatile compounds were expected to be formed;
- 5) n. a. – not analysed;

Distribution of radioactivity



The numbers reported are the average of replicates 1 and 2 for sample days 0, 1, 3, 5 and 7.

Concentrations of FOE Thiadone and propionic acid conjugate of FOE Thiadone

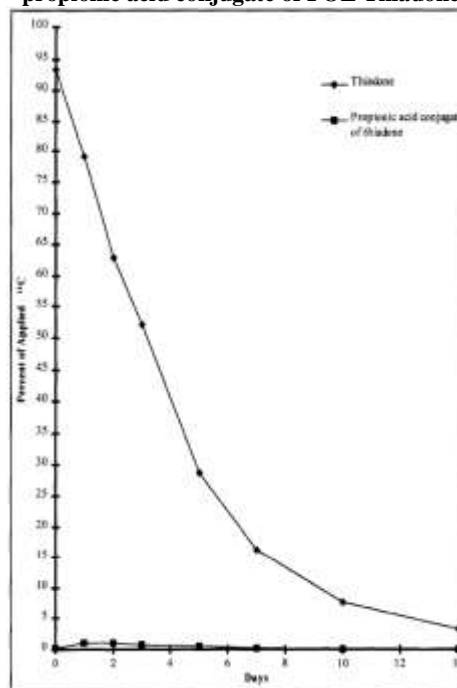


Figure B.8.1.2.1.1._CA-132: The graphical results of the experiment obtained in Nebraska silt loam soil (copied from the study report).

On the basis of the obtained results the transformation pathway of FOE Thiadone radiolabelled in C2 position was proposed in the study report. It is presented below on figure B.8.1.1.2.1.1_CA-133. RMS noted that it is the same as the transformation pathway resulting from the examination of photodegradation of FOE Thiadone in soil (please refer to the summary of the **Study 2** presented under the point B.8.1.1.1.3. of this Assessment Report).

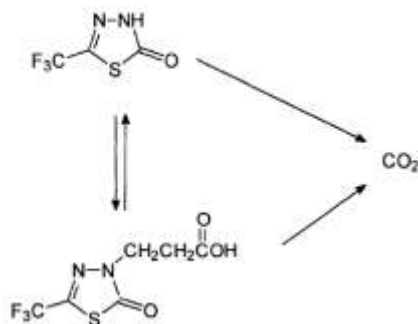


Figure B.8.1.1.2.1.1_CA-133: The transformation pathway of [¹⁴C]-2-FOE Thiadone in soil (copied from the study report).

The data obtained for FOE Thiadone, presented in tables B.8.1.1.2.1.1_CA-241 – B.8.1.1.2.1.1_CA-243, were further kinetically examined. The analysis was performed using first order kinetics and linear-regression model. As it does not comply with the current standards, set by FOCUS Kinetics Guidance (FOCUS, 2006) it is not presented here. The same data set was kinetically examined in a separate study, summarised below as **Study 18**.

Study 18:

Report: Reinken G., Partsch S., (2014): “Kinetic Evaluation of the Degradation of Flufenacet Degradation Product FOE-thiadone under Aerobic Soil conditions in Laboratory according to FOCUS Kinetics Using the KinGUI 2 Tool. FOE-thiadone.”; Bayer CropScience AG, Environmental Safety, Alfred-Nobel-Strasse 50, 40789 Monheim, Germany; unpublished Study Report No. EnSa-12-0579; 2014. 02. 17; study reference number: M-447840-01-1;

Guidelines: The study was declared to be performed to comply with the following guidelines:

- FOCUS (2006): “Guidance Document on Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration.” Report of the FOCUS Work Group on Degradation Kinetics, EC Document Reference SANCO/10058/2005 version 2.0, 434 pp.;
- FOCUS (2011): “Generic guidance for Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration”, version 1.0 (issued on 23 November 2011).

GLP: No, not applicable – this is a modelling study;

RMS comments: RMS verified the study for its compliance with the provisions of the Guidelines listed above. It was stated that the study generally complied with the two evoked Guidance Documents. The study was aimed on the derivation of the modelling kinetic endpoints for FOE Thiadone. It followed modelling approach outlined already in other studies summarised above – **Study 2, Study 7 and Study 8**. The analysis was performed for the results of the summarised above study by [Lentz and Bloomberg; 1999] (**Study 17**). The study was found to be acceptable and is summarised below.

Summary:

The aim of the study was to kinetically examine the data for FOE Thiadone obtained in summarised above as **Study 17** the study by [Lentz and Bloomberg; 1999], in order to derive the kinetic endpoints suitable for use in modelling exposure assessment.

In the source study the the degradation of FOE Thiadone was examined in three soils. Their key properties are presented below in the table B.8.1.1.2.1.1._CA-244. The experimental conditions used in the study are summarised further down, in the table B.8.1.1.2.1.1._CA-245.

Table B.8.1.1.2.1.1._CA-244: The brief characteristic of the test soils.

Soil name	Soil type (USDA classification)	Soil properties			
		pH	OC [%]	Soil microbial biomass at the beginning of the study – [CFU/g soil]	
				bacteria	fungi
Iowa	Loamy sand	7.2	1.11	1.2 E7	3.8 E4
Indiana	Sandy loam	6.5	0.74	9.1 E6	4.8 E4
Nebraska	Silt loam	7.7	0.96	1.0 E7	1.0 E5

Table B.8.1.1.2.1.1._CA-245: The experimental conditions used in each experiment.

Test soil		Experimental conditions			
Name	Type (USDA classification)	Incubation temperature T [°C]	Reference value - % MWHC at ½ bar	Soil moisture	
				In experiment	
				declared	determined
Iowa	Loamy sand	20 ± 1	9.92%	75% of ½ bar	7.44%
Indiana	Sandy loam	20 ± 1	13.27%	75% of ½ bar	9.95%
Nebraska	Silt loam	20 ± 1	24.19%	75% of ½ bar	18.14%

The not-processed input data used in the kinetic analysis are presented below in the table B.8.1.1.2.1.1._CA-246.

Table B.8.1.1.2.1.1._CA-246: The non-processed data obtained in the test soils used as input in kinetic analysis.

Results obtained in Iowa loamy sand soil				Results obtained in Indiana sandy loam soil			
DAT	Concentration [%] of:			DAT	Concentration [%] of:		
	FOE Thiadone	Propionic acid conjugate of FOE Thiadone	Sum		FOE Thiadone	Propionic acid conjugate of FOE Thiadone	Sum
0	98.3	not determined	98.3	0	94.8	not determined	94.8
0.25	81.2	1.3	82.5	0.5	69.1	0.8	69.9
1	57.5	7.5	65.0	1	54.3	4.1	58.4
2	36.6	10.2	46.8	2	29.0	7.0	36.0
3	26.6	7.5	34.1	3	16.7	4.9	21.6
5	16.1	3.1	19.2	5	8.9	2.6	11.5
7	8.9	1.2	10.1	7	4.6	not determined	4.6
10	6.6	0.1	6.7	10	3.0	0.1	3.1

Results obtained in Nebraska silt loam soil				
DAT	Concentration [%] of:			
	FOE Thiadone	Propionic acid conjugate of FOE Thiadone	Sum	
0	93.5	0.2	93.7	
1	79.2	1.3	80.5	
2	62.7	1.1	63.8	
3	52.2	1.0	53.2	
5	28.9	0.7	29.6	
7	16.2	0.2	16.4	
10	7.7	not determined	7.7	
14	3.3	not determined	3.3	

The values presented above as “sum” were subjected to a multistep evaluation procedure almost identical to that already presented above in the summary of the **Study 2**, for convenience repeated below. It consisted of the following steps:

- **Step 1:** Processing of the raw input data;
- **Step 2:** Kinetic evaluation of the processed data using the following 1st – order kinetic models: SFO, FOMC and DFOP, and KinGUI 2 as a modelling tool, in order to determine the appropriate kinetic model.
- **Step 3:** Evaluation of the results of kinetic examination of the data;
- **Step 4:** Reporting of the obtained results, in particular kinetic parameters recommended for modelling.

The data-processing to obtain the input values for kinetic analysis (**Step 1**) was identical to the procedure described in the summary of the **Study 2**, on page 168. The processed data used as input in the kinetic examination are presented below in the table B.8.1.1.2.1.1._CA-247. The Applicant indicated that DAT-0 values were set to total recovery level recorded on that time point.

Table B.8.1.1.2.1.1._CA-247: The processed residue data used in the kinetic analysis.

Results obtained in Iowa Loamy sand soil		Results obtained in Indiana Sandy loam soil		Results obtained in Nebraska Silt loam soil	
DAT	Concentration [%] of FOE Thiadone	DAT	Concentration [%] of FOE Thiadone	DAT	Concentration [%] of FOE Thiadone
0	103.7	0	99.6	0	98.4
0.25	82.5	0.5	69.9	1	80.5
1	65.0	1	58.4	2	63.8
2	46.8	2	36.0	3	53.2
3	34.1	3	21.6	5	29.6
5	19.2	5	11.5	7	16.4
7	10.1	7	4.6	10	7.7
10	6.7	10	3.1	14	3.3

The processed data were kinetically examined using KinGUI ver. 2 modelling tool, developed by Bayer. The optimisation was performed using IRLS (Iteratively Reweighed Nonlinear Least Squares) algorithm. The fitting procedure consisted on the determination of the appropriate kinetic model for FOE Thiadone.

The conceptual metabolic pathway built in the modelling tool was based on the transformation pathway which, in form of a simplified scheme, is presented below on figure B.8.1.1.2.1.1._CA-134.



Figure B.8.1.1.2.1.1._CA-134: The simplified transformation pathway used to create conceptual transformation scheme assumed in the modelling tool (copied from the study report).

The obtained results of the kinetic analysis of the data were evaluated by the Applicant. That was done by means of a detailed statistical analysis comprising the following components:

- visual assessment of the fit;
- χ^2 -error statistics;
- t-test significance;
- correlation analysis.

The detailed characteristic of the evaluation procedure was presented in the summary of the **Study 2** on pages 170 – 171. RMS decided not to repeat it here in order to not overburden the Renewal Assessment Report.

On that basis the following multistep assessment procedure was followed:

- **Step 1:** bearing in mind the aim of the kinetic evaluation of the data – determination of the kinetic parameters used in modelling, the SFO kinetic model was tested as first option and if passed the acceptance criteria (visually acceptable, χ^2 -error not exceeding or not significantly exceeding 15%, *prob. > t* value in t-test less than 0.05 for parent and 0.10 for the degradation products), it was considered acceptable;
- **Step 2:** in case the χ^2 -error was significantly greater than 15%, model parameters were fixed and fitting repeated using SFO model;
- **Step 3:** if the **Step-2** fitting failed the χ^2 -error test, bi-phasic models were included. These were FOMC, DFOP and, possibly, HS. The model with smaller error was indicated as the most appropriate;
- **Step 4:** if none of the bi-phasic model returned significantly improved fit, SFO model was selected if visually acceptable; that was done in order to avoid of an over-parameterised model based on a marginally better fit.

Analysing the proposed assessment procedure RMS stated that it complied with the procedure for determination of the kinetic endpoints for modelling, presented in FOCUS Kinetics Guidance Document [FOCUS; 2006].

The results of the kinetic analysis are presented below, individually for each test soil.

- 1) The results of the kinetic analysis of the data obtained for FOE Thiadone in Iowa Loamy sand soil.

The results of the kinetic analysis performed by the Applicant are presented below, in graphical form on figure B.8.1.1.2.1.1._CA-135 and in numerical form in the table B.8.1.1.2.1.1._CA-248. Additionally the table B.8.1.1.2.1.1._CA-249 provides the kinetic endpoints obtained with each of the kinetic models tested.

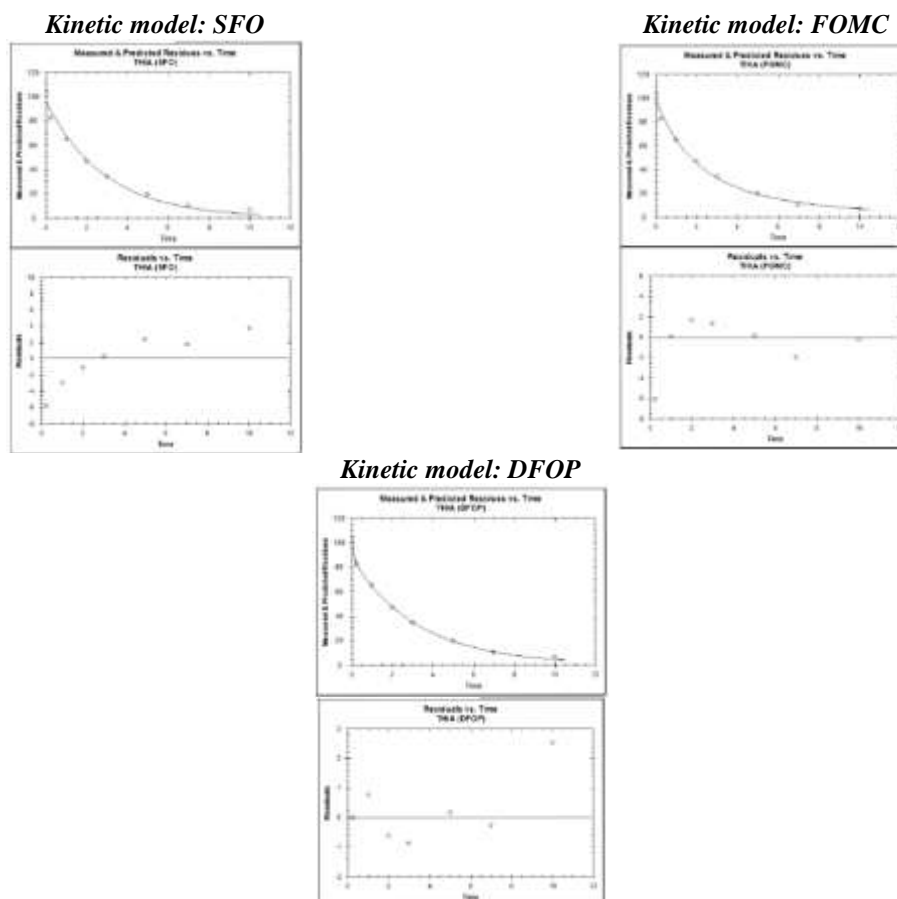


Figure B.8.1.1.2.1.1._CA-135: The graphical results of the kinetic analysis (copied from the study report).

Table B.8.1.1.2.1.1._CA-248: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment ¹⁾
				Lower	Upper			
SFO	M_0	96.430	3.270	90.020	102.839	5.04 E-8	6.725	0.987; Acceptable fit
	k	0.3494	0.02951	0.2915	0.407	1.10 E-5		
FOMC	M_0	99.220	2.997	93.346	105.094	2.36 E-7	5.348	0.992; Good fit
	α	2.6336	1.2352	0.2126	5.055	0.0431		
	β	5.7293	3.4314	-0.9962	12.455	0.0779		
DFOP	M_0	103.699	1.223	101.303	106.096	5.79 E-8	2.023	0.999; Good fit
	k_1	8.8492	5.2636	-1.4674	19.166	0.0840		
	k_2	0.3039	0.01355	0.2774	0.330	1.17 E-5		
	g	0.1606	0.02764	0.1064	0.215	0.00218		

Footnotes to the table:

- 1) Visual assessment of the kinetic curve as proposed by the Applicant.

Table B.8.1.1.2.1.1._CA-249: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested		
		<i>SFO</i>	<i>FOMC</i>	<i>DFOP</i>
<i>FOE Thiadone</i>	DT ₅₀ [days]	1.98	1.72	1.70
	DT ₉₀ [days]	6.59	8.00	7.00

Conclusion:

All three models returned visually and statistically good fits, although Applicant classified SFO fit as only acceptable, most probably due to the distribution of residuals, which is not random. Both FOMC and DFOP returned visually and statistically better fits, DFOP being superior of the three. However, neither FOMC nor DFOP, despite being visually and statistically good fits, can be considered acceptable, because they returned not reliable kinetic parameters. In case of FOMC fit the problem concerned β , not reliable because its CI passed through zero. For DFOP not fully reliable was k_1 , for which the *prob. > t* was higher than 0.05.

Analysing the fits RMS stated that the better fitting results for both bi-phasic models was most probably caused by the fact, that the DAT-0 concentration was adjusted to the procedural recovery, significantly higher than the concentration measured at the next time point – DAT 0.25

As a result, the Applicant stated that SFO model shall be considered as returning the appropriate fit for FOE Thiadone in Iowa Loamy sand soil and hence appropriate to derive persistence and modelling endpoints for that compound in that test soil. RMS accepted that proposal noticing that the compound was very short-living in soil, therefore bi-phasic kinetic behaviour would be hardly explicable in this case.

2) The results of the kinetic analysis of the data obtained for FOE Thiadone in Indiana sandy loam soil.

The results of the kinetic analysis performed by the Applicant are presented below, in graphical form on figure B.8.1.1.2.1.1._CA-136 and in numerical form in the table B.8.1.1.2.1.1._CA-250. Additionally the table B.8.1.1.2.1.1._CA-251 provides the kinetic endpoints obtained with each of the kinetic models tested.

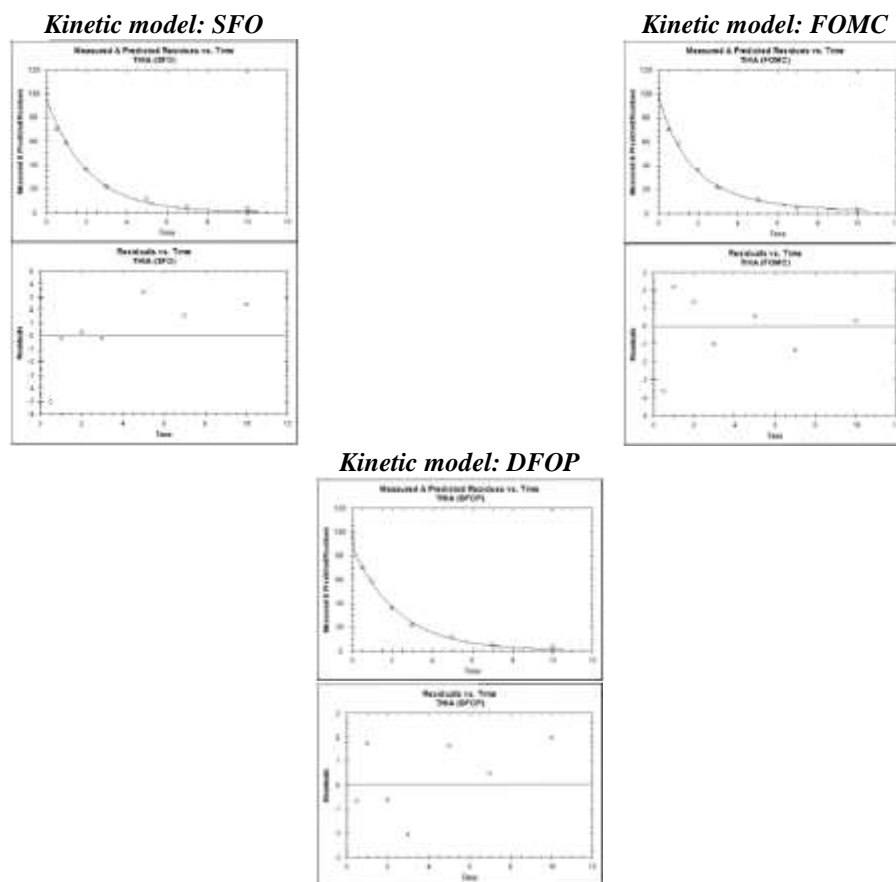


Figure B.8.1.1.2.1.1._CA-136: The graphical results of the kinetic analysis (copied from the study report).

Table B.8.1.1.2.1.1._CA-250: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment ¹⁾
				Lower	Upper			
SFO	M_0	95.989	2.660	90.775	101.203	1.51 E-8	5.67	0.994; Acceptable fit
	k	0.4945	0.03176	0.4323	0.557	2.22 E-6		
FOMC	M_0	98.351	2.113	94.210	102.493	4.32 E-8	3.933	0.997; Good fit
	α	3.6089	1.3854	0.8935	6.324	0.0240		
	β	5.9648	2.7677	0.5401	11.389	0.0419		
DFOP	M_0	99.60	1.548	96.57	102.634	1.75 E-7	3.277	0.999; Good fit
	k_1	28.85	931.1	-1796	1853.682	0.4884		
	k_2	0.4372	0.02621	0.3859	0.489	3.79 E-5		
	g	0.1186	0.0342	0.05153	0.186	0.0128		

Footnotes to the table:

1) Visual assessment of the kinetic curve as proposed by the Applicant.

Table B.8.1.1.2.1.1._CA-251: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested		
		<i>SFO</i>	<i>FOMC</i>	<i>DFOP</i>
<i>FOE Thiadone</i>	DT ₅₀ [days]	1.40	2.93	1.30
	DT ₉₀ [days]	4.66	9.76	4.98

Conclusion:

FOMC and DFOP models returned fits that were classified by the Applicant as visually good. The fit returned by SFO model was classified as acceptable, mainly because of the levels of residuals and their distribution. All three fits were statistically reliable – the χ^2 level for them was well below the threshold value of 15%.

The Applicant indicated the SFO model fit as returning the appropriate fit for determining the kinetic endpoints representing persistence and suitable for modelling.

RMS analysing the results stated that DFOP fit cannot be considered acceptable, because it returned not reliable kinetic parameters. The problem concerned the rate constant k_1 , for which the *prob.* > *t* was very close to 0.5.

FOMC fit was fully reliable.

It shall be pointed out that the inspection of the visual fit performed by the RMS led to the conclusion that also SFO fit should be classified as good.

The better representation of the kinetic behaviour of FOE Thiadone in the test soil by the bi-phasic models may be caused by the fact that the DAT-0 concentration was adjusted to the procedural recovery. Also it shall be noted that for so short-living compound bi-phasic kinetic behaviour is not fully understandable.

The Applicant, indicating that SFO fit was reliable, proposed to consider it as appropriate for deriving persistence and modelling endpoints for FOE Thiadone in Indiana Sandy loam soil. RMS accepted that proposal.

3) The results of the kinetic analysis of the data obtained for FOE Thiadone in Nebraska silt loam soil.

The results of the kinetic analysis performed by the Applicant are presented below, in graphical form on figure B.8.1.1.2.1.1._CA-137 and in numerical form in the table B.8.1.1.2.1.1._CA-252. Additionally the table B.8.1.1.2.1.1._CA-253 provides the kinetic endpoints obtained with each of the kinetic models tested.

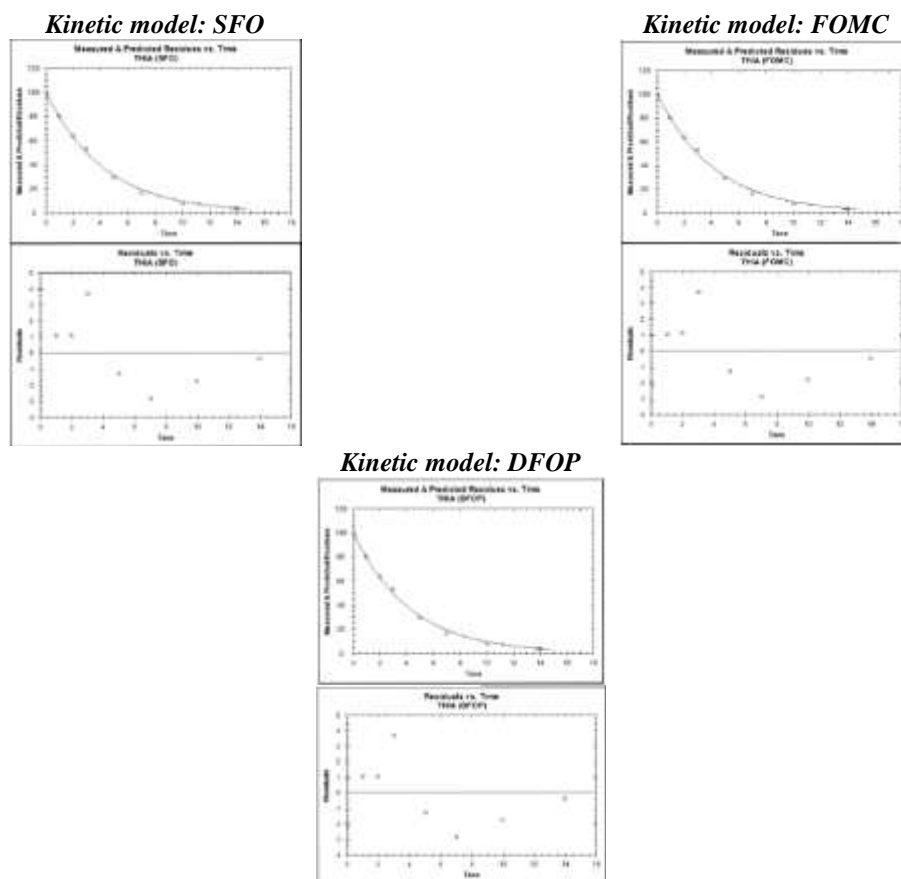


Figure B.8.1.1.2.1.1._CA-137: The graphical results of the kinetic analysis (copied from the study report).

Table B.8.1.1.2.1.1._CA-252: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment ¹⁾
				Lower	Upper			
SFO	M_0	100.6	1.922	96.84	104.377	1.63 E-9	3.709	0.996; Acceptable fit
	k	0.2363	8.967 E-3	0.2187	0.254	9.85 E-8		
FOMC	M_0	100.646	2.089	96.552	104.7	3.64 E-8	4.006	0.996; Acceptable fit
	α	237.143	9.774	217.985	256.3	1.11 E-6		
	β	1000.695	4.228	992.409	1009.0	1.28 E-11		
DFOP	M_0	100.610	8.183	84.571	116.648	1.26 E-3	4.273	0.996; Acceptable fit
	k_1	0.2363	0.01784	0.2013	0.271	9.39 E-5		
	k_2	0.2363	0.3316	-0.4135	0.886	0.2577		
	g	0.9520	2.5414	-4.0291	5.933	0.3635		

Footnotes to the table:

1) Visual assessment of the kinetic curve as proposed by the Applicant.

Table B.8.1.1.2.1.1._CA-253: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested		
		<i>SFO</i>	<i>FOMC</i>	<i>DFOP</i>
<i>FOE Thiadone</i>	DT ₅₀ [days]	2.93	2.93	2.93
	DT ₉₀ [days]	9.74	9.76	9.74

Conclusion:

All three models returned first that were statistically reliable – the χ^2 error for them was well below 15%, but the Applicant classified them as only acceptable in terms of visual assessment. RMS however is of the opinion that all three may be classified as visually good fits.

Of the three SFO was superior, displaying the lowest level of χ^2 error.

RMS also noticed that DFOP fit cannot be classified as acceptable because of the lack of reliability of its two kinetic parameters – k_2 and g , for which the *prob. > t* was higher than 0.1.

As a result it may be stated that the Applicant's proposal to consider SFO fit as appropriately representing persistence of FOE Thiadone in Nebraska Silt loam soil and appropriate for deriving modelling endpoints is acceptable.

Final conclusion of the study:

On the basis of the results of the kinetic analysis presented above was determined the definitive set of the reliable kinetic parameters, presented below in the table B.8.1.1.2.1.1._CA-254.

Table B.8.1.1.2.1.1._CA-254: The definitive set of the kinetic endpoints determined in the study.

Soil		Soil properties		Incubation conditions	Selected best-fit model	Evaluation of the fit		Kinetic parameters		Kinetic endpoints	
<i>Soil name</i>	<i>Soil type (USDA)</i>	<i>OC [%]</i>	<i>pH¹⁾</i>			χ^2 error	<i>Visual fit²⁾</i>	<i>Par.</i>	<i>Value</i>	<i>DT₅₀ [days]</i>	<i>DT₉₀ [days]</i>
<i>Iowa</i>	Loamy sand	1.11	7.2	20.1 ± 1°C; 75% of ½ bar	SFO	6.72	A	<i>k</i>	0.3494	1.98	6.59
<i>Indiana</i>	Sandy loam	0.74	6.5	20.1 ± 1°C; 75% of ½ bar	SFO	5.67	A	<i>k</i>	0.4945	1.40	4.66
<i>Nebraska</i>	Silt loam	0.96	7.7	20.1 ± 1°C; 75% of ½ bar	SFO	3.71	A	<i>k</i>	0.2363	2.93	9.74

Footnotes to the table:

- 1) Measuring medium not given;
- 2) The abbreviations used to describe the visual fit: G. – good, A. – acceptable, P. – poor;

Study 19:

Report: Eckermann N., (2012): “[1-¹⁴C]Trifluoroacetate: Aerobic Degradation in Four European Soils.”; Bayer CropScience AG, BCS-D-EnSa-Testing, 40789 Monheim, Germany; unpublished Study Report No. EnSa-12-0393; 2012. 09. 26; study reference number: M-439283-01-1;

Guidelines: The study was performed to comply with the following Guidelines:

- OECD Guideline for the Testing of Chemicals, No. 307, Aerobic and Anaerobic Transformation in Soil, 2002;
- US. EPA OCSPP Fate, Transport and Transformation Test Guidelines, OPPTS 835.4100 and OPPTS 835.4200, Aerobic and Anaerobic Soil Metabolism, 2008.

Additionally, as the data obtained in the study were kinetically evaluated and the results presented in the study report, it was declared that the following Guideline was used:

- FOCUS (2006): “Guidance Document on Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration.” Report of the FOCUS Work Group on Degradation Kinetics, EC Document Reference SANCO/10058/2005 version 2.0, 434 pp.;

GLP: Yes

RMS comments: This is a new study, submitted specifically for purpose of this assessment. It was verified by the RMS and found acceptable. However, as the full results of the kinetic analysis were presented for only one test soils, considered to be a representative example, RMS had to repeat the kinetic assessment, because it was not possible to fully verify that performed by the Applicant. As a result, RMS decided not to take into account and present in the summary the Applicant’s results, replacing them with those obtained during repeated assessment. The study is summarised below.

Summary:

The aim of the study was to examine the degradation TFA (Trifluoroacetic acid) – a major soil degradation product of Flufenacet, in aerobic soil. The experiment was performed on four EU-soils, used in other studies examining the degradation of Flufenacet and its degradation products in soil. The test soils were taken from the agriculturally used areas, representing different geographical origin and different soil properties, in line with the requirement of the relevant Guideline. The characteristic of the test soils is provided below in the table B.8.1.1.2.1.1._CA-255.

Table B.8.1.2.1.1.CA-255: The characteristic of soils used in the study.

Parameter		Soil			
		<i>Laacher Hof AXxa</i>	<i>Dollendorf II</i>	<i>Hoefchen Am Hohenseh 4a</i>	<i>Laacher Hof Wurmweise</i>
Soil origin		Monheim/ North Rhine-Westphalia /Germany	Blankenheim/ North Rhine-Westphalia /Germany	Burscheid/ North Rhine-Westphalia /Germany	Monheim/ North Rhine-Westphalia /Germany
Soil type (USDA)		Sandy loam	Clay loam	Silt loam	Sandy loam
Particle size distribution	Sand [%]	77	29	25	57
	Silt [%]	14	40	60	26
	Clay [%]	9	31	15	17
pH value	in 0.01M CaCl ₂ (1:2)	6.2	7.3	6.4	5.1
	in H ₂ O (1:1)	6.5	7.5	6.7	5.4
	in 1M KCl (1:1)	6.0	7.1	6.1	4.7
Organic Carbon content (OC) [%]		1.6	5.5	2.4	1.9
Organic Matter content (OM) [%]		2.8	9.5	4.1	3.3
Cation Exchange Capacity – CEC [mEq/100g]		8.7	21.2	13.6	10.0
Water holding capacity [g H ₂ O/ 100 g soil d. w.]	MWHC	46.9	84.9	62.0	57.6
	at pF 2.5 (0.33 bar)	12.9	34.9	26.3	18.2
Soil bulk density (disturbed) [g/cm ³]		1.26	0.97	1.08	1.13
Soil biomass [mg microbial C/ kg soil] ²⁾	DAT-0	536	2930	833	423
	DAT-59	589	3344	844	459
	DAT-120	248	1412	387	424
Soil biomass [% OC] ³⁾	DAT-0	3.35	5.33	3.47	2.22
	DAT-59	3.68	6.08	3.52	2.42
	DAT-120	1.55	2.57	1.61	2.23

Footnotes to the table:

- 1) Determined using the SIR method developed by Anderson & Domsch [1978];
- 2) Values recalculated by the RMS using the OC content reported in the table for each test soil.

The test soils were sampled shortly before being used (14 days before the experiment began) with shovel from 0-20 cm layer of grassland plot. No Plant Protection Products were used on the sampling field for 5 years preceding sampling. The samples of the test soils were transported to the test facility in plastic bags. There they were sieved through 2-mm sieve and stored in the darkness at either $T < 8^{\circ}\text{C}$ or $T = 20^{\circ}\text{C}$ until being used.

The experiment was performed using biometer flasks, presented below on figure B.8.1.1.2.1.1_CA-138, containing 100-g portions of the test soils.

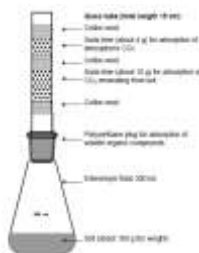


Figure B.8.1.1.2.1.1_CA-138: The biometer flask used in the experiment (copied from the study report).

The experiment started with weighing 100-g (d. w.) portions of the test soil into 300-mL Erlenmeyer test flasks. Next soil in each flask was brought to the designated level of moisture content – 55% MWHC, by addition of the appropriate amount of distilled water. Then the flasks were weighed and pre-incubated in incubation chamber, in the dark at constant temperature $T = 20.0 \pm 0.1^{\circ}\text{C}$, over weekend.

After that period soil in each biometer flask was treated with the test compound.

The test compound used in the experiment was the radiolabelled trifluoroacetic acid in form of its sodium salt. The reason for that was the fact that Trifluoroacetic acid has $pK_a = 1.3$, therefore under environmental conditions it occurs in deprotonated form – as trifluoroacetate (CF_3COO^-). For that reason sodium salt was selected as the relevant deprotonated species. The structural formula of the test compound is presented below on figure B.8.1.1.2.1.1. CA-139. The radiolabelling position is marked with asterisk (*). The test compound had specific activity of 3.48 MBq/mg (94.04 $\mu Ci/mg$) and radiochemical purity, determined by radio-HPLC, of > 98 - 99%. It was delivered to the test facility as a solid sample.

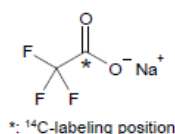


Figure B.8.1.1.2.1.1_CA-139: The structural formula of the test compound used in the experiment (copied from the study report).

The whole delivered sample of the test compound was used to make the **Stock solution**, from which the **Application solution** was prepared. The **Stock solution** was prepared by dissolving the test compound in 11.7 mL of ultrapure water. The so prepared solution had a concentration, expressed in radioactivity units, of 74.1 kBq/mL and radiochemical purity (determined by HPLC) > 99%. The **Stock solution** was stored in the dark, in a freezer until being used.

The **Application solution** was prepared by diluting 2.4 mL of the **Stock solution** with 117.6 mL of ultrapure water to obtain a solution having a concentration 20 µg/mL. That solution was used to treat test soils in biometer flasks. The amount of the **Application solution**, applied in small droplets to the soil surface using 1000-µL

pipette, was 1 mL. That amount resulted in the soil concentration of the test compound 0.2 mg/kg (0.02 mg/100 g soil d.w.). It was determined using the following assumptions:

- field application rate of Flufenacet: 250 g/ha;
- maximum formation level of TFA: 25%;
- molar mass ratio TFA/Flufenacet: 0.3;
- soil bulk density: 1.5 g/cm³;
- depth of the soil layer: 2.5 cm
- factor for increase of application rate: 4.

That factor was declared to be introduced to compensate the analytical limitations. It shall be noted however that the actual formation level of TFA is significantly higher than the proposed 25% and, on the basis of the results of the studies examining the route of degradation of Flufenacet in soil, is expected to reach the level of 75-100% of the applied parent compound, therefore the introduced factor corrected the inaccurate assumption concerning the level of formation of TFA from Flufenacet.

RMS analysing the calculations noticed that the assumed soil layer was ½ of that routinely used to calculate field application rate (in [g/ha]). Therefore the would-be application rate for TFA-Na was recalculated using the standard assumptions:

- soil bulk density: 1.5 g/cm³;
- thickness of the soil layer: 5 cm.

The so calculated theoretical field application rate **A = 150 g TFA-Na/ha**.

Using the measured soil bulk density of each test soil used in the experiment that value would be:

- for Laacherhof AXXa soil: **A = 126 g/ha**;
- for Dollendorf II soil: **A = 97 g/ha**;
- for Höfchen am Hohenseh 4a soil: **A = 108 g/ha**;
- for Wurmweise soil: **A = 113 g/ha**

The level of application and its homogeneity was verified at the beginning, in the middle and at the end of the application procedure, by verification of the concentration of the **Application solution**. For that purpose its 1-mL samples were diluted with ultrapure water to 25- mL and analysed by LSC.

For treatment the pre-incubated biometric flasks were removed from the incubation chamber. After application of the test compound the vessels, except those designated as DAT-0 samples, were fitted with the traps for volatile compounds and returned to incubation chamber to be incubated at constant temperature $T = 20.0 \pm 0.1^{\circ}\text{C}$ and soil moisture level $55 \pm 5\%$ MWHC for up to 120 days. At the designated time points – DAT 3, DAT 7, DAT 14, DAT 28, DAT 34, DAT 59, DAT 92 and DAT 120, duplicate samples of each test soil were removed from the incubation chamber and further processed. At the same time points the soil moisture content was checked and corrected if necessary. That was done by weighing the test vessels without the traps for volatile compounds, calculating the loss of water and, when necessary, readjusting the water content to the designated level by adding the appropriate amount of water.

The samples collected at each sampling point were processed and analysed entirely. The processing of the collected samples followed the procedure presented below on figure B.8.1.1.2.1.1_CA-140. Firstly the biometer flask were placed in a dessicator and the volatile compounds possibly present in the headspace above soil surface were transferred to the trap by evaporating the entire system. Then the flasks were dissected, traps stored for further analysis and soil samples extracted entirely. The extracted soil pellets were freeze-dried, homogenised and analysed for the content of NER fraction.

The recovered traps for volatile compounds were dissected into the PU (Polyurethane Foam) plugs and soda lime traps.

The VOCs possibly retained in PU plugs were extracted by shaking plugs with 50 mL of $\text{CH}_3\text{COC}_2\text{H}_5$. 5-mL aliquots of the obtained extracts were analysed firstly by LSC and then, if necessary, chromatographically.

The soda-lime traps for $^{14}\text{CO}_2$ formed in the experiment were processed in a way identical to that described in details in the summaries of the route-of-degradation studies by [Pangilinan and Smith; 1994a] (aerobic soil route-of-degradation **Study 4**) and by [Kasper and Shadrick; 1995] (soil photolysis **Study 1**), but used also in other studies examining the degradation of Flufenacet in soil under aerobic conditions – e.g. studies [Hein; 2012] (aerobic soil route-of-degradation **Study 5**) and [Hein; 2012 a] (aerobic soil route-of-degradation **Study 6**). The released $^{14}\text{CO}_2$ was absorbed in a scintillation cocktail and analysed by LSC.

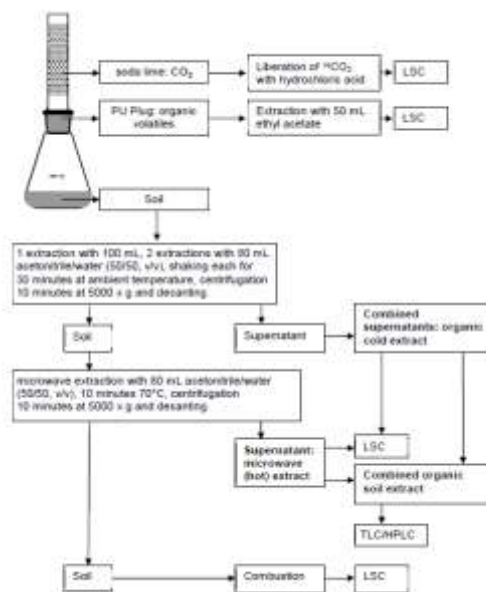


Figure B.8.1.1.2.1.1._CA-140: The sample-processing procedure used in the experiment (copied from the study report).

The extracted soil pellets were analysed for the content of NER fraction. To do that each soil sample was allowed to air-dry overnight, after what its triplicate aliquots (50 – 100 mg) were oxidized by combustion. The formed $^{14}\text{CO}_2$ was trapped in alkaline solution which, after mixing with scintillation cocktail, was analysed by LSC. The further characterisation of NER fraction was not performed, because of its low content – max. 13.5% AR.

All samples were analysed for the content of radioactivity using LSC method. The LSC (Liquid Scintillation Counting) analysis was performed using LS 6500 (Beckmann) or LKB-Wallac 1219 Spectral (Perkin Elmer Life Science) counters.

The radioactivity in solutions was determined in either:

- mini-vials, using the sample aliquots of up to 0.5 mL and 2 mL of Quicksafe® A solution containing 5% of water; the counting was performed using LS 6500 counter, the counting efficiency was 83.07 – 91.01% and the background 13 – 16 cpm;
- maxi-vials, using the sample aliquots of up to 7 mL and 7 mL of Quicksafe® A solution containing 5% of water; the counting was performed using LKB-Wallac 1219 Spectral counter, the counting efficiency was 70.4 – 88.5% and the background 22 – 23 cpm.

The $^{14}\text{CO}_2$ recovered from soda lime was absorbed in 15 mL of Oxysolve C400 and analysed quantitatively using LKB-Wallac 1219 Spectral counter. The counting efficiency was 70.4 – 88.5% and the background 17 – 20 cpm.

The radioactivity in extracts from PU plugs was determined in the same way as in other liquid samples (see above).

The radioactivity in solid samples – extracted soil pellets, was determined after combustion of three 1-g aliquots of dried and homogenised material. The resulting $^{14}\text{CO}_2$ was absorbed in 15 mL of Oxysolve C400 scintillation cocktail and analysed quantitatively using LKB-Wallac 1219 Spectral counter. The counting efficiency was 70.4 – 88.5% and the background 17 – 20 cpm.

The combined organic soil extracts were subjected to chromatographic analysis performed as either:

- radio-TLC analysis – the primary identification and quantitation method used in the study;
- HPLC analysis with radio- and MS detection – conformatory method for TLC analysis.

The TLC analysis was performed on silica gel plates – Si60, F_{254} , 20 cm x 20cm, developed in a chromatographic chamber without solvent saturation, using the following mobile phase:

ethyl acetate/2-propanol/ultrapure water/glacial acetic acid 65:24:11:1 (v/v/v/v). The volume of the analysed sample injected onto the plate was 20 µL. The distribution and quantitation of the radioactivity zones was determined using Bio-Imaging Analyzer BAS 2000, Fuji, Co.

The identification was performed using LC-MS or LC-MS/MS methods characterised below, but the additional identification method was the comparison of the R_f values of the radioactivity zones with those of the known standards, chromatographed in parallel.

The LC/MS analysis was performed using Agilent HP 1100 instrument equipped with Nucleodur C18 Gravity 250 x 2 mm, 3 µm, chromatographic column and UV detector, coupled to Ramona Star radioactivity detector and LTQ Orbitrap XL MS detector. The chromatographic analysis was performed in a gradient mode using a gradient programme presented below in the table B.8.1.1.2.1.1._CA-256. The flow rate was 0.2 mL/min and elution lasted for 35 minutes. The changes in the gradient of mobile phase were linear.

Table B.8.1.1.2.1.1._CA-256: The gradient mode used in the LC-MS analysis.

Time [min]	Solvent ratio	
	<i>Solvent A – Water + 0.1% HCOOH</i>	<i>Solvent B – CH₃CN + 0.1% HCOOH</i>
0	95	5
1	95	5
25	5	95
35	5	95

The method was used to conform the identity of the test compound in application solution and in selected organic extracts.

The radio-RP-HPLC method was used to check the purity of the **Stock solution** and to conform the results of the TLC analysis in selected extracts – the DAT-120 combined organic extracts.

The analysis was performed using Agilent 1100/1200 HPLC instrument equipped with Purospher Star RP18-e 250 x 4.6 mm, 5 µm, chromatographic column preceded by Purospher Star RP18-e 4 x 4 mm, 5 µm guard column, a column oven set to T = 40°C and Agilent VW detector set at $\lambda = 254$ nm. The chromatographic station was coupled with Ramona Star, Raytest, flow-through LS detector.

The elution was performed in a gradient mode, using one of the following two methods:

- Flurtaboden, used to check purity of the **Stock solution**;
 - “KOE78_TFA, used to conform the results of the TLC analysis of DAT-120 combined organic extracts.
- Both methods are characterised below, in the table B.8.1.1.2.1.1._CA-257.

Table B.8.1.1.2.1.1._CA-257: The gradient modes used in the radio-RP-HPLC analysis.

Method 1: “Flurtaboden”		
Time [min]	Solvent ratio	
	<i>Solvent A – Water + 1% HCOOH + 5 mM HCCONH₄</i>	<i>Solvent B – CH₃CN + 1% HCOOH + 5 mM HCCONH₄</i>
0	100	0
5	100	0
10	90	10
35	5	95
40	5	95
45	100	0
55	100	0
Method 1: “KOE78-TFA”		
Time [min]	Solvent ratio	
	<i>Solvent A – Water + 1% HCOOH</i>	<i>Solvent B – CH₃CN + 1% HCOOH</i>
0	100	0
5	100	0
10	90	10
35	5	95
40	5	95
45	100	0
55	100	0
60	100	0

The obtained results are presented below. The determined concentrations of TFA in soil were subjected to the kinetic analysis performed in line with the recommendations given by FOCUS [2006].

Results and their discussion:

The examination of the microbial viability of the test soils showed that they were viable throughout the whole experiment. The detailed results are shown in the table B.8.1.1.2.1.1._CA-255.

The monitoring of incubation temperature showed that the samples were kept in the constant temperature $T = 20 \pm 1^{\circ}\text{C}$. The mean incubation temperature was $T = 20.0^{\circ}\text{C}$ and it ranged from $T = 19.8^{\circ}\text{C}$ to $T = 20.4^{\circ}\text{C}$. The results of the monitoring of the temperature in the incubation chamber are shown below, in the graphical form, on figure B.8.1.1.2.1.1._CA-141.

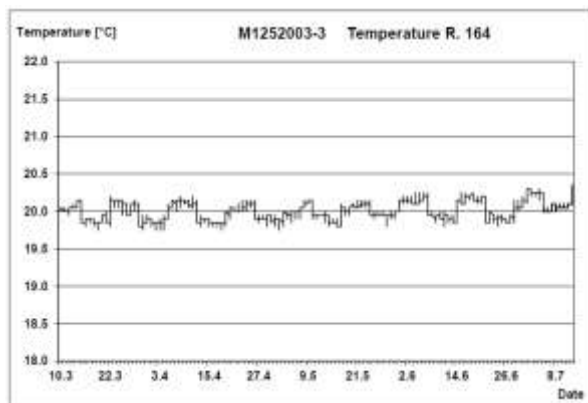


Figure B.8.1.1.2.1.1._CA-141: The temperature recorded in incubation chamber during the experiment (copied from the study report).

The results of the determination of the soil moisture are presented below in the table B.8.1.1.2.1.1._CA-258. These values were subsequently used in normalisation procedure.

Table B.8.1.1.2.1.1._CA-258: The results of the determination of soil moisture content.

Test soil		Soil moisture [g H ₂ O/100 g soil d. w.]			Water addition [ml H ₂ O/100 g soil d. w.]
Soil name	Soil type (USDA)	Actual (air-dried, sieved through 2-mm sieve)	at MWHC	at 55% MWHC	
<i>Laacher Hof AXXa</i>	Sandy loam	16.1	46.9	25.8	10
<i>Dololendorf II</i>	Clay loam	37.5	84.9	46.7	9
<i>Laacher Hof Wurmweise</i>	Silt loam	19.9	57.6	31.7	12
<i>Hoefchen Am Hohenseh 4a</i>	Sandy loam	24.7	62.0	34.1	9

The results of the verification of the application rate and homogeneity of application are presented below in the table B.8.1.1.2.1.1._CA-259. On the basis of the obtained results the value of 72697 Bq, corresponding to 20.89 µg of ¹⁴C equivalents, was regarded as 100% AR for all calculations.

Table B.8.1.1.2.1.1._CA-259: The results of verification of application rate and homogeneity of application.

Sample No.	Sample volume [mL]		Radioactivity [Bq]		¹⁴ C equivalents [µg]
	Total sample volume	Volume of LSC aliquot	Measured in LSC-aliquot	Total in sample	
1	25	0.5	1449.33	72467	20.82
2	25	0.5	1451.01	72551	290.85
3	25	0.5	1451.65	72233	20.76
4	25	0.5	1451.67	72548	20.86
5	25	0.5	1458.26	72913	20.95
6	25	0.5	1446.78	72339	20.79
7	25	0.5	1459.32	72966	20.97
8	25	0.5	1462.91	73146	21.02
9	25	0.5	1461.47	73074	21.00
Mean value				72697	20.89
SD				334	0.10
RSD [%]				----	0.46

The determination of the LOD and LOQ values for LSC and chromatographic analyses resulted in following values:

- the instrumental LOD and LOQ values for LSC analysis were: LOD = 2 times maximum instrument background count rate (0.25 Bq) and LOQ = three times maximum instrument background count rate (0.4 Bq);
- for liquid samples in 2 mL of Quicksafe A scintillation cocktail (mini-vials) LOD = 0.5 Bq and LOQ = 0.8 Bq;
- for liquid samples in 7 mL of Quicksafe A scintillation cocktail (maxi-vials) LOD = 0.8 Bq and LOQ = 1.2 Bq;
- for combustion samples LOD = 0.7 Bq and LOQ = 1.0 Bq;

As a result the corresponding values for entire extracts (worst case) were:

- for organic cold extracts, having volume of 256 mL, LOD = 256 Bq and LOQ = 384 Bq;
- for organic microwave extracts, having volume of 80 mL, LOD = 90 Bq and LOQ = 135 Bq;
- for combustion samples LOD = 80 Bq and LOQ = 121 Bq.

When expressed as % AR that corresponded to LOD < 0.4% AR and LOQ < 0.5% AR for all types of samples.

In case of TLC analysis the determined for combined organic extracts LOD = 0.7% AR and LOQ = 2.1 % AR (3*LOD).

The overview of the key results obtained in the experiment is presented below in the table B.8.1.1.2.1.1._CA-260. The detailed results of the experiment are presented further down the report.

Table B.8.1.1.2.1.1._CA-260: The key results obtained in the study.

Test soil		Determined parameter:				
Soil name	Soil type (USDA)	Total recovery (range) [% AR]	Radioactivity extracted (range) [% AR]	Maximum level of volatiles formed [% AR]	NER level (range) [% AR]	Extraction efficiency on DAT 0 [%]
Laacher Hof AXXa	Sandy loam	98.2 – 102.1	97.5 – 101.4	0.1	0.6 – 0.9	97.7
Dollendorf II	Clay loam	97.8 – 101.9	96.4 – 100.2	0.1	1.2 – 2.0	98.4
Laacher Hof Wurmweise	Silt loam	97.0 – 100.9	95.9 – 99.7	0.1	1.0 – 1.3	98.7
Hoefchen Am Hohenseh 4a	Sandy loam	98.2 – 103.4	97.0 – 102.1	0.1	0.9 – 1.3	99.2

The detailed numerical results of the experiment are presented below, individually for each test soil, in tables B.8.1.1.2.1.1._CA-261 – B.8.1.1.2.1.1._CA-264.

Table B.8.1.1.2.1.1._CA-261: The numerical results of the experiment performed on Laacher Hof AXXa Sandy loam soil.

Radioactivity			Measured on DAT ¹⁾								
			0	3	7	14	28	43	59	92	120
In extract [%AR]	Ambient extract	Rep. 1	96.2	98.0	99.2	98.1	95.8	98.3	99.0	99.7	95.9
		Rep 2.	95.9	97.9	98.4	98.5	95.4	97.8	99.3	99.0	97.0
		Mean	96.1	98.0	98.8	98.3	95.6	98.0	99.1	99.4	96.5
	Microwave extract	Rep. 1	1.6	1.8	1.6	1.8	1.9	1.9	2.3	2.0	2.1
		Rep 2.	1.6	1.7	1.7	2.0	1.9	1.9	2.0	2.0	2.1
		Mean	1.6	1.7	1.7	1.9	1.9	1.9	2.1	2.0	2.1
	Total extracted	Rep. 1	97.8	99.8	100.9	99.9	97.7	100.2	101.3	101.7	98.0
		Rep 2.	97.5	99.6	100.1	100.5	97.3	99.6	101.3	101.0	99.2
		Mean	97.7	99.7	100.5	100.2	97.5	99.9	101.3	101.4	98.6
In extract, identified as [% AR]:	[1- ¹⁴ C] trifluoroacetate	Rep. 1	97.8	99.8	100.9	99.9	97.7	100.2	101.3	101.7	98.0
		Rep 2.	97.5	99.6	100.1	100.5	97.3	99.6	101.3	101.0	99.2
		Mean	97.7	99.7	100.5	100.2	97.5	99.9	101.3	101.4	98.6
	Unidentified/ Diffused radioactivity	Rep. 1	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
		Rep 2.	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
		Mean	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	Total extractable residues	Rep. 1	97.8	99.8	100.9	99.9	97.7	100.2	101.3	101.7	98.0
		Rep 2.	97.5	99.6	100.1	100.5	97.3	99.6	101.3	101.0	99.2
		Mean	97.7	99.7	100.5	100.2	97.5	99.9	101.3	101.4	98.6
Volatile compounds:	CO ₂	Rep. 1	n. a. ³⁾	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
		Rep 2.	n. a. ³⁾	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
		Mean	n. a. ³⁾	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
	VOC ²⁾	Rep. 1	n. a. ³⁾	<0.1	<0.1	0.2	<0.1	<0.1	<0.1	<0.1	<0.1
		Rep 2.	n. a. ³⁾	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
		Mean	n. a. ³⁾	<0.1	<0.1	0.1	<0.1	<0.1	<0.1	<0.1	<0.1
	Total volatiles	Rep. 1	n. a. ³⁾	<0.1	<0.1	0.2	<0.1	<0.1	<0.1	<0.1	<0.1
		Rep 2.	n. a. ³⁾	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
		Mean	n. a. ³⁾	<0.1	<0.1	0.1	<0.1	<0.1	<0.1	<0.1	<0.1
NER fraction [% AR]		Rep. 1	0.6	0.6	0.8	0.7	0.7	0.9	0.7	0.7	0.8
		Rep 2.	0.6	0.6	0.8	0.6	0.7	0.9	0.9	0.6	0.8
		Mean	0.6	0.6	0.8	0.6	0.7	0.9	0.8	0.7	0.8
Total radioactivity recovered [% AR]		Rep. 1	98.4	100.5	101.7	100.8	98.4	101.1	101.9	102.4	98.8
		Rep 2.	98.1	100.3	100.9	101.1	98.1	100.6	102.2	101.7	100.0
		Mean	98.2	100.4	101.3	101.0	98.2	100.9	102.1	102.1	99.4

Footnotes to the table:

- 1) DAT = Days After Treatment;
- 2) VOC = Volatile Organic Compounds;
- 3) n. a. = not analysed – at that time point no volatiles were expected to be formed;
- 4) n. d = not detected.

Table B.8.1.1.2.1.1._CA-262: The numerical results of the experiment performed on Dollendorf II Clay loam soil.

Radioactivity			Measured on DAT ¹⁾								
			0	3	7	14	28	43	59	92	120
In extract [%AR]	Ambient extract	Rep. 1	95.9	96.1	98.2	96.9	93.5	96.5	97.8	97.3	93.4
		Rep 2.	95.8	98.5	97.5	97.0	94.2	97.4	96.6	97.2	94.1
		Mean	95.9	97.3	97.8	96.9	93.9	96.9	97.2	97.2	93.8
	Microwave extract	Rep. 1	2.5	2.5	2.4	2.5	2.5	2.6	2.8	2.9	2.7
		Rep 2.	2.5	2.5	2.3	2.5	2.5	2.3	2.8	3.0	2.7
		Mean	2.5	2.5	2.4	2.5	2.5	2.4	2.8	3.0	2.7
	Total extracted	Rep. 1	98.5	98.6	100.5	99.4	96.0	99.1	100.5	100.3	96.1
		Rep 2.	98.3	101.0	99.9	99.5	96.7	99.6	99.5	100.2	9.68
		Mean	98.4	99.8	100.2	99.4	96.4	99.4	100.0	100.2	96.4
In extract identified as [% AR]:	[1- ¹⁴ C] trifluoroacetate	Rep. 1	98.5	98.6	100.5	99.4	96.0	99.1	100.5	100.3	96.1
		Rep 2.	98.3	101.0	99.9	99.5	96.7	99.6	99.5	100.2	96.8
		Mean	98.4	99.8	100.2	99.4	96.4	99.4	100.0	100.2	96.4
	Unidentified/ Diffused radioactivity	Rep. 1	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
		Rep 2.	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
		Mean	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	Total extractable residues	Rep. 1	98.5	98.6	100.5	99.4	96.0	99.1	100.5	100.3	96.1
		Rep 2.	98.3	101.0	99.9	99.5	96.7	99.6	99.5	100.2	96.8
		Mean	98.4	99.8	100.2	99.4	96.4	99.4	100.0	100.2	96.4
Volatile compounds:	CO ₂	Rep. 1	n. a. ³⁾	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
		Rep 2.	n. a. ³⁾	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
		Mean	n. a. ³⁾	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
	VOC ²⁾	Rep. 1	n. a. ³⁾	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
		Rep 2.	n. a. ³⁾	0.1	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
		Mean	n. a. ³⁾	<0.1	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
	Total volatiles	Rep. 1	n. a. ³⁾	<0.1	0.1	0.1	<0.1	<0.1	<0.1	<0.1	<0.1
		Rep 2.	n. a. ³⁾	0.1	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
		Mean	n. a. ³⁾	0.1	0.1	0.1	<0.1	<0.1	<0.1	<0.1	<0.1
NER fraction [% AR]		Rep. 1	1.3	1.2	1.2	1.3	1.4	1.6	1.7	1.6	2.0
		Rep 2.	1.4	1.2	1.4	1.3	1.5	1.8	1.9	1.8	2.1
		Mean	1.3	1.2	1.3	1.3	1.4	1.7	1.8	1.7	2.0
Total radioactivity recovered [% AR]		Rep. 1	99.8	99.8	101.8	100.8	97.4	100.7	102.2	101.9	98.1
		Rep 2.	99.7	102.3	101.4	100.8	98.2	101.4	101.3	102.0	98.8
		Mean	99.7	101.0	101.6	100.8	97.8	101.1	101.8	101.9	98.5

Footnotes to the table:

- 1) DAT = Days After Treatment;
- 2) VOC = Volatile Organic Compounds;
- 3) n. a. = not analysed – at that time point no volatiles were expected to be formed;
- 4) n. d. = not detected.

Table B.8.1.1.2.1.1. CA-263: The numerical results of the experiment performed on Laacher Hof Wurmwielse Silt loam soil.

Radioactivity			Measured on DAT ¹⁾								
			0	3	7	14	28	43	59	92	120
In extract [%AR]	Ambient extract	Rep. 1	96.7	98.0	97.6	97.3	94.2	97.8	97.8	97.3	94.7
		Rep 2.	97.0	97.6	97.8	96.8	93.4	97.2	96.4	96.6	95.9
		Mean	96.8	97.8	97.7	97.0	93.8	97.5	97.1	96.9	95.3
	Microwave extract	Rep. 1	1.8	1.9	2.0	2.3	2.1	2.1	2.8	2.7	2.3
		Rep 2.	1.9	1.9	2.0	2.0	2.1	2.3	2.4	2.8	2.4
		Mean	1.8	1.9	2.0	2.1	2.1	2.2	2.6	2.7	2.3
	Total extracted	Rep. 1	98.4	99.9	99.6	99.6	96.3	99.9	100.6	100.0	97.0
		Rep 2.	98.9	99.5	99.8	98.8	95.5	99.4	98.9	99.3	98.2
		Mean	98.7	99.7	99.7	99.2	95.9	99.6	99.7	99.7	97.6
In extract identified as [% AR]:	[1- ¹⁴ C] trifluoroacetate	Rep. 1	98.4	99.9	99.6	99.6	96.3	99.9	100.6	100.0	97.0
		Rep 2.	98.9	99.5	99.8	98.8	95.5	99.4	98.9	99.3	98.2
		Mean	98.7	99.7	99.7	99.2	95.9	99.6	99.7	99.7	97.6
	Unidentified/ Diffused radioactivity	Rep. 1	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
		Rep 2.	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
		Mean	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	Total extractable residues	Rep. 1	98.4	99.9	99.6	99.6	96.3	99.9	100.6	100.0	97.0
		Rep 2.	98.9	99.5	99.8	98.8	95.5	99.4	98.9	99.3	98.2
		Mean	98.7	99.7	99.7	99.2	95.9	99.6	99.7	99.7	97.6
Volatile compounds:	CO ₂	Rep. 1	n. a. ³⁾	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
		Rep 2.	n. a. ³⁾	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
		Mean	n. a. ³⁾	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
	VOC ²⁾	Rep. 1	n. a. ³⁾	0.1	<0.1	0.1	<0.1	<0.1	<0.1	<0.1	<0.1
		Rep 2.	n. a. ³⁾	<0.1	<0.1	<0.1	<0.1	<0.1	n. d. ⁴⁾	<0.1	<0.1
		Mean	n. a. ³⁾	0.1	<0.1	0.1	<0.1	<0.1	<0.1	<0.1	<0.1
	Total volatiles	Rep. 1	n. a. ³⁾	0.1	<0.1	0.1	<0.1	<0.1	<0.1	<0.1	<0.1
		Rep 2.	n. a. ³⁾	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
		Mean	n. a. ³⁾	0.1	<0.1	0.1	<0.1	<0.1	<0.1	<0.1	<0.1
NER fraction [% AR]		Rep. 1	1.1	1.0	1.0	0.9	1.1	1.3	1.1	1.1	1.3
		Rep 2.	0.9	1.2	1.1	1.2	1.1	1.2	1.3	1.2	1.3
		Mean	1.0	1.1	1.0	1.0	1.1	1.2	1.2	1.1	1.3
Total radioactivity recovered [% AR]		Rep. 1	99.5	101.1	100.6	100.5	97.4	101.2	101.7	101.1	98.3
		Rep 2.	99.9	100.7	100.9	100.0	96.6	100.6	100.2	100.5	99.6
		Mean	99.7	100.9	100.8	100.3	97.0	100.9	100.9	100.8	99.0

Footnotes to the table:

- 1) DAT = Days After Treatment;
- 2) VOC = Volatile Organic Compounds;
- 3) n. a. = not analysed – at that time point no volatiles were expected to be formed;
- 4) n. d. = not detected.

Table B.8.1.1.2.1.1. CA-264: The numerical results of the experiment performed on Hoefchen am Hohenseh 4a Sandy loam soil.

Radioactivity			Measured on DAT ¹⁾								
			0	3	7	14	28	43	59	92	120
In extract [%AR]	Ambient extract	Rep. 1	96.8	98.8	98.9	97.4	94.7	97.7	99.8	99.6	95.1
		Rep 2.	96.9	97.6	97.8	97.4	94.4	98.4	98.4	98.8	95.9
		Mean	96.9	98.2	98.4	97.4	94.5	98.1	99.1	99.2	95.5
	Microwave extract	Rep. 1	2.3	2.5	2.3	2.6	2.4	2.7	2.7	2.9	2.8
		Rep 2.	2.4	2.4	2.5	2.6	2.5	2.2	2.6	2.9	2.8
		Mean	2.4	2.4	2.4	2.6	2.5	2.4	2.6	2.9	2.8
	Total extracted	Rep. 1	99.1	101.3	101.1	100.0	97.1	100.3	102.5	102.5	97.9
		Rep 2.	99.3	100.0	100.4	100.0	96.9	100.6	101.0	101.7	98.7
		Mean	99.2	100.7	100.7	100.0	97.0	100.5	101.7	102.1	98.3
In extract identified as [% AR]:	[1- ¹⁴ C] trifluoroacetate	Rep. 1	99.1	101.3	101.1	100.0	97.1	100.3	102.5	102.5	97.9
		Rep 2.	99.3	100.0	100.4	100.0	96.9	100.6	101.0	101.7	98.7
		Mean	99.2	100.7	100.7	100.0	97.0	100.5	101.7	102.1	98.3
	Unidentified/ Diffused radioactivity	Rep. 1	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
		Rep 2.	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
		Mean	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	Total extractable residues	Rep. 1	99.1	101.3	101.1	100.0	97.1	100.3	102.5	102.5	97.9
		Rep 2.	99.3	100.0	100.4	100.0	96.9	100.6	101.0	101.7	98.7
		Mean	99.2	100.7	100.7	100.0	97.0	100.5	101.7	102.1	98.3
Volatile compounds:	CO ₂	Rep. 1	n. a. ³⁾	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
		Rep 2.	n. a. ³⁾	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
		Mean	n. a. ³⁾	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
	VOC ²⁾	Rep. 1	n. a. ³⁾	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
		Rep 2.	n. a. ³⁾	<0.1	0.1	0.1	<0.1	<0.1	<0.1	<0.1	<0.1
		Mean	n. a. ³⁾	0.1	0.1	0.1	<0.1	<0.1	<0.1	<0.1	<0.1
	Total volatiles	Rep. 1	n. a. ³⁾	0.1	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
		Rep 2.	n. a. ³⁾	<0.1	0.1	0.1	<0.1	<0.1	<0.1	<0.1	<0.1
		Mean	n. a. ³⁾	0.1	0.1	0.1	<0.1	<0.1	<0.1	<0.1	<0.1
NER fraction [% AR]		Rep. 1	0.9	1.0	1.0	1.0	1.2	1.1	1.3	1.2	1.1
		Rep 2.	0.9	1.1	1.0	0.9	1.1	1.6	1.3	1.3	1.2
		Mean	0.9	1.0	1.0	0.9	1.1	1.3	1.3	1.3	1.2
Total radioactivity recovered [% AR]		Rep. 1	100.0	102.4	102.2	101.1	98.3	101.4	103.8	103.7	99.0
		Rep 2.	100.2	101.1	101.5	101.0	98.0	102.2	102.3	103.0	100.0
		Mean	100.1	101.8	101.8	101.0	98.2	101.8	103.1	103.4	99.5

Footnotes to the table:

- 1) DAT = Days After Treatment;
- 2) VOC = Volatile Organic Compounds;
- 3) n. a. = not analysed – at that time point no volatiles were expected to be formed;
- 4) n. d. = not detected.

The graphical results of the study – the distribution of radioactivity between fractions, is presented below on figure B.8.1.1.2.1.1_CA-142.

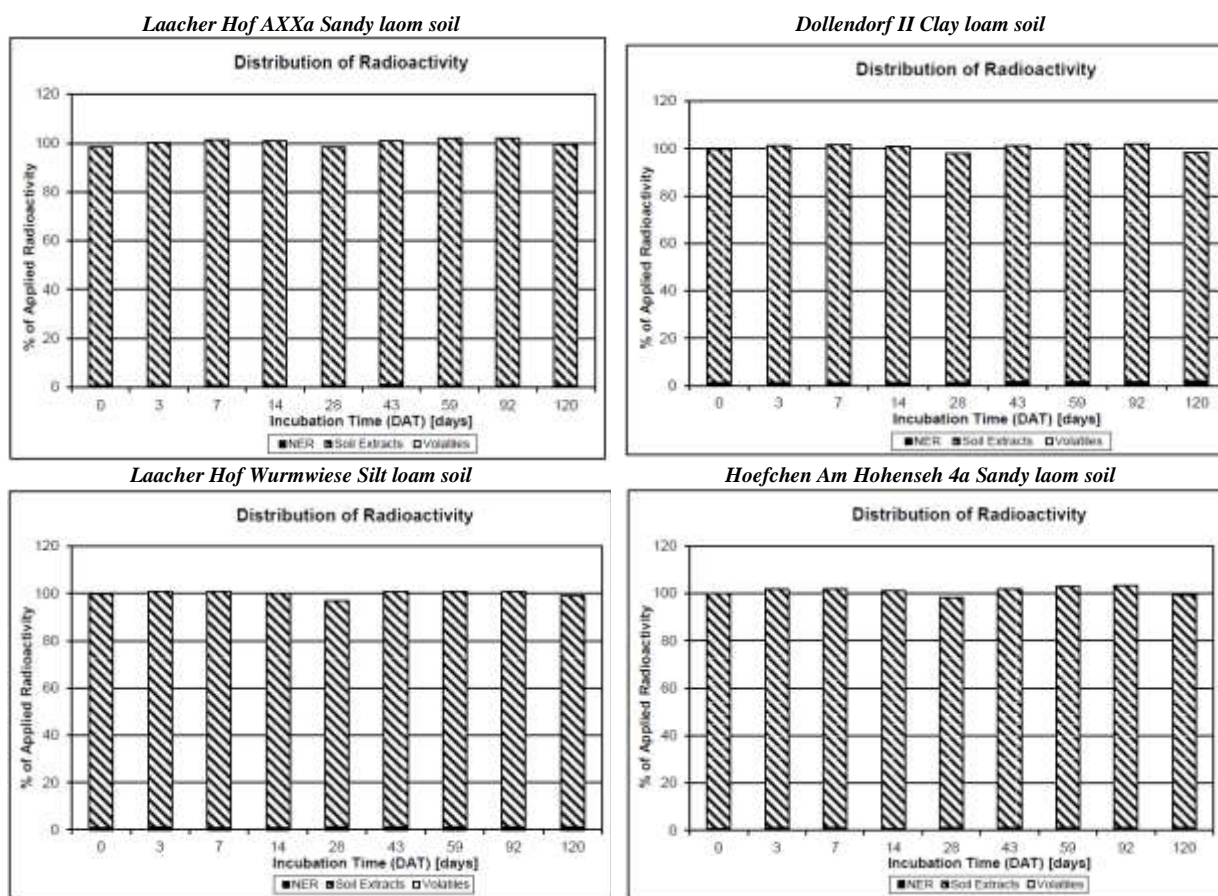


Figure B.8.1.1.2.1.1_CA-142: The distribution of radioactivity between fractions in each test soil (copied from the study report).

The Applicant performed the kinetic analysis of the data obtained for $[1-^{14}\text{C}]$ trifluoroacetate in each test soil, presented in tables B.8.1.1.2.1.1_CA-261 – B.8.1.1.2.1.1_CA-264 above. However, full set of the results, including visual fits, was given only for one soil – Laacher Hof AXXa soil. As a result, the verification of the correctness of the performed kinetic analysis was not possible. Therefore RMS decided not to present the results of the Applicant's kinetic analysis of the data, replacing it with own assessment.

The kinetic analysis was carried out in line with the recommendations given by FOCUS for the determination of the kinetic endpoints suitable for modeling. It followed the approach used by the Applicant and presented in several studies previously summarised in this section (e. g. **Studies 2 – 8**). The data used in the kinetic analysis were the same as presented above in the tables B.8.1.1.2.1.1_CA-261 – B.8.1.1.2.1.1_CA-264. For completeness they are presented below in the table B.8.1.1.2.1.1_CA-265.

Table B.8.1.1.2.1.1_CA-265: The concentrations of TFA in each test soil used in the kinetic analysis performed by the RMS.

Results obtained in <i>Laacher Hof AXXa</i> soil			Results obtained in <i>Dollendorf II</i> soil			Results obtained in <i>Laacher Hof Wurmweise</i> soil			Results obtained in <i>Hoefchen Am Hohenseh 4a</i> soil		
DAT	Concentration of TFA [% AR]		DAT	Concentration of TFA [% AR]		DAT	Concentration of TFA [% AR]		DAT	Concentration of TFA [% AR]	
	Rep. 1	Rep 2.		Rep. 1	Rep 2.		Rep. 1	Rep 2.		Rep. 1	Rep 2.
0	97.8	97.5	0	98.5	98.3	0	98.4	98.9	0	99.1	99.3
3	99.8	99.6	3	98.6	101.0	3	99.9	99.5	3	101.3	100.0
7	100.9	100.1	7	100.5	99.9	7	99.6	99.8	7	101.1	100.4
14	99.9	100.5	14	99.4	99.5	14	99.6	98.8	14	100.0	100.0
28	97.7	97.3	28	96.0	96.7	28	96.3	95.5	28	97.1	96.9
43	100.2	99.6	43	99.1	99.6	43	99.9	99.4	43	100.3	100.6
59	101.3	101.3	59	100.5	99.5	59	100.6	98.9	59	102.5	101.0
92	101.7	101.0	92	100.3	100.2	92	100.0	99.3	92	102.5	101.7
120	98.0	99.2	120	96.1	96.8	120	97.0	98.2	120	97.9	98.7

The presented above data were kinetically examined using CAKE ver. 3.1 modelling tool, developed by Tessella. The optimisation was performed using IRLS (Iteratively Reweighed Nonlinear Least Squares) algorithm. The settings of the optimiser were the defaults of the tool:

- maximum iterations: 100,
- maximum reweighing: 10,
- SANN maximum iterations: 10000,
- convergence tolerance: 1 E-5,
- error variance tolerance: 1 E-5,
- extra solver: yes, if required.

The kinetic analysis was performed using three kinetic models, also used by the Applicant in his analysis – SFO, FOMC and DFOP. RMS however noticed that, because of virtually no degradation of the test compound in all four test soils, only the results obtained with SFO kinetic model will be of any relevance. Never the less, the results of the fitting with FOMC and DFOP models were presented for completeness.

All results of the kinetic analysis of the data are presented below, separately for each test soil.

- 1) The results of the kinetic analysis of the data obtained for Trifluoroacetate in Laacher Hof AXXa soil.

The results of the kinetic analysis are presented below, in graphical form on figure B.8.1.1.2.1.1._CA-143 and in numerical form in the table B.8.1.1.2.1.1._CA-266. Additionally the table B.8.1.1.2.1.1._CA-267 provides the kinetic endpoints obtained with each of the kinetic models tested.

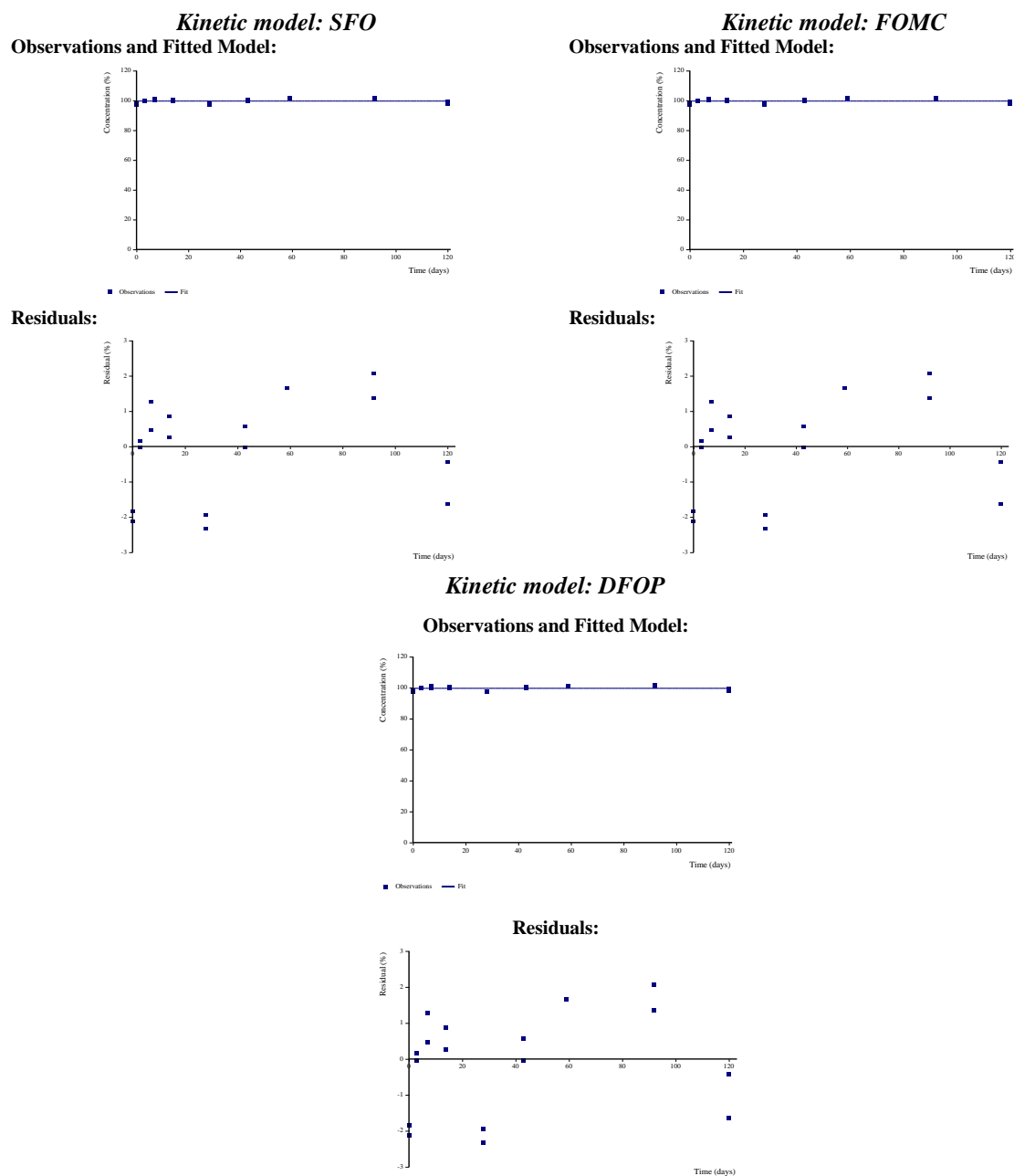


Figure B.8.1.1.2.1.1._CA-143: The graphical results of the kinetic analysis.

Table B.8.1.1.2.1.1._CA-266: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment
				Lower	Upper			
SFO	M_0	99.63	0.495	98.58	100.7	n. c. ¹⁾	1.09	0.0388; Acceptable fit
	k	2.24 E-14	8.72 E-5	-1.848 E-4	0.000	0.5		
FOMC	M_0	99.63	0.358	98.87	100.4	n. c. ¹⁾	1.15	R^2 not determined; Acceptable fit
	α	4.89 E-11	4.72 E-11	-5.16 E-11	0.00	n. d. ²⁾		
	β	9.041	n. d. ²⁾	n. d. ²⁾	n. d. ²⁾	n. d. ²⁾		
DFOP	M_0	99.63	0.527	98.5	100.8	n. c. ¹⁾	1.22	R^2 not determined; Acceptable fit
	k_1	0.00163	1.71 E-4	0.00126	0.002	8.58 E-8		
	k_2	1.45 E-14	9.17 E-5	-1.968 E-4	0.00	0.5		
	g	7.91 E-6	0.00	7.91 E-6	0.00	n. c. ¹⁾		

Footnotes to the table:

1) n. c. = not calculated by the tool;

2) Values were not determined by the model because the covariance matrix could not be created.

Table B.8.1.1.2.1.1._CA-267: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested		
		SFO	FOMC	DFOP
Trifluoroacetate	DT ₅₀ [days]	> 10000	> 10000	> 10000
	DT ₉₀ [days]	> 10000	> 10000	> 10000

Conclusion:

All three models returned fits that were visually acceptable and statistically good. However for none of them the calculated kinetic endpoints may be considered reliable. That was due to the fact that practically no degradation was observed in the experiment. That outcome is in line with available literature data for TFA, stating that the compound is persistent in soil and the sole possible routes of dissipation from that environmental compartment are via volatilisation to air, possible however for the non-dissociated acid, and incorporation to soil matrix.

Therefore RMS proposes to consider SFO as a model giving the acceptable approximate of the kinetic behaviour of TFA in soil. Also for that compound RMS proposes to consider DT₅₀ = 10000 days (~27.4 years) as a kinetic endpoint appropriate to be used as persistence endpoint.

- 2) The results of the kinetic analysis of the data obtained for Trifluoroacetate in Dollendorf II soil.

The results of the kinetic analysis are presented below, in graphical form on figure B.8.1.1.2.1.1._CA-144 and in numerical form in the table B.8.1.1.2.1.1._CA-268. Additionally the table B.8.1.1.2.1.1._CA-269 provides the kinetic endpoints obtained with each of the kinetic models tested.

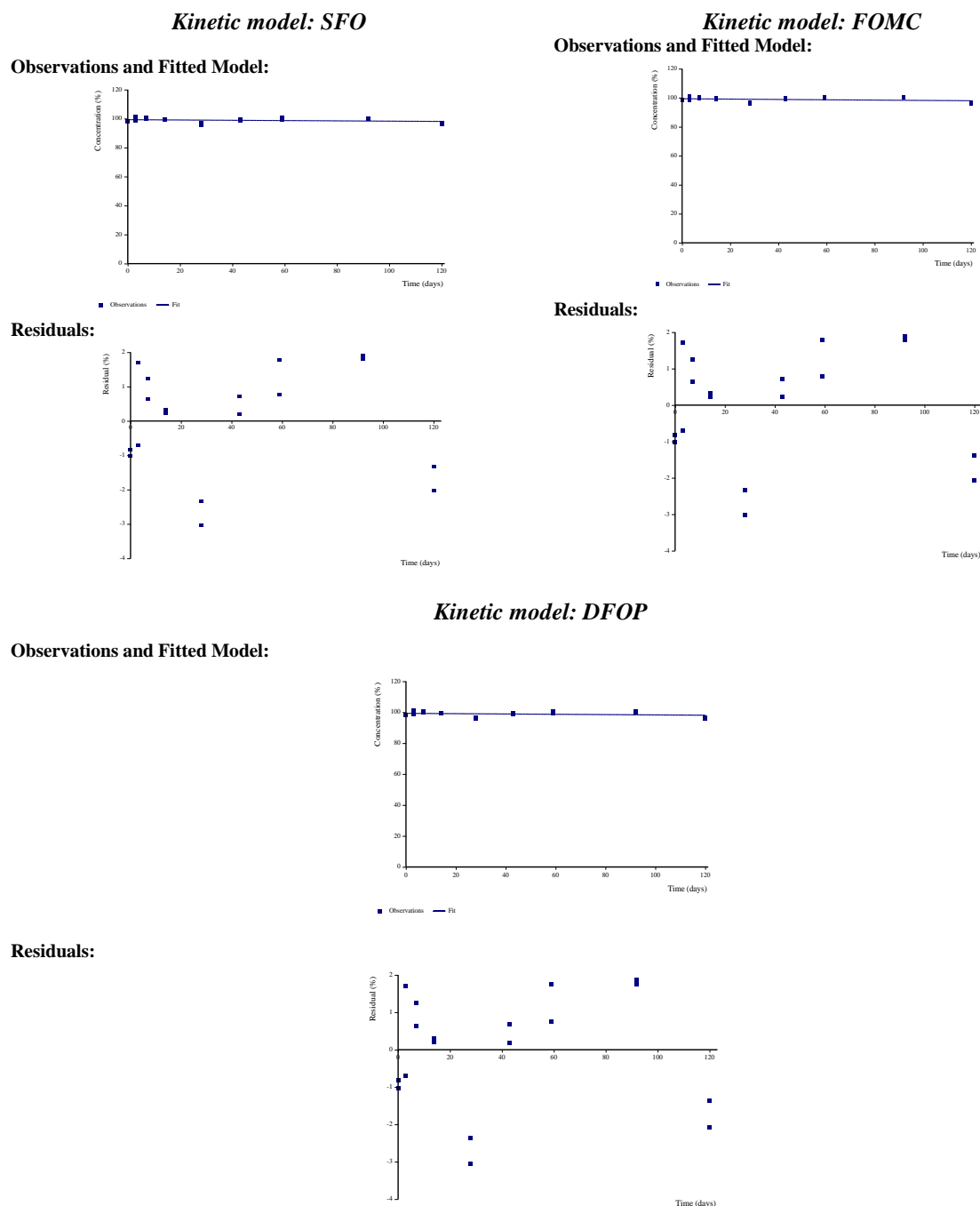


Figure B.8.1.1.2.1.1._CA-144: The graphical results of the kinetic analysis.

Table B.8.1.1.2.1.1._CA-268: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment
				Lower	Upper			
SFO	M_0	99.32	0.526	98.21	100.4	n. c. ¹⁾	1.12	0.0685; Acceptable fit
	k	1.01 E-4	9.34 E-5	-9.70 E-5	0.000	0.1479		
FOMC	M_0	99.40	0.554	98.22	100.6	n. c. ¹⁾	1.19	0.0640; Acceptable fit
	α	0.05807	0.04943	-0.0473	0.163	n. c. ¹⁾		
	β	448.3	89.97	256.6	640.1	n. c. ¹⁾		
DFOP	M_0	99.32	0.560	98.12	100.5	n. c. ¹⁾	1.27	0.0687; Acceptable fit
	k_1	0.002183	0.0126	-0.02484	0.029	0.4325		
	k_2	1.010 E-4	9.82 E-5	-1.098 E-4	0.00	0.161		
	g	3.43 E-9	n. d ²⁾	n. d ²⁾	n. d ²⁾	n. d. ²⁾		

Footnotes to the table:

1) n. c. = not calculated by the tool;

2) Values were not determined by the model because the covariance matrix could not be created.

Table B.8.1.1.2.1.1._CA-269: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested		
		SFO	FOMC	DFOP
Trifluoroacetate	DT ₅₀ [days]	6870	> 10000	6870
	DT ₉₀ [days]	> 10000	> 10000	> 10000

Conclusion:

All three models returned fits that were visually acceptable and statistically good. However for none of them the calculated kinetic endpoints may be considered reliable. That was due to the fact that practically no degradation was observed in the experiment. That outcome is in line with available literature data for TFA stating that the compound is persistent in soil and the sole possible routes of dissipation from that environmental compartment are via volatilisation to air, possible however for the non-dissociated acid, and incorporation to soil matrix.

It shall be noted that for SFO and DFOP kinetic models the modelling tool calculated the DT₅₀ = 6870 days. That value however shall be considered with extreme care as the rate constants used to determine it were of very limited reliability. Therefore more appropriate, in RMS's opinion, would be the default maximum value returned by the model for the remaining soils – DT₅₀ > 10000 days.

Therefore RMS proposes to consider SFO as a model giving the acceptable approximate of the kinetic behaviour of TFA in soil. Also for that compound RMS proposes to consider DT₅₀ = 10000 days (~27.4 years) as a kinetic endpoint appropriate to be used as persistence endpoint.

- 3) The results of the kinetic analysis of the data obtained for Trifluoroacetate in Laacher Hof Wurmwielse soil.

The results of the kinetic analysis are presented below, in graphical form on figure B.8.1.1.2.1.1._CA-145 and in numerical form in the table B.8.1.1.2.1.1._CA-270. Additionally the table B.8.1.1.2.1.1._CA-271 provides the kinetic endpoints obtained with each of the kinetic models tested.

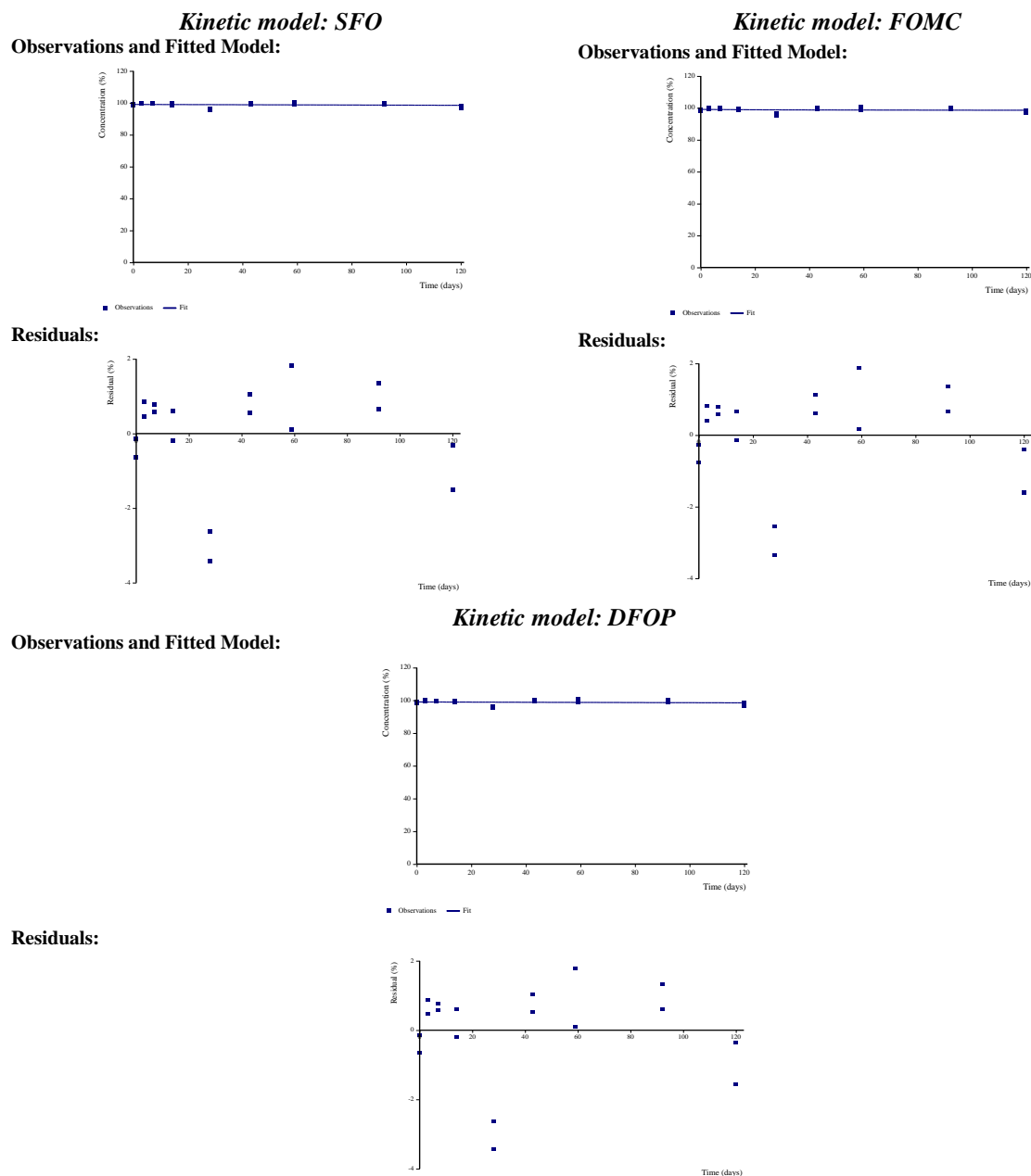


Figure B.8.1.1.2.1.1._CA-145: The graphical results of the kinetic analysis.

Table B.8.1.1.2.1.1._CA-270: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment
				Lower	Upper			
SFO	M_0	99.05	0.467	98.06	100.0	n. c. ¹⁾	0.997	0.0183; Acceptable fit
	k	4.52 E-5	8.29 E-5	-1.305 E-4	0.00	0.2964		
FOMC	M_0	99.16	0.672	97.72	100.6	n. c. ¹⁾	1.05	0.0196; Acceptable fit
	α	1.886 E-3	4.73 E-3	-8.196 E-3	0.012	n. c. ¹⁾		
	β	6.451	38.4	-75.4	88.3	n. c. ¹⁾		
DFOP	M_0	99.05	0.497	97.98	100.1	n. c. ¹⁾	1.12	0.0185; Acceptable fit
	k_1	0.00265	0.0310	-0.0619	0.067	0.4655		
	k_2	4.51 E-5	8.73 E-5	-1.421 E-4	0.00	0.3066		
	g	5.45 E-9	n. d ²⁾	n. d ²⁾	n. d ²⁾	n. c. ¹⁾		

Footnotes to the table:

- 1) n. c. = not calculated by the tool;
 2) Values were not determined by the model because the covariance matrix could not be created.

Table B.8.1.1.2.1.1._CA-271: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested		
		SFO	FOMC	DFOP
Trifluoroacetate	DT ₅₀ [days]	> 10000	> 10000	> 10000
	DT ₉₀ [days]	> 10000	> 10000	> 10000

Conclusion:

All three models returned fits that were visually acceptable and statistically good. However for none of them the calculated kinetic endpoints may be considered reliable. That was due to the fact that practically no degradation was observed in the experiment. That outcome is in line with available literature data for TFA, stating that the compound is persistent in soil and the sole possible routes of dissipation from that environmental compartment are via volatilisation to air, possible however for the non-dissociated acid, and incorporation to soil matrix.

Therefore RMS proposes to consider SFO as a model giving the acceptable approximate of the kinetic behaviour of TFA in soil. Also for that compound RMS proposes to consider DT₅₀ = 10000 days (~27.4 years) as a kinetic endpoint appropriate to be used as persistence endpoint.

- 4) The results of the kinetic analysis of the data obtained for Trifluoroacetate in Hoefchen am Hohenseh 4a soil.

The results of the kinetic analysis are presented below, in graphical form on figure B.8.1.1.2.1.1._CA-146 and in numerical form in the table B.8.1.1.2.1.1._CA-272. Additionally the table B.8.1.1.2.1.1._CA-273 provides the kinetic endpoints obtained with each of the kinetic models tested.

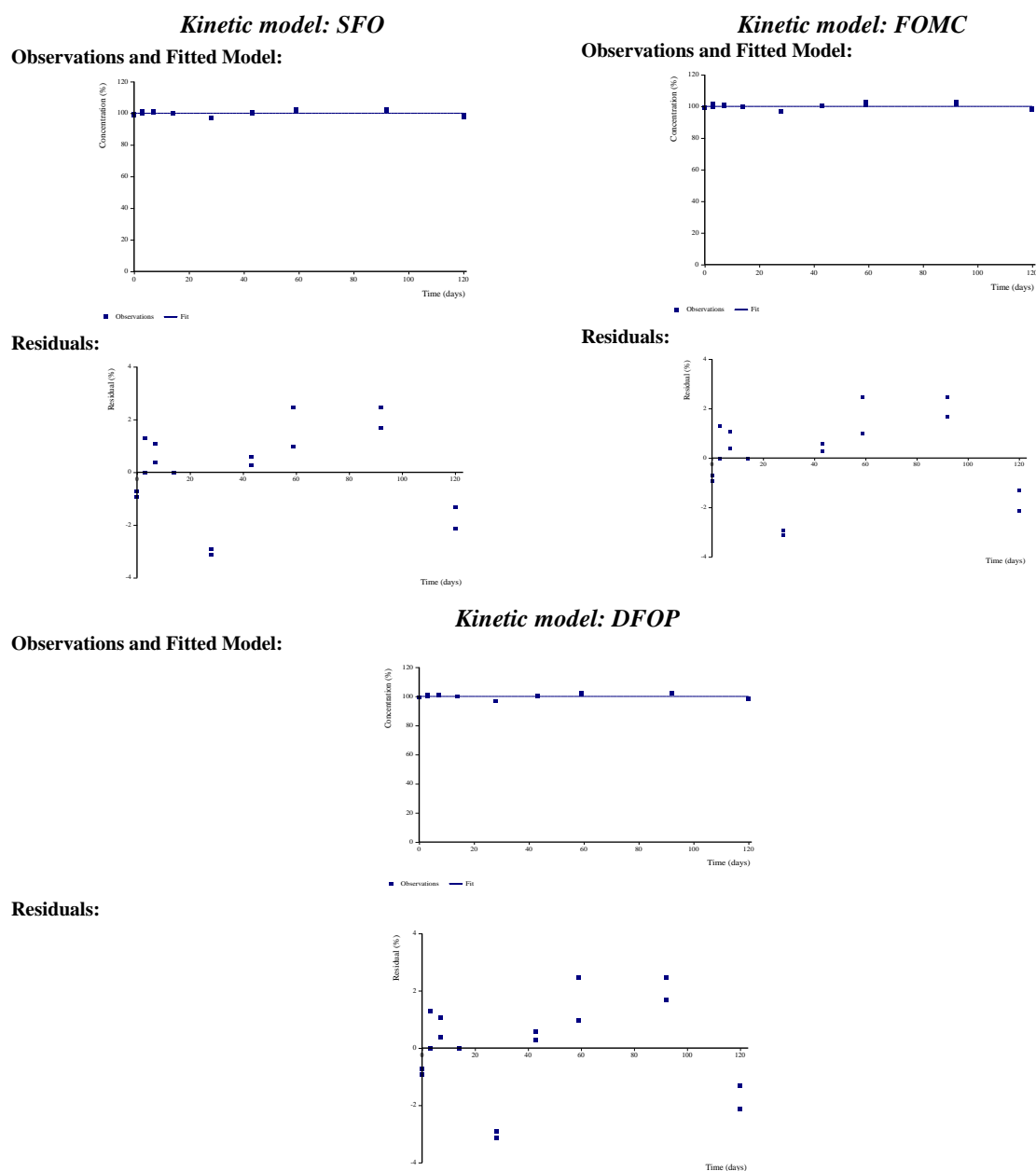


Figure B.8.1.1.2.1.1._CA-146: The graphical results of the kinetic analysis.

Table B.8.1.1.2.1.1._CA-272: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment
				Lower	Upper			
SFO	M_0	100.0	0.566	98.828	101.2	n. c. ¹⁾	1.23	0.0022; Acceptable fit
	k	1.90 E-14	9.93 E-5	-2.105 E-4	0.00	0.5		
FOMC	M_0	100.0	0.410	99.15	100.9	n. c. ¹⁾	1.30	R^2 not determined; Acceptable fit
	α	1.35 E-10	n. d. ²⁾	n. d. ²⁾	n. d. ²⁾	n. d. ²⁾		
	β	9.372	n. d. ²⁾	n. d. ²⁾	n. d. ²⁾	n. d. ²⁾		
DFOP	M_0	100.0	0.603	98.73	101.3	n. c. ¹⁾	1.38	R^2 not determined; Acceptable fit
	k_1	1.929 E-3	1.002 E-3	-2.199 E-4	0.004	3.74 E-2		
	k_2	5.47 E-13	1.05 E-4	-2.241 E-4	0.00	0.5		
	g	7.11 E-6	0.00	7.11 E-6	0.00	n. c. ¹⁾		

Footnotes to the table:

1) n. c. = not calculated by the tool;

2) Values were not determined by the model because the covariance matrix could not be created.

Table B.8.1.1.2.1.1._CA-273: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested		
		SFO	FOMC	DFOP
Trifluoroacetate	DT ₅₀ [days]	> 10000	> 10000	> 10000
	DT ₉₀ [days]	> 10000	> 10000	> 10000

Conclusion:

All three models returned fits that were visually acceptable and statistically good. However for none of them the calculated kinetic endpoints may be considered reliable. That was due to the fact that practically no degradation was observed in the experiment. That outcome is in line with available literature data for TFA, stating that the compound is persistent in soil and the sole possible routes of dissipation from that environmental compartment are via volatilisation to air, possible however for the non-dissociated acid, and incorporation to soil matrix.

Therefore RMS proposes to consider SFO as a model giving the acceptable approximate of the kinetic behaviour of TFA in soil. Also for that compound RMS proposes to consider DT₅₀ = 10000 days (~27.4 years) as a kinetic endpoint appropriate to be used as persistence endpoint.

Final conclusion of the study:

On the basis of the results of the kinetic analysis presented above was determined the definitive set of the reliable kinetic parameters, presented below in the table B.8.1.1.2.1.1._CA-260.

Table B.8.1.1.2.1.1._CA-260: The definitive set of the kinetic endpoints determined in the study.

Soil		Soil properties		Incubation conditions	Selected best-fit model	Evaluation of the fit		Kinetic parameters		Kinetic endpoints ⁴⁾	
Soil name	Soil type (USDA)	OC [%]	pH ¹⁾			χ^2 error	Visual fit ²⁾	Par.	Value	DT ₅₀ [days]	DT ₉₀ [days]
<i>Laacher Hof AXXa</i>	Sandy loam	1.6	6.2	20.0°C/ 55% MWHC	SFO	1.09	A	<i>k</i>	n. d. ³⁾	10000	>10000
<i>Dollendorf II</i>	Clay loam	5.5	7.3	20.0°C/ 55% MWHC	SFO	1.12	A	<i>k</i>	n. d. ³⁾	10000	>10000
<i>Hoefchen Am Hohenseh 4a;</i>	Silt loam	2.4	6.4	20.0°C/ 55% MWHC	SFO	1.23	A	<i>k</i>	n. d. ³⁾	10000	>10000
<i>Laacher Hof Wurmweise</i>	Sandy loam	1.9	5.1	20.0°C/ 55% MWHC	SFO	0.997	A	<i>k</i>	n. d. ³⁾	10000	>10000

Footnotes to the table:

- 1) Measured in 0.01M CaCl₂.
- 2) The abbreviations used to describe the visual fit: G. – good, A. – acceptable, P. – poor;
- 3) The reliable value could not be determined due to the fact that the decline of the test compound was not observed; as a result the corresponding DT₅₀ and DT₉₀ values are the defaults in range with the respective values proposed by the modelling tool;
- 4) For that soil, although the model calculated lower DT₅₀ value, the corresponding rate constant *k* lacked reliability and for that reason the RMS decided to use the default value instead (for justification please refer to the conclusions on the kinetic assessment for that test soil on p. 427).

Study 20:

Report: Eckermann N., (2012): “[1-¹⁴C]Trifluoroacetate: Concentration dependent Mineralization under Aerobic Conditions.”; Bayer CropScience AG, BCS-D-EnSa-Testing, 40789 Monheim, Germany; unpublished Study Report No. EnSa-12-0445; 2012. 10. 11; study reference number: M-441101-01-1;

Guidelines: The study was performed to comply with the following Guidelines:

- OECD Guideline for the Testing of Chemicals, No. 307, Aerobic and Anaerobic Transformation in Soil, 2002;
- US. EPA OCSPP Fate, Transport and Transformation Test Guidelines, OPPTS 835.4100 and OPPTS 835.4200, Aerobic and Anaerobic Soil Metabolism, 2008.

GLP: Yes

RMS comments: This is a new study, submitted specifically for purpose of this assessment. It was indicated by the Applicant to be supplementary to the summarised above study examining the degradation of TFA in soil, with specific aim to examine the possible influence of concentration of the test compound on its rate of degradation in soil. It was verified by the RMS and found acceptable. The study is summarised below.

Summary:

The study is a supplementary to the summarised above **Study 19** ([Eckermann; 2012]) examining rate of degradation of Trifluoroacetate (dissociated form of TFA) in soil. The aim of the present study was to further investigate the rate of degradation of TFA in soil, by verifying whether the process was not concentration-dependent. That was done by examining the mineralisation level of TFA in function of concentration and time.

The experiment was performed on four EU-soils, used in other studies examining the degradation of Flufenacet and its degradation products in soil. The test soils were taken from the agriculturally used areas, representing different geographical origin and different soil properties, in line with the requirement of the relevant Guideline. The characteristic of the test soils is provided below in the table B.8.1.1.2.1.1_CA-274.

Table B.8.1.2.1.1_CA-274: The characteristic of soils used in the study.

Parameter		Soil			
		<i>Laacher Hof AXXa</i>	<i>Dollendorf II</i>	<i>Hoefchen Am Hohenseh 4a</i>	<i>Laacher Hof Wurmwiess</i>
Soil origin		Monheim/ North Rhine-Westphalia /Germany	Blankenheim/ North Rhine-Westphalia /Germany	Burscheid/ North Rhine-Westphalia /Germany	Monheim/ North Rhine-Westphalia /Germany
Soil type (USDA)		Sandy loam	Clay loam	Silt loam	Sandy loam
Particle size distribution	Sand [%]	77	29	25	57
	Silt [%]	14	40	60	26
	Clay [%]	9	31	15	17
pH value	in 0.01M CaCl ₂ (1:2)	6.2	7.3	6.4	5.1
	in H ₂ O (1:1)	6.5	7.5	6.7	5.4
	in 1M KCl (1:1)	6.0	7.1	6.1	4.7
Organic Carbon content (OC) [%]		1.6	5.5	2.4	1.9
Organic Matter content (OM) [%]		2.8	9.5	4.1	3.3
Cation Exchange Capacity – CEC [mEq/100g]		8.7	21.2	13.6	10.0
Water holding capacity [g H ₂ O/ 100 g soil d. w.]	MWHC	46.9	84.9	62.0	57.6
	at pF 2.5 (0.33 bar)	12.9	34.9	26.3	18.2
Soil bulk density (disturbed) [g/cm ³]		1.26	0.97	1.08	1.13
Soil biomass [mg microbial C/ kg soil] ²⁾	DAT-0	536	2930	833	423
	DAT-59	589	3344	844	459
	DAT-120	248	1412	387	424
Soil biomass [% OC] ³⁾	DAT-0	3.35	5.33	3.47	2.22
	DAT-59	3.68	6.08	3.52	2.42
	DAT-120	1.55	2.57	1.61	2.23

Footnotes to the table:

- 1) Determined using the SIR method developed by Anderson & Domsch [1978];
- 2) Values recalculated by the RMS using the OC content reported in the table for each test soil;

The test soils were sampled shortly before being used (7 days before the experiment began) with shovel from 0-20 cm layer of grassland plot. No Plant Protection Products were used on the sampling field for 5 years preceding sampling. The samples of the test soils were transported to the test facility in plastic bags. There they were sieved through 2-mm sieve and stored in the darkness at either $T < 8^{\circ}\text{C}$ or $T = 20^{\circ}\text{C}$ until being used.

The experiment was performed using biometer flasks containing 100-g portions of the test soils, the example of which is presented below on figure B.8.1.1.2.1.1._CA-147.

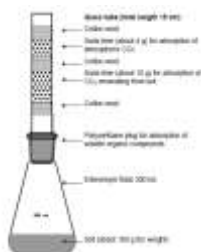


Figure B.8.1.1.2.1.1._CA-147: The biometer flask used in the experiment (copied from the study report).

The experiment started with weighing 100-g (d. w.) aliquots of each test soil into 300-mL Erlenmeyer test flask. Next the test soils in each flask were brought to the designated level of moisture content – 55% MWHC, by addition of the appropriate amount of distilled water. Then the flasks were weighed and pre-incubated in incubation chamber, in the dark at constant temperature $T = 20.0 \pm 0.1^{\circ}\text{C}$, over weekend. After that period soil in each biometer flask was treated with the test compound.

The test compound used in the experiment was the radiolabelled trifluoroacetic acid in form of its sodium salt. The reason for that was the fact that Trifluoroacetic acid has $\text{pK}_{\text{a}} = 1.3$, therefore under environmental conditions it is present in deprotonated form – as trifluoroacetate (CF_3COO^-). For that reason sodium salt was selected as the relevant deprotonated species. The structural formula of the test compound is presented below on figure B.8.1.1.2.1.1._CA-148. The radiolabelling position is marked with asterisk (*). The test compound had specific activity of 3.48 MBq/mg (94.04 $\mu\text{Ci/mg}$) and radiochemical purity, determined by radio-HPLC, $> 98 - 99\%$. It was delivered to the test facility as a solid sample.

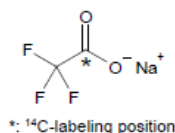


Figure B.8.1.1.2.1.1._CA-148: The structural formula of the test compound used in the experiment (copied from the study report).

The whole delivered sample of the test compound was used to prepare the **Stock solution**, from which three **Application solutions** were prepared. The **Stock solution** was prepared by dissolving the test compound in 11.7 mL of ultrapure water. The so prepared solution had a concentration, expressed in radioactivity units, 74.1 kBq/mL and radiochemical purity (determined by HPLC) $> 99\%$. The **Stock solution** was stored in the dark, in a freezer until being used.

The characterised above **Stock solution** was used to prepare three following **Application solutions**:

- **Application solution KOE7903A**, having a nominal concentration 20 μg test compound/mL;
- **Application solution KOE7903B**, having a nominal concentration 1 μg test compound/mL;
- **Application solution KOE7903C**, having a nominal concentration 0.1 μg test compound/mL.

Application solution KOE7903A, was prepared by diluting 1.4 mL of the **Stock solution** with 68.6 mL of ultrapure water (the dilution ratio was 1:50). The exact concentration, expressed in radioactivity units, was determined using LSC, while the identity of the test item in the solution by HPLC-MS and HPLC-MS/MS. The purity of the solution, determined using HPLC, was $\geq 99.7\%$ and when determined using TLC it was 100%.

Application solution KOE7903B, was prepared by diluting 3.5 mL of the **Application solution KOE7903A** with 66.5 mL of ultrapure water (the dilution ratio was 1:20). The exact concentration, expressed in radioactivity units, was determined using LSC.

Application solution KOE7903C, was prepared by diluting 6.0 mL of the **Application solution KOE7903B** with 54.0 mL of ultrapure water (the dilution ratio was 1:10). The exact concentration, expressed in radioactivity units, was determined using LSC.

The **Application solutions** characterised above were used to treat the test soils in each pre-equilibrated incubation vessels. That was done by applying 1 mL of the given **Application solution** to the soil surface in small droplets using the 1000- μ L Eppendorf pipette. The experimentally determined levels of fortification were following:

- for samples treated with **Application solution KOE7903A** – 20.9 μ g/vessel, which was the equivalent to 72591 Bq;
- for samples treated with **Application solution KOE7903B** – 1.05 μ g/vessel, which was the equivalent to 3668 Bq;
- for samples treated with **Application solution KOE7903C** – 0.10 μ g/vessel, which was the equivalent to 356.8 Bq;

The amount of radioactivity determined as application dose for each concentration variant and presented above was regarded as 100% AR for calculations.

The level of application and its homogeneity was verified at the beginning, in the middle and at the end of the application procedure by verification of the concentration of each of **Application solutions**. For that purpose its 1-mL samples were diluted with ultrapure water to 25 mL with CH₃CN/ultrapure water (1:1) and analysed by LSC.

For treatment the pre-incubated biometric flasks were removed from the incubation chamber. After application of the test compound the vessels, except those designated as DAT-0 samples, were fitted with the traps for volatile compounds and returned to the incubation chamber, to be incubated at constant temperature $T = 20.0 \pm 0.1^\circ\text{C}$ and soil moisture level $55 \pm 5\%$ MWHC, for up to 120 days. At the designated time points – DAT 30, DAT 59 and DAT 120, duplicate samples of each test soil were removed from the incubation chamber and further processed. At the same time points the soil moisture content was checked and corrected if necessary. That was done by weighing the test vessels without the traps for volatile compounds, determining the loss of water and, when necessary readjusting the water content to the designated level by adding the appropriate amount of water. The samples for the determination of biomass content were set alongside the treated samples. These were prepared in duplicate for each test soil and taken for analysis on DAT 0, DAT 59 and DAT 120.

Additionally for each test soil spare samples, incubated for up to 120 days were set.

The samples collected at each sampling point were processed and analysed following the procedure presented below on figure B.8.1.1.2.1.1._CA-149.

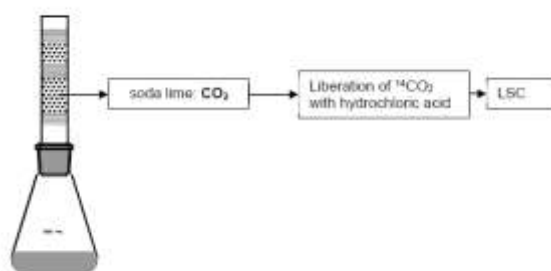


Figure B.8.1.1.2.1.1._CA-149: The sample-processing procedure used in the experiment (copied from the study report).

It shall be noted that, due to the aim of the study, only the volatile traps were analysed, while the soil in Erlenmeyer flasks was not further processed. Firstly the biometer flask were placed in a dessicator and the volatile compounds possibly present in the headspace above soil surface were transferred to the trap by evaporating the entire system. Then the flask were dissected and traps stored for further analysis, which occurred within 1 to 8 days after sampling.

The recovered traps for volatile compounds were dissected into the PU (Polyurethane Foam) plugs and soda lime traps.

The soda-lime traps for $^{14}\text{CO}_2$ formed in the experiment were processed in a way identical to that described in detail in the summaries of route-of-degradation studies by [Pangilinan and Smith; 1994a] (aerobic soil route-of-degradation **Study 4**) and by [Kasper and Shadrack; 1995] (soil photolysis **Study 1**), but used also in other studies examining the degradation of Flufenacet in soil under aerobic conditions – e.g. studies [Hein; 2012] (aerobic soil route-of-degradation **Study 5**) and [Hein; 2012 a] (aerobic soil route-of-degradation **Study 6**). The released $^{14}\text{CO}_2$ was absorbed in a scintillation cocktail and analysed by LSC.

All liquid samples were analysed for the content of radioactivity using LSC method. The LSC (Liquid Scintillation Counting) analysis was performed using LS 6500 (Beckmann) or LKB-Wallac 1219 Spectral (Perkin Elmer Life Science) counters.

The radioactivity in solutions was determined in either:

- a) mini-vials, using the sample aliquots of up to 0.5 mL and 2 mL of Quicksafe® A solution containing 5% of water; the counting was performed using LS 6500 counter, the counting efficiency was 87.9 – 88.0% and the background 15 cpm;
- b) maxi-vials, using the sample aliquots of up to 7 mL and 7 mL of Quicksafe® A solution containing 5% of water; the counting was performed using LKB-Wallac 1219 Spectral counter, the counting efficiency was 73.8 – 88.4% and the background 22 – 23 cpm.

The $^{14}\text{CO}_2$ recovered from soda lime was absorbed in 15 mL of Oxysolve C400 and analysed quantitatively using LKB-Wallac 1219 Spectral counter. The counting efficiency was 73.8 – 88.4% and the background 17 – 18 cpm.

The purity of the **Stock solution** and **Application solution KOE7903A** was verified chromatographically using the following techniques:

- radio-TLC analysis – method used to determine the purity of the **Application solution KOE7903A**;
- HPLC analysis with radio- and MS detection – method used to determine the purity of the **Stock solution** and **Application solution KOE7903A**, and to conform the identity of the test item – trifluoroacetate, in Application solution.

The TLC analysis was performed on silica gel plates – Si60, F₂₅₄, 20 cm x 20cm, developed in a chromatographic chamber without solvent saturation, using the following mobile phase: ethyl acetate/2-propanol/ultrapure water/glacial acetic acid 65:24:11:1 (v/v/v/v). For the purpose of the analysis the solution was diluted two times in parallel in a ratio 1:10 (v/v). The volume of each analysed dilution injected onto the plate was 20 µL. The distribution and quantitation of the radioactivity zones was determined using Bio-Imaging Analyzer BAS 2000, Fuji, Co.

The HPLC analysis was performed using Agilent HP 1100/1200 instrument equipped with chromatographic column oven, UV detector – Agilent VWD working at $\lambda = 254$, Ramona Star radioactivity detector and LTQ Orbitrap XL MS detector. The chromatographic analysis was performed as RP-chromatography and in a gradient mode using one of the following two methods:

- method “**Flurtaboden**” used to check the purity of the **Stock solution**;
- method “**Flurtaboden2**” used to check the purity of the **Application solution KOE7903A**.

In the method “**Flurtaboden**” chromatographic separation was performed on Purospher Star RP18-e 250 x 4.6 mm, 5 µm, chromatographic column preceded by Purospher Star RP18-e 4 x 4 mm, 5 µm guard column, placed in a chromatographic column oven set to $T = 40^\circ\text{C}$. The elution was performed in a gradient mode and lasted for 55 minutes. The flow rate was set to 1 mL/min. The characteristic of the gradient mode is presented below in the table B.8.1.1.2.1.1._CA-275.

Table B.8.1.1.2.1.1._CA-275: The gradient mode used in the chromatographic method “Flurtaboden”.

Time [min]	Solvent ratio	
	<i>Solvent A – Water + 1% HCOOH + 5 mM HCCONH₄</i>	<i>Solvent B – CH₃CN + 1% HCOOH + 5 mM HCCONH₄</i>
0	100	0
5	100	0
10	90	10
35	5	95
40	5	95
45	100	0
55	100	0

In the method “Flurtaboden2” chromatographic separation was performed on Nucleodur C18 Gravity 250 x 4.0 mm, 5 µm, chromatographic column (guard column was not used), placed in a chromatographic column oven set to T = 40°C. The elution was performed in a gradient mode and lasted for 55 minutes. The flow rate was set to 1 mL/min. The characteristic of the gradient mode ins presented below in the table B.8.1.1.2.1.1._CA-276.

Table B.8.1.1.2.1.1._CA-276: The gradient mode used in the chromatographic method “Flurtaboden2”.

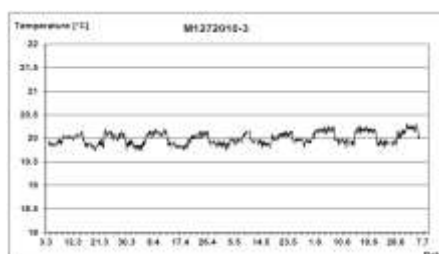
Time [min]	Solvent ratio	
	<i>Solvent A – Water + 1% HCOOH</i>	<i>Solvent B – CH₃CN + 1% HCOOH</i>
0	100	0
5	100	0
10	90	10
35	5	95
40	5	95
45	100	0
55	100	0

The obtained results are presented below. Kinetic analysis of the obtained results was not performed.

Results and their discussion:

The examination of the microbial viability of the test soils showed that they were viable throughout the whole experiment. The detailed results are shown in the table B.8.1.1.2.1.1._CA-274.

The monitoring of incubation temperature showed that the samples were kept in the constant temperature T = 20 ± 1°C. The mean incubation temperature was T = 20.0°C and it ranged from T = 19.8°C to T = 20.3°C. The results of the monitoring of the temperature in the incubation chamber are shown below, it the graphical form on figure B.8.1.1.2.1.1._CA-150.

**Figure B.8.1.1.2.1.1._CA-150:** The temperature recorded in incubation chamber during the experiment (copied from the study report).

The results of the determination of the soil moisture were identical to those obtained in the previously summarised **Study 19** and presented in the table B.8.1.1.2.1.1._CA-258. RMS decided to not reproduce them in order to not overburden the Assessment Report.

The results of the verification of the application rate and homogeneity of application are presented below, individually for each **Application solution** used in the experiment.

The results obtained for **Application solution KOE7903A** are given below in the table B.8.1.1.2.1.1._CA-277. On the basis of the obtained results the value of 72591 Bq, corresponding to 20.86 µg of ¹⁴C equivalents, was regarded as 100% AR for all calculations.

Table B.8.1.1.2.1.1._CA-277: The results of verification of application rate and homogeneity of application for **Application solution KOE7903A**.

Sample No.	Sample volume [mL]		Radioactivity [Bq]		¹⁴ C equivalents [µg]
	Total sample volume	Volume of LSC aliquot	Measured in LSC-aliquot	Total in sample	
1	25	0.5	1458.85	72943	20.96
2	25	0.5	1435.82	71791	20.63
3	25	0.5	1453.54	72677	20.88
4	25	0.5	1462.61	73131	21.01
5	25	0.5	1410.61	70531	20.27
6	25	0.5	1464.09	73205	21.04
7	25	0.5	1473.39	73670	21.17
8	25	0.5	1441.37	72069	20.71
9	25	0.5	1466.07	73304	21.06
Mean value				72591	20.86
SD				976	0.28
RSD [%]				----	1.35

The results obtained for **Application solution KOE7903B** are given below in the table B.8.1.1.2.1.1._CA-278. On the basis of the obtained results the value of 3668 Bq, corresponding to 1.05 µg of ¹⁴C equivalents, was regarded as 100% AR for all calculations.

Table B.8.1.1.2.1.1._CA-278: The results of verification of application rate and homogeneity of application for **Application solution KOE7903B**.

Sample No.	Sample volume [mL]		Radioactivity [Bq]		¹⁴ C equivalents [µg]
	Total sample volume	Volume of LSC aliquot	Measured in LSC-aliquot	Total in sample	
1	25	0.5	73.35	3668	1.05
2	25	0.5	73.30	3665	1.05
3	25	0.5	72.38	3619	1.04
4	25	0.5	73.19	3660	1.05
5	25	0.5	73.24	3662	1.05
6	25	0.5	73.73	3687	1.06
7	25	0.5	74.24	3712	1.07
8	25	0.5	73.25	3663	1.05
9	25	0.5	73.47	3674	1.06
Mean value				3668	1.05
SD				25	0.01
RSD [%]				----	0.67

The results obtained for **Application solution KOE7903C** are given below in the table B.8.1.1.2.1.1._CA-279. On the basis of the obtained results the value of 356.83 Bq, corresponding to 0.103 µg of ¹⁴C equivalents, was regarded as 100% AR for all calculations.

Table B.8.1.1.2.1.1_CA-279: The results of verification of application rate and homogeneity of application for Application solution KOE7903C.

Sample No.	Sample volume [mL]		Radioactivity [Bq]		¹⁴ C equivalents [µg]
	Total sample volume	Volume of LSC aliquot	Measured in LSC-aliquot	Total in sample	
1	----	1.0	354.00	354.00	0.102
2	----	1.0	355.15	355.15	0.102
3	----	1.0	356.20	356.20	0.102
4	----	1.0	356.09	356.09	0.102
5	----	1.0	357.53	357.53	0.103
6	----	1.0	356.92	356.92	0.103
7	----	1.0	359.02	359.02	0.103
8	----	1.0	358.53	358.53	0.103
9	----	1.0	358.52	358.52	0.103
Mean value				356.83	0.103
SD				1.63	0.0005
RSD [%]				----	0.458

The determination of the LOD and LOQ values for LSC and chromatographic analyses resulted in following values:

- the instrumental LOD and LOQ values for LSC analysis were: LOD = 2 times maximum instrument background count rate (0.25 Bq) and LOQ = three times maximum instrument background count rate (0.4 Bq);
- for liquid samples in 2 mL of Quicksafe A scintillation cocktail (mini-vials) LOD = 0.5 Bq and LOQ = 0.8 Bq;
- for liquid samples in 7 mL of Quicksafe A scintillation cocktail (maxi-vials) LOD = 0.8 Bq and LOQ = 1.2 Bq;
- for ¹⁴CO₂ samples in 15 mL Oxysolve C400 scintillation cocktail LOD = 0.6 Bq and LOQ = 0.9 Bq;

The detailed results of the study – the level of mineralisation in each test soil in function of time and different initial concentration of the test item, are provided below, individually for each test soil, in tables B.8.1.1.2.1.1_CA-280 – B.8.1.1.2.1.1_CA-283.

Table B.8.1.1.2.1.1_CA-280: The level of mineralisation of [1-¹⁴C] Trifluoroacetate determined in Laacher Hof AXXa Sandy loam test soil.

Time point - DAT	Level of mineralisation – ¹⁴ CO ₂ in soda traps, determined for the treatment level:											
	20.9 µg TFA/100 g soil (d. w.)				1.1 µg TFA/100 g soil (d. w.)				0.1 µg TFA/100 g soil (d. w.)			
	in Bq		as % AR		in Bq		as % AR		in Bq		as % AR	
	Rep. 1	Rep. 2	Rep. 1	Rep. 2	Rep. 1	Rep. 2	Rep. 1	Rep. 2	Rep. 1	Rep. 2	Rep. 1	Rep. 2
30	4.46	4.48	0.0061	0.0062	0.34	0.22	0.0093	0.0060	0	0.09	0	0.025
59	5.31	5.34	0.0073	0.0074	0.31	0.54	0.0085	0.0147	0.64	0.79	0.179	0.221
120	5.35	5.22	0.0074	0.0072	0.4	0.57	0.0109	0.0155	0.44	0.39	0.123	0.109

Table B.8.1.1.2.1.1_CA-281: The level of mineralisation of [1-¹⁴C] Trifluoroacetate determined in Dollendorf II Clay loam test soil.

Time point - DAT	Level of mineralisation – ¹⁴ CO ₂ in soda traps, determined for the treatment level:											
	20.9 µg TFA/100 g soil (d. w.)				1.1 µg TFA/100 g soil (d. w.)				0.1 µg TFA/100 g soil (d. w.)			
	in Bq		as % AR		in Bq		as % AR		in Bq		as % AR	
	Rep. 1	Rep. 2	Rep. 1	Rep. 2	Rep. 1	Rep. 2	Rep. 1	Rep. 2	Rep. 1	Rep. 2	Rep. 1	Rep. 2
30	4.88	4.96	0.0067	0.0068	0.51	0.72	0.0139	0.0196	0.15	0.02	0.042	0.006
59	5.44	5.73	0.0075	0.0079	0.37	0.56	0.0101	0.0153	0.81	0.17	0.0227	0.048
120	5.26	5.55	0.0072	0.0076	1.56	0.58	0.0425	0.0158	0.82	0.46	0.230	0.129

Table B.8.1.1.2.1.1_CA-282: The level of mineralisation of [$1\text{-}^{14}\text{C}$] Trifluoroacetate determined in Laacher Hof Wurmwiess Sandy loam test soil.

Time point - DAT	Level of mineralisation – $^{14}\text{CO}_2$ in soda traps, determined for the treatment level:											
	20.9 $\mu\text{g TFA}/100\text{ g soil (d. w.)}$				1.1 $\mu\text{g TFA}/100\text{ g soil (d. w.)}$				0.1 $\mu\text{g TFA}/100\text{ g soil (d. w.)}$			
	in Bq		as % AR		in Bq		as % AR		in Bq		as % AR	
	Rep. 1	Rep. 2	Rep. 1	Rep. 2	Rep. 1	Rep. 2	Rep. 1	Rep. 2	Rep. 1	Rep. 2	Rep. 1	Rep. 2
30	4.68	4.99	0.0064	0.0069	0.28	0.24	0.0076	0.0065	0.14	0.0	0.039	0.00
59	5.24	5.49	0.0072	0.0076	0.49	0.45	0.0134	0.0123	0.06	0.16	0.017	0.045
120	6.04	5.81	0.0083	0.0080	0.57	0.71	0.0155	0.0194	1.24	0.34	0.348	0.095

Table B.8.1.1.2.1.1_CA-283: The level of mineralisation of [$1\text{-}^{14}\text{C}$] Trifluoroacetate determined in Hoefchen Am Hohenseh 4a Silt loam test soil.

Time point - DAT	Level of mineralisation – $^{14}\text{CO}_2$ in soda traps, determined for the treatment level:											
	20.9 $\mu\text{g TFA}/100\text{ g soil (d. w.)}$				1.1 $\mu\text{g TFA}/100\text{ g soil (d. w.)}$				0.1 $\mu\text{g TFA}/100\text{ g soil (d. w.)}$			
	in Bq		as % AR		in Bq		as % AR		in Bq		as % AR	
	Rep. 1	Rep. 2	Rep. 1	Rep. 2	Rep. 1	Rep. 2	Rep. 1	Rep. 2	Rep. 1	Rep. 2	Rep. 1	Rep. 2
30	4.96	4.77	0.0068	0.0066	2.82	0.41	0.0769	0.0112	0.41	0.25	0.115	0.070
59	5.39	5.44	0.0074	0.0075	0.42	0.26	0.0115	0.0071	0.31	0.58	0.087	0.163
120	5.06	5.24	0.0070	0.0072	0.74	0.86	0.0202	0.0234	0.55	0.39	0.154	0.109

The results clearly indicate that the level of mineralisation was generally very low, not surpassing 0.3% AR. The Applicant in conclusion to the study stated that “No significant mineralization ($\geq 1\%$ AR) could be detected”. The conclusion related to it stated that:

“No significant amounts of CO_2 could be measured. Therefore, a kinetic evaluation was not performed.”

RMS analysing the results presented in the tables above stated that several values expressed in radioactivity units – Bq, were below the declared LOD level – 0.6 Bq. There were several other values that were above that level, but below the declared LOQ = 0.9 Bq. Such values should not be reported as the level of uncertainty associated to them is very high. Nowhere in the study report the Applicant provided the clarification concerning the way of derivation of the values either < LOD or < LOQ. RMS decided to keep those results, but marked those < LOD by giving them in italics.

It shall be noted however that this, being a clear deficiency of the study, does not change the final conclusion drawn from it.

Conclusion (RMS):

On the basis of the results presented above it can be stated that the test compound – Trifluoroacetate (a dissociated form of TFA) will not undergo significant mineralisation in soil over conceivable period of time, therefore it shall be considered persistent in that environmental compartment. It may be also stated that the concentration would have negligible influence on the level of the would-be mineralisation.

The results of the study, although indirectly, conform the appropriateness of the kinetic endpoints proposed by the RMS as the outcome of the previously summarised **Study 19**.

Study 21:

Report: Schäfer H. (1995): “Calculation of DT-50 values of two metabolites of FOE 5043 in soil under aerobic conditions.”; Bayer AG; unpublished Report No. MR-1085/95; 11. 10. 1995; study reference number: M-004479-02-1;

Guidelines: None declared.

GLP: No, not applicable – this is a modelling study;

RMS comments: The study had been evaluated for the previous authorisation of Flufenacet in the EU. Its brief summaries can be found under the point B.7.1.2.1.1.2.2., in section B.7 of the Annex B to the Monograph and under the point B.7.1.2.1.1.2. of the Addendum to the DAR for Flufenacet issued in January 2003, both prepared by the then-RMS – France. For the purpose of the current assessment the study was evaluated for its compliance with the following Guidelines:

- FOCUS (2006): “Guidance Document on Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration.” Report of the FOCUS Work Group on Degradation Kinetics, EC Document Reference SANCO/10058/2005 version 2.0, 434 pp.;
- FOCUS (2011): “Generic guidance for Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration”, version 1.0 (issued on 23 November 2011).

RMS stated that the study did not comply with the Guidelines listed above. For that reason it was decided not to provide its extensive summary. Instead below was given the summary that was placed in the Addendum to the DAR for Flufenacet prepared by the then-RMS – France. For clarity RMS – Poland, decided also to present the methodology used in the assessment. The summary is presented for informative purposes and its results will not be used in the further assessment.

Summary:

Below is presented the summary of the study written by the then-RMS – France for the purpose of the first authorisation of that compound in the EU, presented in the Addendum to the DAR for Flufenacet issued in January 2003 under the point B.7.1.2.1.1.2. N.b. RMS noted that this summary provides more detailed information than the summary of the same study available in the Draft Assessment Report for Flufenacet, under the point B.7.1.2.1.1.2.2., in section B.7 of the Annex B to the Monograph.

Schafer H. (1995), report MR-1085/95

This study was included in the monograph but it was briefly presented. Therefore more details are given below. DT50 for the major metabolites FOE sulfonic acid and FOE oxalate were calculated using data from the Kelly et al. (1995a) parent study reported in the monograph (report MR 106664). Four routes of degradation were assumed leading to sulfonic acid, oxalate, thioglycolate sulfoxide and methylsulfone, respectively. These metabolites were assumed to be further degraded to CO₂ and bound residues. Assuming first order kinetics, a set of differential equations was written according to the proposed degradation pathway. This equation system was numerically solved to fit the experimental data (SIMUSOLV program package). DT50 values were derived from the estimated rate constants. For FOE oxalate DT50 was calculated to be 7 d in the Hofchen soil, 4 d in the BBA 2.2 soil and 18 d in the the Laacherhof soil (acceptable visual fit). For FOE sulfonic acid, no reliable DT50 values could be obtained (no decline).

The methodology used in the kinetic assessment is given below, as it was presented in the source study report.

1. Method

For the calculation of kinetic data of metabolites by using metabolism studies the knowledge of the degradation pathways is necessary. Based on a metabolism studies conducted by Panglilan et al. /3/ and Kelley et al. /1/ the degradation pathways can be described as depicted in figure 1:

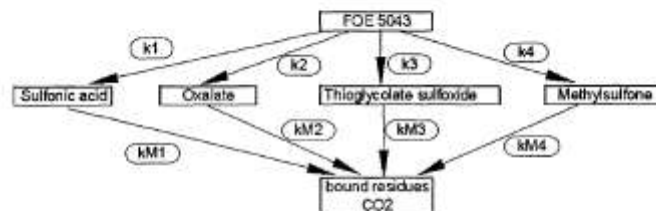


Figure 1: degradation pathways of FOE 5043 (chemical formulas see chapter abbreviations)

Assuming first order kinetics for the all reaction steps the following rate equations can be deduced:

$$r_1 = k_1 \cdot c_{FOE} \quad (1)$$

$$r_2 = k_2 \cdot c_{FOE} \quad (2)$$

$$r_3 = k_3 \cdot c_{FOE} \quad (3)$$

$$r_4 = k_4 \cdot c_{FOE} \quad (4)$$

$$r_{M1} = k_{M1} \cdot c_{SA} \quad (5)$$

$$r_{M2} = k_{M2} \cdot c_{OX} \quad (6)$$

$$r_{M3} = k_{M3} \cdot c_{TGS} \quad (7)$$

$$r_{M4} = k_{M4} \cdot c_{MS} \quad (8)$$

This leads to mass balance equations for each species. The concentrations are expressed in percent of applied radioactivity. Since the reaction of one radio labeled molecule leads again to only one radio labeled molecule, no stoichiometric coefficients have to be considered in the mass balance equations.

$$R_{FOE} = \frac{dc_{FOE}}{dt} = -(k_1 + k_2 + k_3 + k_4) \cdot c_{FOE} \quad (9)$$

$$R_{SA} = \frac{dc_{SA}}{dt} = k_1 \cdot c_{FOE} - k_{M1} \cdot c_{SA} \quad (10)$$

$$R_{OX} = \frac{dc_{OX}}{dt} = k_2 \cdot c_{FOE} - k_{M2} \cdot c_{OX} \quad (11)$$

$$R_{TGS} = \frac{dc_{TGS}}{dt} = k_3 \cdot c_{FOE} - k_{M3} \cdot c_{TGS} \quad (12)$$

$$R_{MS} = \frac{dc_{MS}}{dt} = k_4 \cdot c_{FOE} - k_{M4} \cdot c_{MS} \quad (13)$$

$$R_{REST} = \frac{dc_{REST}}{dt} = k_{M1} \cdot c_{SA} + k_{M2} \cdot c_{OX} + k_{M3} \cdot c_{TGS} + k_{M4} \cdot c_{MS} \quad (14)$$

$REST = CO_2 + \text{Bound residues}$

The coupled differential equation system is solved numerically. The calculated concentrations are fitted to experimental data by adjusting the parameters k_1 to k_4 and k_{M1} to k_{M4} . The fitting algorithm and the numerical solution of the differential equation is computed by using the "SIMUSOLV" program package /2/. For the problem definition within SIMUSOLV a FORTRAN-like language is used (see appendix 1).

The results of the parameter fitting are summarized in a report. The report consists of information on the parameter estimation, a comparison of observed and predicted data, a statistical summary, the correlation matrix, and the variance-covariance matrix (see appendices 2, 3, and 4).

The DT-50 values for sulfonic acid can then be obtained by:

$$DT50_{SA} = \frac{\ln 2}{k_{M1}} \quad (15)$$

and for oxalate by:

$$DT50_{OX} = \frac{\ln 2}{k_{M2}} \quad (16)$$

Study 22:

Report: Schäfer H. (1998): “Amendment to Report MR-1085/95.”; Bayer AG; unpublished Report No. MR-037/98; 15. 01. 1998; study reference number: M-004479-02-1;

Guidelines: None declared.

GLP: No, not applicable – this is a modelling study;

RMS comments: The study had been evaluated for the previous authorisation of Flufenacet in the EU. Its brief summary can be found under the point B.7.1.2.1.1.2. of the Addendum to the DAR for Flufenacet issued in January 2003, prepared by the then-RMS – France. For the purpose of the current assessment the study was evaluated for its compliance with the following Guidelines:

- FOCUS (2006): “Guidance Document on Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration.” Report of the FOCUS Work Group on Degradation Kinetics, EC Document Reference SANCO/10058/2005 version 2.0, 434 pp.;
- FOCUS (2011): “Generic guidance for Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration”, version 1.0 (issued on 23 November 2011).

RMS stated that the study did not comply with the Guidelines listed above. For that reason it was decided not to provide its extensive summary. Instead below was given the summary that was placed in the Addendum to the DAR for Flufenacet prepared by the then-RMS – France. For clarity RMS – Poland, decided also to present the methodology used in the assessment. The summary is presented for informative purposes and its results will not be used in the further assessment.

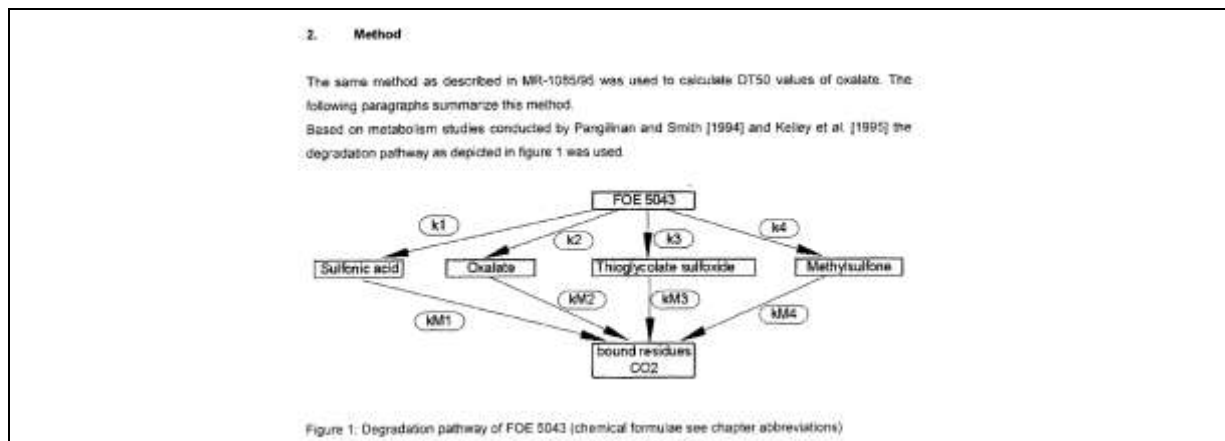
Summary:

Below is presented the summary of the study written by the then-RMS – France for the purpose of the first authorisation of that compound in the EU, presented in the Addendum to the DAR for Flufenacet issued in January 2003 under the point B.7.1.2.1.1.2.

Schafer H. (1998), report MR-037/98 (amendment to Report MR-1085/95)

The rate of degradation of the metabolite FOE oxalate was estimated as described above but the measured rate constants for FOE sulfonic acid (Hellpointner, 1996a, report PF 4110) were used. Under these conditions, DT50 values were estimated to be 5 d in the BBA 2.2 soil (measured DT50 189 d for sulfonic acid), 17 d in the Laacherhof soil (measured DT50 247 d for sulfonic acid) and 12 d in the Hoefchen soil (DT50 for sulfonic acid not measured in this soil, the mean value of 235 d for 3 studied soils was used). These values are deemed to be the most reliable.

The methodology used in the kinetic assessment is given below, as it was presented in the source study report.



Assuming first order kinetics for the all reaction steps the following rate equations and the following mass balances were derived:

Rate equations:

$$r_1 = k_1 \cdot c_{FOE} \quad (1)$$

$$r_2 = k_2 \cdot c_{FOE} \quad (2)$$

$$r_3 = k_3 \cdot c_{FOE} \quad (3)$$

$$r_4 = k_4 \cdot c_{FOE} \quad (4)$$

$$r_{MI} = k_{M1} \cdot c_{SA} \quad (5)$$

$$r_{MO} = k_{M2} \cdot c_{OX} \quad (6)$$

$$r_{MI} = k_{M3} \cdot c_{TOS} \quad (7)$$

$$r_{MI} = k_{M4} \cdot c_{MS} \quad (8)$$

Mass balances:

$$\frac{dc_{FOE}}{dt} = -(k_1 + k_2 + k_3 + k_4) \cdot c_{FOE} \quad (9)$$

$$\frac{dc_{SA}}{dt} = k_1 \cdot c_{FOE} - k_{M1} \cdot c_{SA} \quad (10)$$

$$\frac{dc_{OX}}{dt} = k_2 \cdot c_{FOE} - k_{M2} \cdot c_{OX} \quad (11)$$

$$\frac{dc_{TOS}}{dt} = k_3 \cdot c_{FOE} - k_{M3} \cdot c_{TOS} \quad (12)$$

$$\frac{dc_{MS}}{dt} = k_4 \cdot c_{FOE} - k_{M4} \cdot c_{MS} \quad (13)$$

$$\frac{dc_{MI}}{dt} = k_{M1} \cdot c_{SA} + k_{M2} \cdot c_{OX} + k_{M3} \cdot c_{TOS} + k_{M4} \cdot c_{MS} \quad (14)$$

$$\frac{dc_{MI}}{dt} = k_{M1} \cdot c_{SA} + k_{M2} \cdot c_{OX} + k_{M3} \cdot c_{TOS} + k_{M4} \cdot c_{MS} \quad (15)$$

$$\frac{dc_{MI}}{dt} = k_{M1} \cdot c_{SA} + k_{M2} \cdot c_{OX} + k_{M3} \cdot c_{TOS} + k_{M4} \cdot c_{MS} \quad (16)$$

$$\frac{dc_{MI}}{dt} = k_{M1} \cdot c_{SA} + k_{M2} \cdot c_{OX} + k_{M3} \cdot c_{TOS} + k_{M4} \cdot c_{MS} \quad (17)$$

REST=CO₂ + Bound residues

The coupled differential equation system is solved numerically. The calculated concentrations are fitted to experimental data by adjusting the parameters k_1 to k_4 and k_{M2} to k_{M4} . The fitting algorithm and the numerical solution of the differential equation is computed by using ACSL Optimize [1998].

Appendix 1 shows the program code used.

The DT50 values for oxalate can then be obtained by:

$$DT50_{OX} = \frac{\ln 2}{k_{M2}} \quad (15)$$

As mentioned before the method used now is identical to method reported in MR-1085/96. The only difference is that now the rate constant k_{M1} which describes the degradation of sulfonic acid is not fitted to experimental data but fixed to values observed by Hellpointner [1998].

Study 23:

Report: Reinken G. Porschewski R., (2014): “Flufenacet Core PECsoil and Accumulation: Modelling Core Info Document for Soil Exposure Assessment in Europe.”; Bayer CropScienceAG, Environmental Safety, Alfred-Nobel-Straße 50, 40789 Monheim, Germany; unpublished Report No. EnSa-13-1007; 2014. 02. 25; study reference number: M-478418-01-1;

Guidelines: Not specified, it was stated however that the assessment of the kinetic endpoints for Flufenacet and its major soil degradation products to select those suitable for calculating PEC_{SOIL} was performed to comply with the recommendations for modelling input selection given by the EU Commission, FOCUS and EFSA.

GLP: No, not applicable, modelling study

RMS comments: The study was performed as a supportive study to the main study presenting the results of the model exposure assessment for the soil compartment performed by the Applicant for Flufenacet and its major soil degradation products. It provides, for each compound of interest, the list of determined reliable DT_{50} values, the analysis of the data set aimed on the identification of potential outliers and identification, with justification, of the value considered suitable in calculation of PEC_{SOIL} values.

RMS evaluated the study and found it acceptable, although some of the conclusions drawn by the Applicant had to be modified as a result of the repeated kinetic analysis performed by the RMS. The study, although intended by the Applicant to be supportive for model exposure assessment for the soil compartment, is summarised here, as in RMS’s opinion it is closely related to the issues presented in this section, summarising the results of all studies presented under the point B.8.1.1.2.1.1.

Summary:

The aim of the study was to summarise the substance data used for the purpose of soil exposure and soil accumulation calculations, selected in line with the recommendations given by EU Commission, FOCUS and EFSA. It provided lists of the kinetic endpoints – DT_{50} values, together with the corresponding kinetic model, considered as appropriately representing persistence of Flufenacet and its major soil degradation products – FOE Sulfonic acid, FOE Oxalate, FOE Methylsulfone, FOE Thiadone, FOE 5043-Trifluoroethanesulfonic acid (TFESA) and Trifluoroacetic acid (TFA), in aerobic soil.

The conceptual compartmental scheme of transformation of Flufenacet in aerobic soil is presented below on figure B.8.1.1.2.1.1._CA-151.

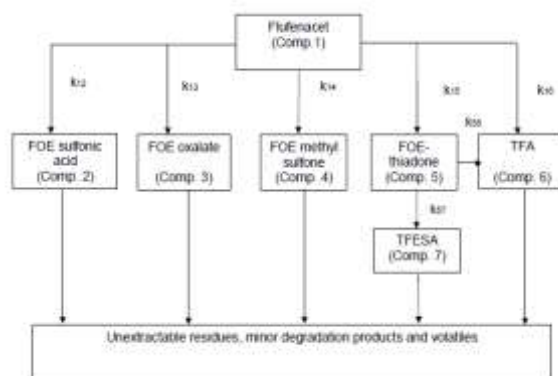


Figure B.8.1.1.2.1.1._CA-151: The conceptual compartmental scheme of transformation of Flufenacet in aerobic soil (copied from the study report).

The results of the kinetic analysis – the kinetic endpoints obtained for each of the compounds presented on the above scheme, were given in tables. They are presented below, individually for each of the compounds, also in tabularised form. Due to the fact, that in some cases RMS repeated the kinetic analysis, which resulted in different kinetic endpoints, the tables will contain additional column presenting the values found acceptable by

the RMS. In case the values proposed by the Applicant were changed by the RMS, the appropriate justification will be given under the table. Additionally, the Applicant's values not accepted by the RMS were marked italics.

a) The persistence kinetic endpoints obtained for Flufenacet:

In the study report the Applicant stated that the degradation of Flufenacet in aerobic soil was examined in six studies: [Kelley et al.; 1995], [Pangilinan and Smith; 1994], [Pangilinan and Smith; 1994a], [Hellpointner; 1999], [Hein; 2012] and [Hein; 2012a]. The kinetic analysis of the results obtained in these studies was performed and its results presented by Reinken and Partsch in five study reports. The Applicant decided to present the results obtained in three of them – [Reinken and Partsch; 2014], [Reinken and Partsch; 2014c] and [Reinken and Partsch; 2014d], in this report. That analysis resulted in the set of ten persistence kinetic endpoint determined in nine test soils. They are given below in the table B.8.1.1.2.1.1._CA-284. It shall be noted that while in case of Howe Indiana soil two DT₅₀ values are available for the same soil incubated under the same conditions, these values cannot be averaged, because they were determined in two separate studies, differing substantially in analytical protocol (soil processing and extracts quantitative analysis). As a result, the values cannot be regarded as replicates for the same soil but rather as separate values.

Table B.8.1.1.2.1.1._CA-284: The persistence kinetic endpoints – DT₅₀ values, determined for Flufenacet.

Study	Test soil data				Results obtained by the Applicant		Results verified and accepted by RMS	
	Soil name	Soil type (USDA)	Key soil properties		Kinetic model	DT ₅₀ [days]	Kinetic model	DT ₅₀ [days]
			pH	OC [%]				
<i>Kelley et al.; 1995</i>	BBA 2.2	Loamy sand	6.2	2.58	SFO	31.9	SFO	31.9
	Laacherhof AIII	Silt loam	7.3	0.9	SFO	<i>15.2</i>	SFO	16.9
	Hoefchen im Tal	Silt loam	5.8	2.4	SFO	20.4	SFO	20.44
<i>Pangilinan and Smith; 1994</i>	Howe, Indiana	Sandy loam	6.2	0.35	SFO	32.2	SFO	32.21
<i>Pangilinan and Smith; 1994a</i>	Howe, Indiana	Sandy loam	6.2	0.35	SFO	55.0	SFO	57.63
<i>Hellpointner; 1999</i>	Laacherhof AXXa	Sandy loam	6.1	1.41	SFO	7.3	SFO	7.35
<i>Hein; 2012</i>	Hoefchen am Hohenseh 4a	Silt loam	6.7	2.5	SFO	15.9	SFO	15.84
<i>Hein; 2012a</i>	Laacherhof AXXa	Loamy sand	6.1	2.4	SFO	19.9	SFO	19.85
	Dollendorf II	Clay loam	7.2	5.3	SFO	16.3	SFO	16.30
	Laacherhof Wurmweise	Loam	5.4	2.2	SFO	14.9	SFO	14.91

The Applicant performing the further statistical analysis of the data set stated that the DT₅₀ value obtained in Howe, Indiana Sandy loam soil in the study by [Pangilinan and Smith; 1994a] should be considered as an outlier and as a result not taken into account in determining the DT₅₀ value suitable for the soil exposure assessment. The justification for that were the results of the statistical analysis presented below on the figure B.8.1.1.2.1.1._CA-152. However, RMS, having analysed the justification, did not agree on the rejection of the challenged value solely on the basis of the statistical assessment, moreover because another value, second highest one, determined for the same soil and the same experimental conditions, was maintained in the data base in spite of some substantial deficiencies of both studies.

Additionally, at the last stage of assessment of the data set, the Applicant averaged two DT₅₀ values obtained in Laacherhof AXXa soil. It shall be noted however that the values were determined in two soils having a common name, but being different in many other aspects – one Laacherhof AXXa soil is a Sandy loam, having pH = 6.1 and OC = 1.41, while the other is a Loamy sand, although having the same pH = 6.1, but different OC = 2.4. Additionally, the values were derived using the data coming from two separate studies, having different analytical protocol with regard to sample processing and analysing.

As a result, the values cannot be considered replicates for the same soil, but used as individual values in calculating the averaged kinetic endpoint.

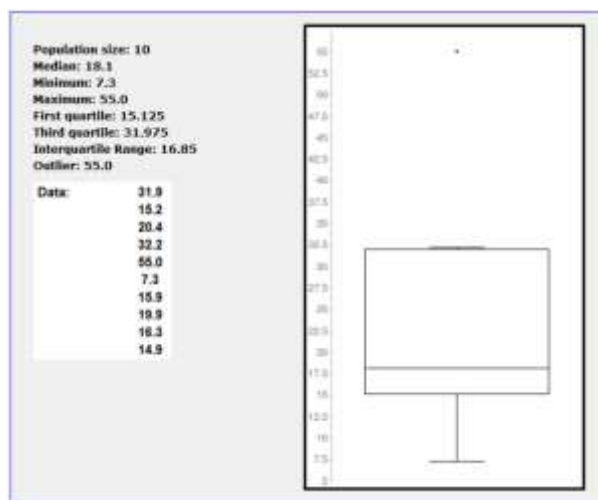


Figure B.8.1.1.2.1.1_CA-152: The results of the statistical analysis of the data set aimed on the identification of the outliers (copied from the study report).

Conclusion:

As a result of the evaluation presented above RMS identified the $DT_{50} = 57.63$ days, determined in Howe, Indiana, Sandy loam soil (study by [Pangilinan and Smith; 1994]) as appropriate value to be used in the exposure assessment for soil compartment performed for Flufenacet.

b) The persistence kinetic endpoints obtained for FOE Sulfonic acid:

The data on the persistence of FOE Sulfonic acid in soil were obtained in two studies with Flufenacet applied as parent compound and FOE Sulfonic acid forming as one of the primary major degradation products – [Kelley et al.; 1995] and [Pangilinan and Smith; 1994], and in four additional studies in which FOE Sulfonic acid was applied to soil as a parent compound – [Hellpointner; 1996], [Hellpointner; 2003], [Hein; 2013] and [Ströch and Junge; 2013]. The results of the studies by [Kelley et al.; 1995] and by [Pangilinan and Smith; 1994] were kinetically examined and the outcome presented in the study report [Reinken and Partsch; 2014]. The results obtained in the studies by [Hellpointner; 1996] and [Hellpointner; 2003] were subjected to subsequent kinetic analysis, the results of which were presented in another study report by Reinken and Partsch – [Reinken and Partsch; 2014e]. The two remaining studies – [Hein; 2013] and [Ströch and Junge; 2013], contain the appropriate kinetic analysis of the data.

That analysis resulted in the set of seventeen persistence kinetic endpoints, determined in seventeen test soils. The Applicant presenting the data set, initially divided it into two parts, presented separately in two tables. In one table were given the results obtained in the trials with Flufenacet applied as a parent compound – studies by [Kelley et al.; 1995] and [Pangilinan and Smith; 1994]. Second table contained the results obtained in the trials in which FOE Sulfonic acid was applied to test soils as a parent compound – studies by [Hellpointner; 1996], [Hellpointner; 2003], [Hein; 2013] and [Ströch and Junge; 2013].

Further analysing the data the Applicant stated that in case of the two soils used in the experiments with Flufenacet applied to soil – soils BBA 2.2 and Laacherhof AIII (both used in the study by [Kelley et al.; 1995]), the results for identical studies were available in the trials with FOE Sulfonic acid applied as parent compound (study by [Hellpointner; 1996]). For that reason the results were excluded from the data set. RMS however stated, having examined the data set, that the soils were similar but not identical. Additionally, the results were obtained in two separate studies. For that reason the results obtained in the study by [Kelley et al.; 1995] cannot be excluded from the data set on the basis of the justification provided by the Applicant. The Applicant also proposed to average the DT_{50} values, by calculating their geometric mean, obtained in soil Laacherhof AIII in studies by [Hellpointner; 1996] and [Hellpointner; 2003], and in soil Laacherhof AXXa in the same studies. The justification was not provided, but most probably it was based on the fact that the soils, bearing the same name were considered to be the same. RMS however, having analysed the data set, stated that the Applicant's proposal is not acceptable, because the soils for which averaging of the DT_{50} values was performed were not identical.

While soils bearing the name Laacherhof AIII were similar, belonging to the same textural class, but at the same time having different pH and OC, in case of the soil Laacherhof AXXa it was stated that the used soils not only differed in pH and OC, but also belonged to different textural classes.

Applicant also performed statistical analysis of the DT_{50} -data set, aimed on the identification of the would-be outliers. The analysis was performed in the same way as for Flufenacet and its results were presented in graphical form, reproduced below on figure B.8.1.1.2.1.1._CA-153. On their basis the Applicant stated that the DT_{50} values obtained in soils Hoefchen im Tal (study by [Kelley et al.; 1995]) and Howe, Indiana (study by [Pangilinan and Smith; 1994]), both having the value $DT_{50} = 1000$ days, should not be taken into account in selection of DT_{50} suitable for calculation of PEC_{SOIL} values, being outliers. RMS, having analysed the data set, came to similar conclusion with regard to these two values, but with different justification, presented further down this evaluation.

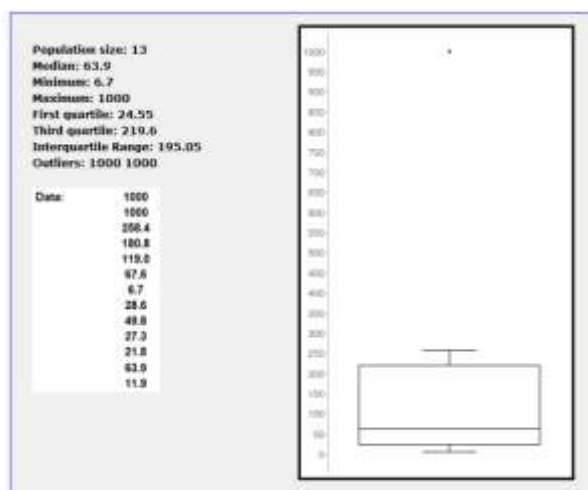


Figure B.8.1.1.2.1.1._CA-153: The results of the statistical analysis of the data set aimed on the identification of the outliers (copied from the study report).

Finally, the values proposed as definitive persistence kinetic endpoints (DT_{50} values) by the Applicant were compared with those found acceptable by the RMS. The results are presented below in the table B.8.1.1.2.1.1._CA-285. It shall be noted that in case of one trial – that on Laacherhof AIII in the study by [Hellpointner; 1996], the results of the repeated kinetic analysis demonstrated that it was not possible to obtain reliable kinetic fit. As a result RMS decided to replace the value by the mark “n. d.” – “not determined”. In case of the results of two studies – [Kelley et al; 1995] and [Pangilinan and Smith; 1994], the kinetic curve for FOE Sulfonic acid did not reach the decline phase. Therefore the default values $DT_{50} = 1000$ days were proposed in absence of those experimentally derived. It shall be noted however that, as they do not represent the reliable estimates of persistence of FOE Sulfonic acid in soil, they were not taken into account in determination of the DT_{50} value appropriate as input parameter in exposure assessment for the soil compartment and are presented here only for completeness. For that reason they are given in italics.

Table B.8.1.1.2.1.1_CA-285: The persistence kinetic endpoints – DT_{50} values, determined for FOE Sulfonic acid.

Study	Test soil data				Results obtained by the Applicant		Results verified and accepted by RMS	
	Soil name	Soil type (USDA)	Key soil properties		Kinetic model	DT_{50} [days]	Kinetic model	DT_{50} [days]
			pH	OC [%]				
<i>Kelley et al.; 1995</i>	BBA 2.2	Loamy sand	6.2	2.58	SFO	> 1000	SFO	> 1000
	Laacherhof AIII	Silt loam	7.3	0.9	SFO	> 1000	SFO	> 1000
	Hoefchen im Tal	Silt loam	5.8	2.4	SFO	> 1000	SFO	> 1000
<i>Pangilinan and Smith; 1994</i>	Howe, Indiana	Sandy loam	6.2	0.35	SFO	> 1000	SFO	> 1000
<i>Hellpointner; 1996</i>	BBA 2.1	Sand	5.3	0.57	SFO	258.4	SFO	318
	BBA 2.2	Loamy sand	6.3	2.48	SFO	180.8	SFO	211
	Laacherhof AIII	Silt loam	7.3	0.9	SFO	234.9	SFO	n. d.
<i>Hellpointner; 2003</i>	Laacherhof AXXa	Sandy loam	6.3	1.47	SFO	62.3	SFO	62.31
	Laacherhof AIII	Silt loam	6.8	0.88	SFO	60.3	SFO	60.26
<i>Hein; 2013</i>	Laacherhof AXXa	Loamy sand	6.2	1.7	SFO	73.4	SFO	73.38
	Dollendorf II	Loam	7.0	4.6	SFO	6.7	SFO	6.71
	Hoefchen am Hohenseh 4a	Silt loam	6.7	2.5	SFO	28.6	SFO	28.58
	Wurmweise	Sandy loam	5.0	1.8	SFO	49.8	SFO	49.77
<i>Ströch and Junge; 2013</i>	Hanscheider Hof	Loam	5.6	2.8	SFO	27.3	SFO	27.30
	Frankenforst	Silt loam	6.8	1.8	SFO	21.8	SFO	21.79
	LUFA 2.3	Sandy loam	6.8	1.1	SFO	63.9	SFO	63.87
	LUFA 6S	Clay	7.0	1.9	SFO	37.7	SFO	37.71

Conclusion:

As a result of the evaluation presented above RMS identified the $DT_{50} = 318$ days, determined in BBA 2.1 Sand soil (study by [Hellpointner; 1996]) as appropriate value to be used in the exposure assessment for soil compartment performed for FOE Sulfonic acid.

c) The persistence kinetic endpoints obtained for FOE Oxalate:

The data on the persistence of FOE Oxalate in soil were obtained in two studies with Flufenacet applied as parent compound and FOE Oxalate forming as one of the primary major degradation products – [Kelley et al.; 1995], and [Pangilinan and Smith; 1994]. The results of these studies were kinetically examined and the outcome presented in two study reports – [Reinken and Partsch; 2014] and [Reinken and Partsch; 2014a]. That analysis resulted in the set of four persistence kinetic endpoint determined in four test soils. RMS, having analysed the data, stated that in case of one soil it was not possible to determine the reliable kinetic endpoints, because the decline phase was not reached in course of the study. Therefore for that soil the value reported by the Applicant was replaced by the mark “n. d.” – “not determined”. The results of the comparative analysis of the Applicant’s persistence kinetic endpoints and those found acceptable by the RMS are presented below in the table B.8.1.1.2.1.1_CA-286.

Table B.8.1.1.2.1.1._CA-286: The persistence kinetic endpoints – DT_{50} values, determined for FOE Oxalate.

Study	Test soil data				Results obtained by the Applicant		Results verified and accepted by RMS	
	Soil name	Soil type (USDA)	Key soil properties		Kinetic model	DT_{50} [days]	Kinetic model	DT_{50} [days]
			pH	OC [%]				
<i>Kelley et al.; 1995</i>	BBA 2.2	Loamy sand	6.2	2.58	SFO	6.9	SFO	6.7
	Laacherhof AIII	Silt loam	7.3	0.9	SFO	20.7	SFO	18.9
	Hoefchen im Tal	Silt loam	5.8	2.4	SFO	13.1	SFO	13.09
<i>Pangilinan and Smith; 1994</i>	Howe, Indiana	Sandy loam	6.2	0.35	SFO	19.4	SFO	n. d.

Conclusion:

As a result of the evaluation presented above RMS identified the $DT_{50} = 18.9$ days, determined in Laacherhof AIII Silt loam soil (study by [Hellpointner; 1996]) as appropriate value to be used in the exposure assessment for soil compartment performed for FOE Sulfonic acid.

d) The persistence kinetic endpoints obtained for FOE Methylsulfone:

The data on the persistence of FOE Methylsulfone in soil were obtained in one study with Flufenacet applied as parent compound and FOE Methylsulfone forming as one of the primary major degradation products – [Kelley et al.; 1995], and in two additional studies in which FOE Methylsulfone was applied to soil as a parent compound – [Traub; 2012; 2013] and [Ströch and Junge; 2013a]. The results of the study by [Kelley et al.; 1995] were kinetically examined and the outcome presented in the study report [Reinken and Partsch; 2014]. The results obtained in the study by [Traub; 2012] were subjected to subsequent kinetic analysis, the results of which were presented in another study report by Reinken and Partsch – [Reinken and Partsch; 2014f]. The remaining study – [Ströch and Junge; 2013a], contain the appropriate kinetic analysis of the data.

That analysis resulted in the set of eleven persistence kinetic endpoints, determined in eleven test soils. The Applicant presenting the data set, initially divided it into two parts, presented separately in two tables. In one table were given the results obtained in the trials with Flufenacet applied as a parent compound – study [Kelley et al.; 1995]. Second table contained the results obtained in the trials in which FOE Methylsulfone was applied to test soils as a parent compound – studies by [Traub; 2012] and [Ströch and Junge; 2013a].

Applicant also performed statistical analysis of the DT_{50} -data set, aimed on the identification of the would-be outliers. The analysis was performed in the same way as for Flufenacet and its results were presented in graphical form, reproduced below on figure B.8.1.1.2.1.1._CA-154. On their basis the Applicant stated that the DT_{50} values obtained in soils BBA 2.2 and Hoefchen im Tal in the study by [Kelley et al.; 1995], both having the value $DT_{50} = 1000$ days, should not be considered in selection of DT_{50} suitable for calculation of PEC_{SOIL} values, being outliers. RMS, having analysed the data set came to similar conclusion with regard to these two values, but with different justification. In RMS's opinion the reason for not taking into account the kinetic endpoints reported for BBA 2.2 and Hoefchen im Tal soils is the fact that for these two soils the decline phase of the kinetic curve for FOE Methylsulfone was not reached, hence it cannot be stated whether the proposed kinetic endpoints can be considered the reliable estimates for the persistence of FOE Methylsulfone in those two soils.

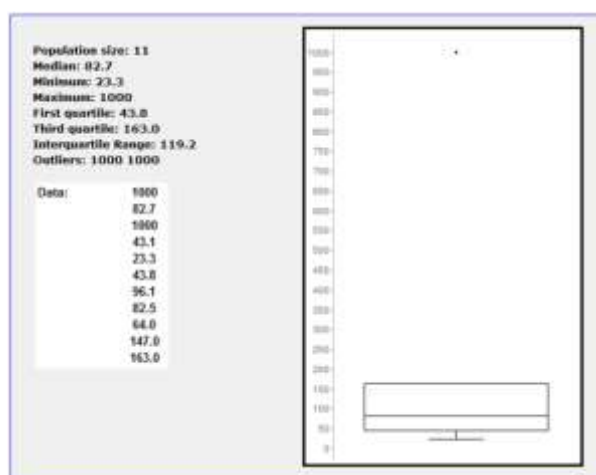


Figure B.8.1.1.2.1.1_CA-154: The results of the statistical analysis of the data set aimed on the identification of the outliers (copied from the study report).

Finally, the values proposed as definitive persistence kinetic endpoints (DT_{50} values) by the Applicant were compared with those found acceptable by the RMS. The results are presented below in the table B.8.1.1.2.1.1_CA-287. The kinetic endpoints for BBA 2.2 and Hoefchen im Tal soils are considered as not representing the reliable estimates of persistence of FOE Methylsulfone in soil. For that reason they were not taken into account in the determination of the DT_{50} value appropriate as input parameter in exposure assessment for the soil compartment and are presented here only for completeness. Therefore they are given in italics.

Table B.8.1.1.2.1.1_CA-287: The persistence kinetic endpoints – DT_{50} values, determined for FOE Methylsulfone.

Study	Test soil data				Results obtained by the Applicant		Results verified and accepted by RMS	
	Soil name	Soil type (USDA)	Key soil properties		Kinetic model	DT_{50} [days]	Kinetic model	DT_{50} [days]
			pH	OC [%]				
<i>Kelley et al.; 1995</i>	BBA 2.2	Loamy sand	6.2	2.58	SFO	> 1000	SFO	> 1000
	Laacherhof AIII	Silt loam	7.3	0.9	SFO	82.7	SFO	174
	Hoefchen im Tal	Silt loam	5.8	2.4	SFO	> 1000	SFO	> 1000
<i>Traub; 2012</i>	Laacherhof AXXa	Loamy sand	6.2	1.7	SFO	43.1	SFO	43.14
	Dollendorf II	Loam	7.0	4.6	SFO	23.2	SFO	23.30
	Hoefchen Am Hohenseh 4a	Silt loam	6.1	2.0	SFO	43.8	SFO	43.84
	Laacherhof Wurmweise	Sandy loam	5.0	1.8	SFO	96.1	SFO	96.13
<i>Ströch and Junge; 2013a</i>	Hanscheider Hof	Loam	5.6	2.8	SFO	82.5	SFO	82.53
	Frankenforst	Silt loam	6.8	1.8	SFO	64.0	SFO	63.98
	LUFA 2.3	Sandy loam	6.8	1.1	SFO	147.0	SFO	146.78
	LUFA 6S	Clay	7.0	1.9	SFO	163.0	SFO	163.06

Conclusion:

As a result of the evaluation presented above RMS identified the $DT_{50} = 174$ days, determined in Laacherhof AIII Silt loam soil (study by [Kelley et al.; 1995]) as appropriate value to be used in the exposure assessment for soil compartment performed for FOE Methylsulfone.

e) The persistence kinetic endpoints obtained for FOE Thiadone:

The data on the persistence of FOE Thiadone in soil were obtained in three studies with Flufenacet applied as parent compound and FOE Thiadone forming as one of the primary major degradation products – [Pangilinan and Smith; 1994a], [Hein; 2012] and [Hein; 2012a], as well as in one additional study in which FOE Thiadone was applied to soil as a parent compound – [Lentz and Bloomberg; 1999]. The results of the study by [Pangilinan and Smith; 1994a] were kinetically examined and the outcome presented in the study report [Reinken and Partsch; 2014d], those obtained in the studies by [Hein; 2012] and [Hein; 2012a] in the study report by [Reinken and Partsch; 2014c] and finally those obtained in the study by [Lentz and Bloomberg; 1999] in the study report by [Reinken and Partsch; 2014g].

That analysis resulted in the set of seven persistence kinetic endpoints, determined in eight test soils. No reliable kinetic endpoint could be determined in soil Howe, Indiana (study by [Pangilinan and Smith; 1994a]), due to the poor results of the fitting. RMS however was able to derive the reliable persistence kinetic endpoint for that soil as well using the top-down approach.

The values proposed as definitive persistence kinetic endpoints (DT_{50} values) by the Applicant were compared with those found acceptable by the RMS. The results are presented below in the table B.8.1.1.2.1.1_CA-288.

Table B.8.1.1.2.1.1_CA-288: The persistence kinetic endpoints – DT_{50} values, determined for FOE Thiadone.

Study	Test soil data				Results obtained by the Applicant		Results verified and accepted by RMS	
	Soil name	Soil type (USDA)	Key soil properties		Kinetic model	DT_{50} [days]	Kinetic model	DT_{50} [days]
			pH	OC [%]				
<i>Lentz and Bloomberg; 1999</i>	Iowa	Loamy sand	7.2	1.91	SFO	2.0	SFO	1.98
	Indiana	Sandy loam	6.5	1.28	SFO	1.4	SFO	1.40
	Nebraska	Silt loam	7.7	1.66	SFO	2.9	SFO	2.93
<i>Pangilinan and Smith; 1994a</i>	Howe, Indiana	Sandy loam	6.2	0.35	SFO	n. d.	SFO	15.9
<i>Hein; 2012</i>	Hoefchen am Hohenseh 4a	Silt loam	6.7	2.5	SFO	1.1	SFO	1.34
<i>Hein; 2012a</i>	Laacherhof AXXa	Loamy sand	6.1	2.4	SFO	1.4	SFO	1.13
	Dollendorf II	Clay loam	7.2	5.3	SFO	2.8	SFO	2.84
	Laacherhof Wurmwiiese	Loam	5.4	2.2	SFO	2.0	SFO	1.99

Conclusion:

As a result of the evaluation presented above RMS identified the $DT_{50} = 15.9$ days, determined in Howe, Indiana Sandy loam soil (study by [Pangilinan and Smith; 1994a]), as appropriate value to be used in the exposure assessment for soil compartment performed for FOE Thiadone.

f) The persistence kinetic endpoints obtained for FOE 5043-Trifluoroethanesulfonic acid (TFESA):

The data on the persistence of FOE 5043-Trifluoroethanesulfonic acid in soil were obtained in two studies with Flufenacet applied as parent compound and FOE 5043-Trifluoroethanesulfonic acid forming as a secondary major degradation products – [Hein; 2012] and [Hein; 2012a]. The results of these studies were kinetically examined and the outcome presented in the study report by [Reinken and Partsch; 2014c].

That analysis resulted in the set of four persistence kinetic endpoint determined in four test soils. The values proposed as definitive persistence kinetic endpoints (DT_{50} values) by the Applicant were compared with those found acceptable by the RMS. The results are presented below in the table B.8.1.1.2.1.1_CA-289. It shall be noted that in case of two test soils – Dollendorf II Clay loam soil and Laachehof Wurmwiiese Loam soil, the Applicant's and RMS's values are significantly different. That is due to the fact that, because of the poor fitting results, RMS repeated the analysis using the top-down approach.

Table B.8.1.1.2.1.1._CA-289: The persistence kinetic endpoints – DT₅₀ values, determined for FOE 5043-Trifluoroethanesulfonic acid (TFESA).

Study	Test soil data				Results obtained by the Applicant		Results verified and accepted by RMS	
	Soil name	Soil type (USDA)	Key soil properties		Kinetic model	DT ₅₀ [days]	Kinetic model	DT ₅₀ [days]
			pH	OC [%]				
Hein; 2012	Hoefchen am Hohenseh 4a	Silt loam	6.7	2.5	SFO	9.1	SFO	9.10
Hein; 2012a	Laacherhof AXXa	Loamy sand	6.1	2.4	SFO	4.5	SFO	4.48
	Dollendorf II	Clay loam	7.2	5.3	SFO	22.5	SFO	20.9
	Laacherhof Wurmweise	Loam	5.4	2.2	SFO	7.6	SFO	2.24

Conclusion:

As a result of the evaluation presented above RMS identified the **DT₅₀ = 20.9 days**, determined in Dollendorf II Clay loam soil (study by [Hein; 2012a]), as appropriate value to be used in the exposure assessment for soil compartment performed for FOE 5043-Trifluoroethanesulfonic acid (TFESA).

g) The persistence kinetic endpoints obtained for Trifluoroacetic acid (TFA):

The data on the persistence of Trifluoroacetic acid – TFA, were obtained in two studies Flufenacet applied as parent compound and TFA forming as secondary and ternary major degradation product – [Hein; 2012] and [Hein; 2012a], as well as in one additional study in which TFA was applied to soil as a parent compound – [Eckermann; 2012]. The results of the studies by [Hein; 2012] and [Hein; 2012a] were kinetically examined and the outcome presented in the study report [Reinken and Partsch; 2014c]. The kinetic analysis of the data obtained in the study by [Eckermann; 2012] was found incomplete by RMS, therefore repeated and the hence the reliable persistence kinetic endpoints reported here are those determined by the RMS.

The values proposed as definitive persistence kinetic endpoints (DT₅₀ values) by the Applicant were compared with those found acceptable by the RMS. The results are presented below in the table B.8.1.1.2.1.1._CA-277.

Table B.8.1.1.2.1.1._CA-290: The persistence kinetic endpoints – DT₅₀ values, determined for Trifluoroacetic acid – TFA.

Study	Test soil data				Results obtained by the Applicant		Results verified and accepted by RMS	
	Soil name	Soil type (USDA)	Key soil properties		Kinetic model	DT ₅₀ [days]	Kinetic model	DT ₅₀ [days]
			pH	OC [%]				
Hein; 2012	Hoefchen am Hohenseh 4a	Silt loam	6.7	2.5	SFO	> 1000	SFO	> 1000
Hein; 2012a	Laacherhof AXXa	Loamy sand	6.1	2.4	SFO	> 1000	SFO	> 1000
	Dollendorf II	Clay loam	7.2	5.3	SFO	> 1000	SFO	> 1000
	Laacherhof Wurmweise	Loam	5.4	2.2	SFO	> 1000	SFO	> 1000
Eckermann; 2012	Laacher Hof AXXa	Sandy loam	6.2	1.6	SFO	> 1000	SFO	> 10000
	Dollendorf II	Clay loam	7.3	5.5	SFO	> 1000	SFO	> 10000
	Hoefchen Am Hohenseh 4a	Silt loam	6.4	2.4	SFO	> 1000	SFO	> 10000
	Laacher Hof Wurmweise	Sandy loam	5.1	1.9	SFO	> 1000	SFO	> 10000

Conclusion:

As a result of the evaluation presented above RMS identified the default **DT₅₀ = 10000 days** as appropriate value to be used in the exposure assessment for soil compartment performed for Trifluoroacetic acid. That extreme value is considered appropriate because not only the relevant study demonstrated no degradation of TFA in soil, but also the literature data indicate that the compound is extremely persistent in that compartment.

Study 24:

Report: Reinken G. Porschewski R., (2014): “Flufenacet Core PEC_{gw} FOCUS EU: Modelling Core Info Document for Groundwater Risk Assessment in Europe.”; Bayer CropScienceAG, Environmental Safety, Alfred-Nobel-Straße 50, 40789 Monheim, Germany, unpublished Report No. EnSa-13-1006; 2014. 02. 25; study reference number: M-478214-01-1;

Guidelines: Not specified, it was stated however that the assessment of the kinetic endpoints for Flufenacet and its major soil degradation products to select those suitable for calculating PEC_{GW} was performed to comply with the recommendations for modelling input selection given by the EU Commission, FOCUS and EFSA.

GLP: No, not applicable, modelling study

RMS comments: The study was performed as a supportive study to the main study presenting the results of the model exposure/risk assessment for the groundwater compartment, performed by the Applicant for Flufenacet and its major soil degradation products. It provides, for each compound of interest, the list of determined reliable soil DT₅₀ values and adsorption parameters (K_f, K_{fOC} and 1/n values), the analysis of the data sets aimed on the identification of potential outliers and identification, with justification, of the endpoints considered suitable in calculation of PEC_{GW} values, as well as their normalisation.

RMS evaluated the study and found it generally acceptable, although some of the conclusions drawn by the Applicant had to be modified as a result of the repeated kinetic analysis performed by the RMS. Also refined was the normalisation procedure – calculated correction fraction, presented by the Applicant. The study, although intended by the Applicant to be supportive for model risk assessment for the groundwater compartment is summarised here in its part dealing with the analysis of the kinetic endpoints derived for soil compartment. That is due to the fact that in RMS opinion the study in that area it is closely related to the issues presented in this section, summarising the results of all studies presented under the point B.8.1.1.2.1.1.

Summary:

The aim of the study was to provide a summary of modelling input values for Flufenacet and its major soil degradation products selected for PEC_{GW} calculations, in line with the recommendations given by EU Commission, FOCUS and EFSA. In the area of the degradation in soil it provided lists of the normalised kinetic endpoints – DT₅₀ values, together with the corresponding kinetic model, considered as appropriately representing degradation rate of Flufenacet and its major soil degradation products – FOE Sulfonic acid, FOE Oxalate, FOE Methylsulfone, FOE Thiadone, FOE 5043-Trifluoroethanesulfonic acid (TFESA) and Trifluoroacetic acid (TFA) in aerobic soil. The normalisation of DT₅₀ values to the standard conditions – T = 20°C and soil moisture equal to FC (Field Capacity), was performed in line with the recommendations provided by the relevant EU Guidelines. The correction for temperature was performed using the recommended by EFSA Q₁₀ = 2.58. The normalisation factor f_T was calculated using the equation presented below (copied from the study report):

$$f_T = Q_{10}^{(T - T_{ref})/10}$$

The normalisation for the soil moisture was performed using the Walker equation presented below (copied from the study report) and Walker moisture exponent $\beta = 0.7$:

$$f_\theta = \begin{cases} \left(\frac{\theta}{\theta_{ref}} \right)^\beta & \theta \leq \theta_{ref} \\ 1 & \theta > \theta_{ref} \end{cases}$$

The results of the normalisation – correction factors calculated by the Applicant, are provided below in the table B.8.1.1.2.1.1_CA-291.

Table B.8.1.1.2.1.1_CA-291: The results of the normalisation procedure performed by the Applicant – calculated temperature and moisture correction factors.

Study	Test soil		Experimental conditions		Temperature normalisation		Moisture content normalisation					RMS evaluation – acceptability of the correction factor	
	Name ¹⁾	Textural class (USDA) ²⁾	T [°C]	Soil moist.	T [°C] ³⁾	Corr. factor	Experimental conditions [%]		Reference value - θ_{ef} at pF2 [%]		Corr. factor		
							MWHC	θ	measured	FOCUS			
Kelley et al; 1995	BBA 2.2	LS	20	40% MWHC	20	1.0	53.8	21.52	----	14	1.0	Yes	Yes
	LH AIII	SiL	20	40% MWHC	20	1.0	48.6	19.44	----	26	0.82	Yes	Yes
	HT	SiL	20	40% MWHC	20	1.0	71.6	28.64	----	26	1.0	Yes	Yes
Pangilinan and Smith; 1994	Howe, Indiana	SaL	21	75% of 1/3 bar	21	1.10	----	----	----	19	1.0	Yes	No
Pangilinan and Smith; 1994a	Howe, Indiana	SaL	21	75% of 1/3 bar	20	1.0	----	----	----	19	1.0	No	No
Hellpointner; 1999	LH AXXa	SaL	20.3	50% MWHC	20	1.0	34.4	17.2	----	19	0.93	No	Yes
Hein; 2012	HH	SiL	19.7	55% MWHC	20	1.0	61.1	33.61	29.8	----	1.00	No	Yes
Hein; 2012a	LH AXXa	LS	19.8	55% MWHC	20	1.0	49.1	27.01	18.7	----	1.00	No	Yes
	DD	CL	19.8	55% MWHC	20	1.0	79.8	43.89	46.0	----	0.97	No	Yes
	LW	Lo	19.8	55% MWHC	20	1.0	59.9	32.95	23.3	----	1.00	No	Yes
Hellpointner; 1996	BBA 2.1	Sa	20	40% MWHC	20	1.0	----	9.0	----	12	0.82	Yes	Yes
	BBA 2.2	LS	20	40% MWHC	20	1.0	----	17.9	----	14	1.00	Yes	Yes
	LH AIII	SiL	20	40% MWHC	20	1.0	----	14.0	----	26	0.65	Yes	Yes
Hellpointner; 2003	LH AXXa	SaL	20	40% MWHC	20	1.0	34.42	13.77	----	19	0.80	Yes	Yes
	LH AIII	SiL	20	40% MWHC	20	1.0	36.4	14.56	----	26	0.67	Yes	Yes
Hein; 2013	LH AXXa	LS	19.6	55% MWHC	19.6	0.96	48.5	26.7	12.9	----	1.00	Yes	Yes
	DD	Lo	19.6	55% MWHC	19.6	0.96	79.1	43.5	45.4	----	0.97	Yes	Yes
	HH	SiL	19.6	55% MWHC	19.6	0.96	54.8	30.1	33.1	----	0.94	Yes	Yes
	WW	SaL	19.6	55% MWHC	19.6	0.96	56.3	31.0	19.8	----	1.00	Yes	Yes
Ströch and Junge; 2013	HaH	Lo	19.9	55% MWHC	19.9	0.99	64.4	35.4	30.1	----	1.00	Yes	Yes
	FF	SiL	19.9	55% MWHC	19.9	0.99	56.7	31.2	30.5	----	1.00	Yes	Yes
	LUFA 2.3	SaL	19.9	55% MWHC	19.9	0.99	39.3	21.6	17.8	----	1.00	Yes	Yes
	LUFA 6S	Cl	19.9	55% MWHC	19.9	0.99	48.3	26.6	32.8	----	0.86	Yes	Yes
Traub; 2012	LH AXXa	LS	19.7	55% MWHC	20	1.0	48.5	26.675	----	14	1.00	No	Yes
	DD	Lo	19.7	55% MWHC	20	1.0	79.1	43.505	----	25	1.00	No	Yes
	HH	SiL	19.7	55% MWHC	20	1.0	54.8	30.14	----	26	1.00	No	Yes
	LW	SaL	19.7	55% MWHC	20	1.0	56.3	30.695	----	19	1.00	No	Yes
Lentz and Bloomberg; 1999	Iowa	LS	20	75% of 1/3 bar	20	1.0	----	9.92	----	14	0.79	Yes	No
	Indiana	SaL	20	75% of 1/3 bar	20	1.0	----	13.27	----	19	0.78	Yes	No
	Nebraska	SiL	20	75% of 1/3 bar	20	1.0	----	24.19	----	26	0.95	Yes	No
Ströch and Junge; 2013a	HaH	Lo	19.9	55% MWHC	19.9	0.99	64.4	35.4	30.1	----	1.00	Yes	Yes
	FF	SiL	19.9	55% MWHC	19.9	0.99	56.7	31.2	30.5	----	1.00	Yes	Yes
	LUFA 2.3	SaL	19.9	55% MWHC	19.9	0.99	39.3	21.6	17.8	----	1.00	Yes	Yes
	LUFA 6S	Cl	19.9	55% MWHC	19.9	0.99	48.3	26.6	32.8	----	0.86	Yes	Yes

Footnotes to the table:

- 1) For the soil names the following abbreviations were used:
 - LH AIII: Laaaherhof AIII/Laacher Hof AIII;
 - HT: Hoefchen im Tal (Höfchen im Tal);
 - LH AXXa: Laacherhof AXXa/Laacher Hof AXXa;
 - HH: Hoefchen am Hohenseh 4a/ Höfchen am Hohenseh 4a;
 - DD: Dollendorf II;
 - LW: Laaaherhof Wurmwielse;
 - WW: Wurmwielse;
 - HaH: Hanscheider Hof;
 - FF: Frankenforst;
- 2) For the soil textural class the following abbreviations were used:
 - LS: Loamy sand;
 - SiL: Silt loam;
 - SaL: Sandy loam;
 - Cl: Clay;
 - Lo: Loam;
 - Sa: Sand;
 - CL: Clay loam.
- 3) Temperature reported by the Applicant

These values were verified by the RMS. The following things were stated:

- The normalisation for the temperature was not accepted in case of Howe Indiana soil in the study [Pangilinan and Smith; 1994a], because the Applicant used the wrong incubation temperature – $T = 20^{\circ}\text{C}$ instead of $T = 21^{\circ}\text{C}$ declared in the study and hence incorrectly assumed the correction factor of 1.00.
- In case of Howe, Indiana, Sandy loam soil for both experiments – by [Pangilinan and Smith; 1994] and [Pangilinan and Smith; 1994a], normalisation for the soil moisture cannot be accepted because the Applicant incorrectly stated that there was no soil moisture data available in the study. In fact in the study report were given both soil moisture content measured at the level of $\frac{1}{3}$ bar – 13.1%, and at 75% of $\frac{1}{3}$ bar – 8.95%. Therefore it was possible to carry out proper normalisation and hence it was not necessary to assume worst case conditions – 100% FC, as did the Applicant.
- In case of the study by [Lentz and Bloomberg; 1999] normalisation for the soil moisture content was carried out incorrectly: the Applicant as the values of soil moisture during the experiment used those determined at the level of $\frac{1}{3}$ bar instead of the values at 75% of $\frac{1}{3}$ bar – the actual soil moisture content during incubation. That in turn resulted in underestimated correction factors.
- The temperature normalisation performed for the studies [Hellpointner; 1999], [Hein; 2012], [Hein; 2012a] and [Traub; 2012] was not accepted by the RMS because of the inconsistency of the Applicant's approach. For these three studies the incubation temperature was set to $T = 20^{\circ}\text{C}$, while in fact the average incubation temperature was different: $T = 20.3^{\circ}\text{C}$ in case of the study by [Hellpointner; 1999], $T = 19.7^{\circ}\text{C}$ in case of the study by [Hein; 2012], $T = 19.8^{\circ}\text{C}$ in case of the study by [Hein; 2012a] and $T = 19.7^{\circ}\text{C}$ in case of the study by [Traub; 2012]. These deviations from the assumed temperature $T = 20 \pm 1^{\circ}\text{C}$ were minimal and it may be therefore stated that the correction for the temperature was not necessary, however the Applicant performed the temperature correction of the kinetic endpoints in case of three other studies – by [Hein; 2013], where the average $T = 19.6^{\circ}\text{C}$ and by [Ströch and Junge; 2013] and [Ströch and Junge; 2013a], for both of which the average $T = 19.9^{\circ}\text{C}$, so the difference between the assumed $T = 20^{\circ}\text{C}$ and the averaged measured incubation temperature was $<0.5^{\circ}\text{C}$, so within the assumed error margin $\pm 1.0^{\circ}\text{C}$. In RMS's opinion for none of these studies the normalisation for temperature was required, but to maintain the consistency of the approach the RMS decided to normalise for temperature the results of the studies by [Hellpointner; 1999], [Hein; 2012], [Hein; 2012a] and [Traub; 2012].
- No normalisation was performed for the experiment by [Eckermann; 2012], but that may be explained by the fact that it was not necessary since no degradation of the compound was observed in any test soil, so the default DT_{50} values were proposed, for which any normalisation would be meaningless.

The verified correction factors used in normalisation of the kinetic endpoints are provided below in the table B.8.1.1.2.1.1._CA-292.

Table B.8.1.1.2.1.1_CA-292: The results of the updated normalisation procedure performed by the RMS – temperature and moisture correction factors.

Study	Test soil		Experimental conditions		Temperature normalisation		Moisture content normalisation					
	Name ¹⁾	Textural class (USDA) ²⁾	T [°C]	Soil moist.	T [°C]	Corr. factor	Experimental conditions [%]			Reference value - θ_{ref} at pF2 [%]		Corr. factor
							MWHC	at ½ bar	θ	measured	FOCUS	
<i>Kelley et al; 1995</i>	BBA 2.2	LS	20	40% MWHC	20	1.0	53.8	----	21.52	----	14	1.0
	LH AIII	SiL	20	40% MWHC	20	1.0	48.6	----	19.44	----	26	0.82
	HT	SiL	20	40% MWHC	20	1.0	71.6	----	28.64	----	26	1.0
<i>Pangilinan and Smith; 1994</i>	Howe, Indiana	SaL	21	75% of ½ bar	21	1.10	----	13.1	8.95	----	19	0.59
<i>Pangilinan and Smith; 1994a</i>	Howe, Indiana	SaL	21	75% of ½ bar	21	1.10	----	13.1	8.95	----	19	0.59
<i>Hellpointner; 1999</i>	LH AXXa	SaL	20.3	50% MWHC	20.3	1.03	34.4	----	17.2	----	19	0.93
<i>Hein; 2012</i>	HH	SiL	19.7	55% MWHC	19.7	0.97	61.1	----	33.61	29.8	----	1.00
<i>Hein; 2012a</i>	LH AXXa	LS	19.8	55% MWHC	19.8	0.98	49.1	----	27.01	18.7	----	1.00
	DD	CL	19.8	55% MWHC	19.8	0.98	79.8	----	43.89	46.0	----	0.97
	LW	Lo	19.8	55% MWHC	19.8	0.98	59.9	----	32.95	23.3	----	1.00
<i>Hellpointner; 1996</i>	BBA 2.1	Sa	20	40% MWHC	20	1.0	----	----	9.0	----	12	0.82
	BBA 2.2	LS	20	40% MWHC	20	1.0	----	----	17.9	----	14	1.00
	LH AIII	SiL	20	40% MWHC	20	1.0	----	----	14.0	----	26	0.65
<i>Hellpointner; 2003</i>	LH AXXa	SaL	20	40% MWHC	20	1.0	34.42	----	13.77	----	19	0.80
	LH AIII	SiL	20	40% MWHC	20	1.0	36.4	----	14.56	----	26	0.67
<i>Hein; 2013</i>	LH AXXa	LS	19.6	55% MWHC	19.6	0.96	48.5	----	26.7	12.9	----	1.00
	DD	Lo	19.6	55% MWHC	19.6	0.96	79.1	----	43.5	45.4	----	0.97
	HH	SiL	19.6	55% MWHC	19.6	0.96	54.8	----	30.1	33.1	----	0.94
	WW	SaL	19.6	55% MWHC	19.6	0.96	56.3	----	31.0	19.8	----	1.00
<i>Ströck and Junge; 2013</i>	HaH	Lo	19.9	55% MWHC	19.9	0.99	64.4	----	35.4	30.1	----	1.00
	FF	SiL	19.9	55% MWHC	19.9	0.99	56.7	----	31.2	30.5	----	1.00
	LUFA 2.3	SaL	19.9	55% MWHC	19.9	0.99	39.3	----	21.6	17.8	----	1.00
	LUFA 6S	Cl	19.9	55% MWHC	19.9	0.99	48.3	----	26.6	32.8	----	0.86
<i>Traub; 2012</i>	LH AXXa	LS	19.7	55% MWHC	19.7	0.97	48.5	----	26.675	----	14	1.00
	DD	Lo	19.7	55% MWHC	19.7	0.97	79.1	----	43.505	----	25	1.00
	HH	SiL	19.7	55% MWHC	19.7	0.97	54.8	----	30.14	----	26	1.00
	LW	SaL	19.7	55% MWHC	19.7	0.97	56.3	----	30.695	----	19	1.00
<i>Lentz and Bloomberg; 1999</i>	Iowa	LS	20	75% of ½ bar	20	1.0	----	9.92	7.44	----	14	0.64
	Indiana	SaL	20	75% of ½ bar	20	1.0	----	13.27	9.95	----	19	0.64
	Nebraska	SiL	20	75% of ½ bar	20	1.0	----	24.19	18.14	----	26	0.78
<i>Ströck and Junge; 2013a</i>	HaH	Lo	19.9	55% MWHC	19.9	0.99	64.4	----	35.4	30.1	----	1.00
	FF	SiL	19.9	55% MWHC	19.9	0.99	56.7	----	31.2	30.5	----	1.00
	LUFA 2.3	SaL	19.9	55% MWHC	19.9	0.99	39.3	----	21.6	17.8	----	1.00
	LUFA 6S	Cl	19.9	55% MWHC	19.9	0.99	48.3	----	26.6	32.8	----	0.86

Footnotes to the table:

- 1) For the soil names the following abbreviations were used:
 - LH AIII: Laacherhof AIII/Laacher Hof AIII;
 - HT: Hoefchen im Tal (Höfchen im Tal);
 - LH AXXa: Laacherhof AXXa/Laacher Hof AXXa;
 - HH: Hoefchen am Hohenseh 4a/ Höfchen am Hohenseh 4a;
 - DD: Dollendorf II;
 - LW: Laacherhof Wurmwielse;
 - WW: Wurmwielse;
 - HaH: Hanscheider Hof;
 - FF: Frankenforst;
- 2) For the soil textural class the following abbreviations were used:
 - LS: Loamy sand;
 - SiL: Silt loam;
 - SaL: Sandy loam;
 - Cl: Clay;
 - Lo: Loam;
 - Sa: Sand;
 - CL: Clay loam.

The correction factors presented above in the table B.8.1.1.2.1.1_CA-292 were subsequently used to normalise the DT_{50} values for GW and SW modelling.

The Applicant presented in the study report the determined kinetic formation fractions – ff for each degradation product and the normalised kinetic endpoints – individual DT_{50} values for each test soil and the calculated geomean values. RMS noticed that the normalised values were determined using the persistence DT_{50} values, identical with those characterised in the previously summarised **Study 23**. As the RMS changed the conclusions of that study, also the results obtained there by the Applicant changed. Therefore RMS decided not to present the values obtained by the Applicant, even for the comparative purposes, in order to not overburden the Assessment Report.

As an introduction to the whole analysis the conceptual compartmental scheme of transformation of Flufenacet in aerobic soil was presented, shown below on figure B.8.1.1.2.1.1_CA-155.

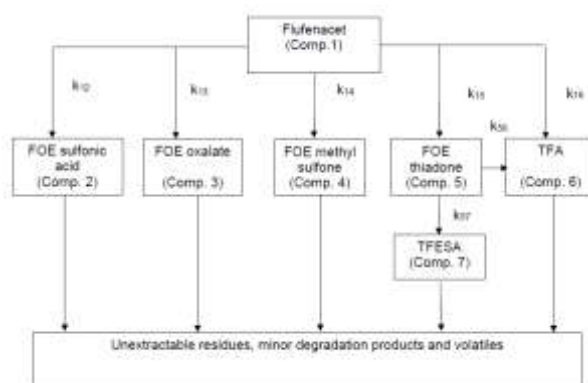


Figure B.8.1.1.2.1.1_CA-155: The conceptual compartmental scheme of transformation of Flufenacet in aerobic soil (copied from the study report).

Next are presented the results of the normalisation of DT_{50} values for each compound and, for the degradation products, the determined kinetic formation fractions ff . To maintain the consistency between the two summaries, the RMS used exactly the same order of presenting the data for each individual compound as in the previous summary (**Study 23**).

a) The kinetic endpoints determined for Flufenacet:

The degradation of Flufenacet in aerobic soil was examined in six studies: [Kelley et al.; 1995], [Pangilinan and Smith; 1994], [Pangilinan and Smith; 1994a], [Hellpointner; 1999], [Hein; 2012] and [Hein; 2012a]. The kinetic analysis of the results obtained in these studies was performed and its results presented by Reinken and Partsch in five study reports, of which three were found to contain relevant kinetic endpoints – [Reinken and Partsch; 2014], [Reinken and Partsch; 2014c] and [Reinken and Partsch; 2014d]. That analysis resulted in the set of ten pairs of persistence kinetic endpoints – DT_{50} and DT_{90} values, determined in nine test soils. The DT_{50}

values representing persistence were subsequently normalised in order to obtain the modelling DT_{50} values. All of them are given below in the table B.8.1.1.2.1.1._CA-293. It shall be noted that while in case of Howe Indiana soil two DT_{50} values are available for the same soil incubated under the same conditions, these values cannot be averaged, because they were determined in two separate studies, differing substantially in analytical protocol (soil processing and extracts quantitative analysis). As a result, the values cannot be regarded as replicates for the same soil but rather as separate values.

The Applicant rejected both sets of kinetic endpoints obtained in Howe, Indiana, Sandy loam soil. The kinetic endpoints obtained in the study by [Pangilinan and Smith; 1994] were rejected from the data set as outliers already at initial stage and not taken at all into consideration for the selection of DT_{50} values for PEC_{GW} calculations. That conclusion was supported by the results of the statistical analysis, the results of which are presented in graphical form below, on figure B.8.1.1.2.1.1._CA-156. Such approach is however inconsistent, because the values determined for degradation products – FOE Sulfonic acid and FOE Oxalate, were included into the data set undergoing further statistical analysis. The results of the normalisation showed that the value was in good agreement with other DT_{50} values, therefore there is no reason for not including it into the data set.

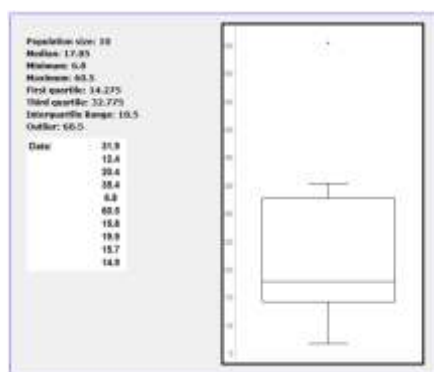


Figure B.8.1.1.2.1.1._CA-156: The results of the initial statistical analysis of the data set aimed on the identification of the outliers (copied from the study report).

Applicant also stated that the second set of kinetic endpoints obtained in Howe, Indiana, Sandy loam soil, in the study by [Pangilinan and Smith; 1994a] should be considered as an outlier and not taken into account in calculating the geomean DT_{50} value to be used in GW modelling. RMS however did not agree with that approach, moreover because no justification was provided and the results of the statistical analysis, presented above on figure B.8.1.1.2.1.1._CA-156, did not demonstrate that the value significantly differed from the other values within the data set.

Finally, it was noticed that the Applicant averaged two DT_{50} values obtained in Laacherhof AXXa soil before calculating the overall geomean normalised DT_{50} value. However, that approach is not acceptable, since the two Laacherhof AXXa soils bear a common name, but are different in many other aspects – one Laacherhof AXXa soil is a Sandy loam, having pH = 6.1 and OC = 1.41, while the other is a Loamy sand, although having the same pH = 6.1, but different OC = 2.4. Additionally, the values were derived using the data coming from two separate studies, having different analytical protocol with regard to sample processing and analysing.

As a result, the values cannot be considered replicates for the same soil, but should be used as individual values in calculating the averaged kinetic endpoint.

As signalled above, the resulting ultimate data set is presented below in the table B.8.1.1.2.1.1._CA-293.

Table B.8.1.1.2.1.1_CA-293: The persistence and modelling kinetic endpoints – DT₅₀ and DT₉₀ values, determined for Flufenacet.

Study	Test soil data				Persistence kinetic endpoints			Kinetic endpoints recommended for modelling
	Soil name	Soil type (USDA)	Key soil properties		Kinetic model	DT ₅₀ [days]	DT ₉₀ [days]	DT ₅₀ [days]
			pH	OC [%]				
<i>Kelley et al.; 1995</i>	BBA 2.2	Loamy sand	6.2	2.58	SFO	31.9	106.1	31.9
	Laacherhof AIII	Silt loam	7.3	0.9	SFO	16.9	56.0	13.86
	Hoefchen im Tal	Silt loam	5.8	2.4	SFO	20.44	67.90	20.44
<i>Pangilinan and Smith; 1994</i>	Howe, Indiana	Sandy loam	6.2	0.35	SFO	32.21	107.0	20.90
<i>Pangilinan and Smith; 1994a</i>	Howe, Indiana	Sandy loam	6.2	0.35	SFO	57.63	191.42	37.40
<i>Hellpointner; 1999</i>	Laacherhof AXXa	Sandy loam	6.1	1.41	SFO	7.35	24.42	7.04
<i>Hein; 2012</i>	Hoefchen am Hohenseh 4a	Silt loam	6.7	2.5	SFO	15.84	52.61	15.36
<i>Hein; 2012a</i>	Laacherhof AXXa	Loamy sand	6.1	2.4	SFO	19.85	65.93	19.45
	Dollendorf II	Clay loam	7.2	5.3	SFO	16.30	54.18	15.49
	Laacherhof Wurmweise	Loam	5.4	2.2	SFO	14.91	49.54	14.61
Geomean (n = 10)						20.23	67.20	17.89
Median (n = 10)						18.38	60.97	17.47

The report also contained the data on the soil sorption of Flufenacet, which are beyond the scope of this summary therefore not presented here, and on the kinetic formation fractions determined for the degradation products of Flufenacet. In case of these values RMS decided to present and evaluate them in the relevant sections of this summary, dealing individually with each degradation product.

Conclusion:

As a result of the evaluation presented above RMS determined the normalised geomean **DT₅₀ = 17.89 days**, value for Flufenacet, recommended to be used in GW (and SW) model exposure assessment. Also the median normalised **DT₅₀ = 17.47 days** was calculated, which can be alternatively used for the same purpose.

b) The kinetic endpoints determined for FOE Sulfonic acid:

The data on the persistence of FOE Sulfonic acid in soil were obtained in two studies with Flufenacet applied as parent compound and FOE Sulfonic acid forming as one of the primary major degradation products – [Kelley et al.; 1995] and [Pangilinan and Smith; 1994], and in four additional studies in which FOE Sulfonic acid was applied to soil as a parent compound – [Hellpointner; 1996], [Hellpointner; 2003], [Hein; 2013] and [Ströch and Junge; 2013]. The results of the studies by [Kelley et al.; 1995], [Pangilinan and Smith; 1994] were kinetically examined and the outcome presented in the study report [Reinken and Partsch; 2014]. The results obtained in the studies by [Hellpointner; 1996] and [Hellpointner; 2003] were subjected to subsequent kinetic analysis, the results of which were presented in another study report by Reinken and Partsch – [Reinken and Partsch; 2014e]. The two remaining studies – [Hein; 2013] and [Ströch and Junge; 2013], contain the appropriate kinetic analysis of the data.

That analysis resulted in the set of seventeen persistence kinetic endpoint determined in seventeen test soils. The Applicant presenting the data set, initially divided it into two parts, presented separately in two tables. In one table were given the results obtained in the studies with Flufenacet applied as a parent compound – studies by [Kelley et al.; 1995] and [Pangilinan and Smith; 1994]. Second table contained the results obtained in studies in which FOE Sulfonic acid was applied to test soils as a parent compound – studies by [Hellpointner; 1996], [Hellpointner; 2003], [Hein; 2013] and [Ströch and Junge; 2013].

Further analysing the data the Applicant stated that in case of the two soils used in the experiments with Flufenacet applied to soil – soils BBA 2.2 and Laacherhof AIII (both used in the study by [Kelley et al.; 1995]) the results for identical soils were available in the trials with FOE Sulfonic acid applied as parent compound (study by [Hellpointner; 1996]). For that reason the results were excluded from the data set. RMS however stated, having examined the data set, that the soils were similar but not identical. Additionally, the results were obtained in two separate studies. For that reason the results obtained in the study by [Kelley et al.; 1995] cannot be excluded from the data base on the basis of the justification provided by the Applicant. The Applicant also proposed to average the DT_{50} values, by calculating their geometric mean, obtained in soil Laacherhof AIII in studies by [Hellpointner; 1996] and [Hellpointner; 2003] and in soil Laacherhof AXXa in the same studies. The justification was not provided, but most probably it was based on the fact that the soils, bearing the same name should be the same. RMS however, having analysed the data set, stated that the Applicant's proposal is not acceptable, because the soils for which averaging of the DT_{50} values was performed were not identical. While soils bearing name Laacherhof AIII were similar, belonging to the same textural class, but at the same time having different pH and OC, in case of the soil Laacherhof AXXa it was stated that the used soil samples not only differed in pH and OC, but also belonged to different textural classes.

Applicant also performed statistical analysis of the DT_{50} -data set aimed on the identification of the would-be outliers. The analysis was performed in the same way as for Flufenacet and its results presented in graphical form, reproduced below on figure B.8.1.1.2.1.1_CA-157. On their basis the Applicant stated that the DT_{50} values obtained in soils Hoefchen im Tal (study by [Kelley et al.; 1995]) and Howe, Indiana (study by [Pangilinan and Smith; 1994]), both having the value $DT_{50} = 1000$ days, should not be considered in selection of DT_{50} suitable for calculation of PEC_{GW} values, being outliers. RMS having analysed the data set came to similar conclusion with regard to these two values, but with different justification, presented further down this evaluation.

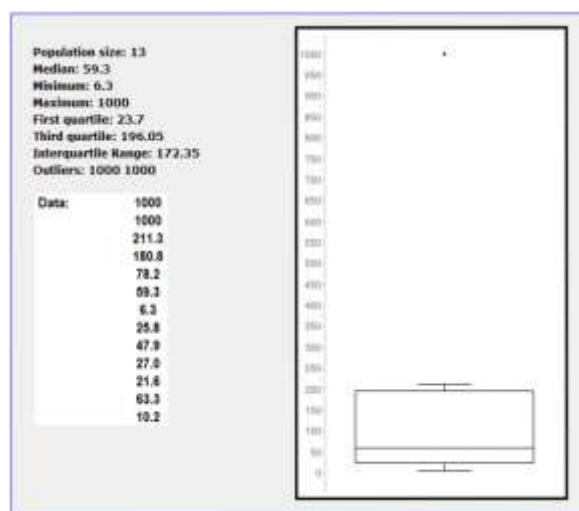


Figure B.8.1.1.2.1.1_CA-157: The results of the statistical analysis of the data set aimed on the identification of the outliers (copied from the study report).

RMS decided not to include the kinetic endpoints obtained as a result of the kinetic examination of the data coming from the studies by [Kelley et al; 1995] and [Pangilinan and Smith; 1994]. That is due to the fact that the decline phase for FOE Sulfonic acid was not reached in any of the test soils used in these studies. Therefore, although the persistence kinetic endpoints were proposed, set to the default value $DT_{50}/DT_{90} > 1000$ days, they cannot be considered as reliable and were given only for completeness. For that reason RMS decided not to present the results for these studies in the summary table presenting the persistence and modelling kinetic endpoints, given below as table B.8.1.1.2.1.1_CA-294. Also the whole data set for soil Laacherhof AIII in the study by [Hellpointner; 1996] was not presented in that table. That was due to the fact that in the repeated kinetic analysis performed by the RMS it was not possible to obtain reliable kinetic fit and hence kinetic endpoints.

Table B.8.1.1.2.1.1._CA-294: The persistence and modelling kinetic endpoints – DT₅₀ and DT₉₀ values, determined for FOE Sulfonic acid.

Study	Test soil data				Persistence kinetic endpoints			Kinetic endpoints recommended for modelling
	Soil name	Soil type (USDA)	Key soil properties		Kinetic model	DT ₅₀ [days]	DT ₉₀ [days]	DT ₅₀ [days]
			pH	OC [%]				
<i>Hellpointner; 1996</i>	BBA 2.1	Sand	5.3	0.57	SFO	318	1060	260.76
	BBA 2.2	Loamy sand	6.3	2.48	SFO	211	701	211.00
<i>Hellpointner; 2003</i>	Laacherhof AXXa	Sandy loam	6.3	1.47	SFO	62.31	206.99	49.85
	Laacherhof AIII	Silt loam	6.8	0.88	SFO	60.26	200.18	40.37
<i>Hein; 2013</i>	Laacherhof AXXa	Loamy sand	6.2	1.7	SFO	73.38	243.77	70.44
	Dollendorf II	Loam	7.0	4.6	SFO	6.71	22.30	6.25
	Hoefchen am Hohenseh 4a	Silt loam	6.7	2.5	SFO	28.58	94.95	25.79
	Wurmwielse	Sandy loam	5.0	1.8	SFO	49.77	165.32	47.78
<i>Ströch and Junge; 2013</i>	Hanscheider Hof	Loam	5.6	2.8	SFO	27.30	90.70	27.03
	Frankenforst	Silt loam	6.8	1.8	SFO	21.79	72.39	21.57
	LUFA 2.3	Sandy loam	6.8	1.1	SFO	63.87	212.61	63.23
	LUFA 6S	Clay	7.0	1.9	SFO	37.71	125.28	32.11
Geomean (n = 12)						50.15	166.67	45.11
Median (n = 12)						55.02	182.75	44.08

In addition the Applicant presented also the normalised kinetic endpoints derived for FOE Sulfonic acid from field dissipation studies. These values will be dealt with separately, under the point B.8.1.1.2.2.1. – Soil dissipation studies.

The study report also provided the kinetic formation fractions determined for FOE Sulfonic acid. These are presented, together with the respective values considered reliable by the RMS, below in the table B.8.1.1.2.1.1._CA-295.

Table B.8.1.1.2.1.1._CA-295: The kinetic formation fraction values – *ff*, determined by the Applicant and verified by the RMS.

Study	Test soil data				Kinetic formation fractions - <i>ff</i>		
	Soil name	Soil type (USDA)	Key soil properties		Value proposed by the Applicant	Value accepted by RMS	Precursor
			pH	OC [%]			
<i>Kelley et al.; 1995</i>	BBA 2.2	Loamy sand	6.2	2.58	0.257	0.257	Flufenacet
	Laacherhof AIII	Silt loam	7.3	0.9	0.259	0.272	Flufenacet
	Hoefchen im Tal	Silt loam	5.8	2.4	0.143	0.143	Flufenacet
<i>Pangilinan and Smith; 1994</i>	Howe, Indiana	Sandy loam	6.2	0.35	0.108	0.108	Flufenacet
Arithmetic mean (n = 4)						0.195	Flufenacet

The report also contained the data on the soil sorption of FOE Sulfonic acid. As they are however beyond the scope of this summary they were not presented here.

Conclusion:

As a result of the evaluation presented above RMS determined the normalised geomean **DT₅₀ = 45.11 days**, value for FOE Sulfonic acid, recommended to be used in GW (and SW) model exposure assessment. Also the median normalised **DT₅₀ = 44.08 days** was calculated, which can be alternatively used for the same purpose.

The kinetic formation fraction recommended to be used in GW model exposure assessment is ***ff* = 0.195**.

c) The kinetic endpoints determined for FOE Oxalate:

The data on the persistence of FOE Oxalate in soil were obtained in two studies with Flufenacet applied as parent compound and FOE Oxalate forming as one of the primary major degradation products – [Kelley et al.; 1995], and [Pangilinan and Smith; 1994]. The results of these studies were kinetically examined and the outcome presented in two study reports – [Reinken and Partsch; 2014] and [Reinken and Partsch; 2014a]. That analysis resulted in the set of four persistence kinetic endpoint determined in four test soils. RMS having analysed the data stated that in case of Howe, Indiana, Sandy loam soil used in the study by [Pangilinan and Smith; 1994], it was not possible to determine the reliable kinetic endpoints as the decline phase was not reached in course of the study. Therefore the whole data set was for that soil was removed from the summary table. The summary table presenting the persistence and modelling kinetic endpoints for FOE Oxalate is given below as table B.8.1.1.2.1.1_CA-296. Although the geomean values were calculated for all kinetic endpoints, they are not recommended to be used in modelling, because the data base consists of only three individual values, therefore it may not be considered fully representative.

Table B.8.1.1.2.1.1_CA-296: The persistence and modelling kinetic endpoints – DT_{50} and DT_{90} values, determined for FOE Oxalate.

Study	Test soil data				Persistence kinetic endpoints			Kinetic endpoints recommended for modelling
	Soil name	Soil type (USDA)	Key soil properties		Kinetic model	DT_{50} [days]	DT_{90} [days]	DT_{50} [days]
			pH	OC [%]				
Kelley et al.; 1995	BBA 2.2	Loamy sand	6.2	2.58	SFO	6.9	22.80	6.9
	Laacherhof AIII	Silt loam	7.3	0.9	SFO	18.9	62.90	15.5
	Hoefchen im Tal	Silt loam	5.8	2.4	SFO	13.09	43.48	13.09
Geomean (n = 3)						11.83	39.65	11.08

The study report also provided the kinetic formation fractions determined for FOE Oxalate. These are presented, together with the respective values considered reliable by the RMS, below in the table B.8.1.1.2.1.1_CA-297.

Table B.8.1.1.2.1.1_CA-297: The kinetic formation fraction values – ff , determined by the Applicant and verified by the RMS.

Study	Test soil data				Kinetic formation fractions - ff		
	Soil name	Soil type (USDA)	Key soil properties		Value proposed by the Applicant	Value accepted by RMS	Precursor
			pH	OC [%]			
Kelley et al.; 1995	BBA 2.2	Loamy sand	6.2	2.58	0.448	0.448	Flufenacet
	Laacherhof AIII	Silt loam	7.3	0.9	0.375	0.422	Flufenacet
	Hoefchen im Tal	Silt loam	5.8	2.4	0.350	0.350	Flufenacet
Pangilinan and Smith; 1994	Howe, Indiana	Sandy loam	6.2	0.35	0.484	0.484	Flufenacet
Arithmetic mean (n = 4)						0.426	Flufenacet

Conclusion:

As a result of the evaluation presented above RMS stated that it was possible to determine the normalised geomean $DT_{50} = 11.08$ days, value for FOE Oxalate, recommended to be used in GW (and SW) model exposure assessment. However, it shall be pointed out that because the supporting data base consisted of only three values, more conservative value – the longest normalised $DT_{50} = 15.5$ days, may also be used for that purpose.

The kinetic formation fraction recommended to be used in GW model exposure assessment is $ff = 0.426$.

d) The kinetic endpoints determined for FOE Methylsulfone:

The data on the persistence of FOE Methylsulfone in soil were obtained in one study with Flufenacet applied as parent compound and FOE Methylsulfone forming as one of the primary major degradation products – [Kelley et al.; 1995], and in two additional studies in which FOE Methylsulfone was applied to soil as a parent compound – [Traub; 2012; 2013] and [Ströch and Junge; 2013a]. The results of the study by [Kelley et al.; 1995] were kinetically examined and the outcome presented in the study report [Reinken and Partsch; 2014]. The results obtained in the study by [Traub; 2012] were subjected to subsequent kinetic analysis, the results of which were presented in another study report by Reinken and Partsch – [Reinken and Partsch; 2014f]. The remaining study – [Ströch and Junge; 2013a], contain the appropriate kinetic analysis of the data.

That analysis resulted in the set of eleven persistence kinetic endpoint determined in eleven test soils. The Applicant presenting the data set, initially divided it into two parts, presented separately in two tables. In one table were given the results obtained in the studies with Flufenacet applied as a parent compound – study [Kelley et al.; 1995]. Second table contained the results obtained in studies in which FOE Methylsulfone was applied to test soils as a parent compound – studies by [Traub; 2012] and [Ströch and Junge; 2013a].

Applicant also performed statistical analysis of the DT₅₀-data set aimed on the identification of the would-be outliers. The analysis was performed in the same way as for Flufenacet and its results were presented in graphical form, reproduced below on figure B.8.1.1.2.1.1._CA-158. On their basis the Applicant stated that the DT₅₀ values obtained in soils BBA 2.2 and Hoefchen im Tal in the study by [Kelley et al.; 1995], both having the value DT₅₀ = 1000 days, should not be considered in selection of DT₅₀ suitable for calculation of PEC_{GW} values, being outliers. RMS having analysed the data set came to similar conclusion with regard to these two values, but with different justification. In RMS's opinion the reason for not taking into account the kinetic endpoints reported for BBA 2.2 and Hoefchen im Tal soils is the fact that for these two soils the decline phase of the kinetic curve for FOE Methylsulfone was not reached, hence it cannot be stated whether the proposed kinetic endpoints can be considered as reliable estimates for the persistence of FOE Methylsulfone in those two soils. As a results the data for these two soils were removed from the summary table presenting the persistence (not normalised) and modelling (normalised) kinetic endpoints for FOE Methylsulfone.

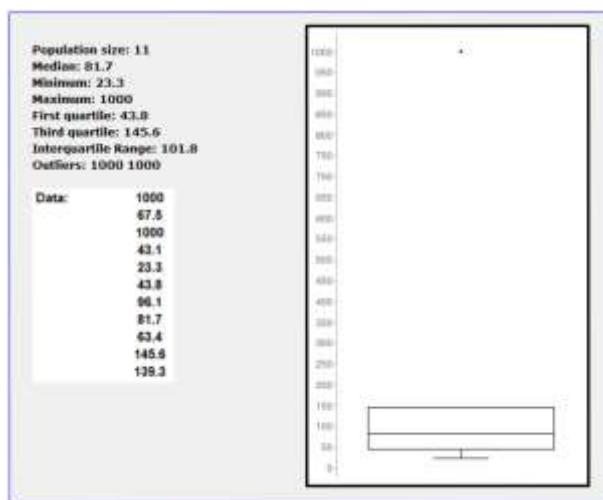


Figure B.8.1.1.2.1.1._CA-158: The results of the statistical analysis of the data set aimed on the identification of the outliers (copied from the study report).

The summary table presenting the persistence and modelling kinetic endpoints for FOE Methylsulfone is given below as table B.8.1.1.2.1.1._CA-298.

Table B.8.1.1.2.1.1._CA-298: The persistence and modelling kinetic endpoints – DT₅₀ and DT₉₀ values, determined for FOE Methylsulfone.

Study	Test soil data				Persistence kinetic endpoints			Kinetic endpoints recommended for modelling
	Soil name	Soil type (USDA)	Key soil properties		Kinetic model	DT ₅₀ [days]	DT ₉₀ [days]	DT ₅₀ [days]
			pH	OC [%]				
<i>Kelley et al.; 1995</i>	Laacherhof AIII	Silt loam	7.3	0.9	SFO	174	576	142.68
<i>Traub; 2012</i>	Laacherhof AXXa	Loamy sand	6.2	1.7	SFO	43.14	143.3	41.85
	Dollendorf II	Loam	7.0	4.6	SFO	23.30	77.41	22.60
	Hoefchen Am Hohenseh 4a	Silt loam	6.1	2.0	SFO	43.84	145.6	42.52
	Laacherhof Wurmwise	Sandy loam	5.0	1.8	SFO	96.13	319.32	93.25
<i>Ströch and Junge; 2013a</i>	Hanscheider Hof	Loam	5.6	2.8	SFO	82.53	274.14	81.70
	Frankenforst	Silt loam	6.8	1.8	SFO	63.98	212.53	63.34
	LUFA 2.3	Sandy loam	6.8	1.1	SFO	146.78	487.60	145.31
	LUFA 6S	Clay	7.0	1.9	SFO	163.06	541.68	138.83
Geomean (n = 9)						76.82	255.08	72.57
Median (n = 9)						82.53	274.14	81.7

The study report also provided the kinetic formation fractions determined for FOE Methylsulfone. These are presented, together with the respective values considered reliable by the RMS, below in the table B.8.1.1.2.1.1._CA-299.

Table B.8.1.1.2.1.1._CA-299: The kinetic formation fraction values – *ff*, determined by the Applicant and verified by the RMS.

Study	Test soil data				Kinetic formation fractions - <i>ff</i>		
	Soil name	Soil type (USDA)	Key soil properties		Value proposed by the Applicant	Value accepted by RMS	Precursor
			pH	OC [%]			
<i>Kelley et al.; 1995</i>	BBA 2.2	Loamy sand	6.2	2.58	0.061	0.061	Flufenacet
	Laacherhof AIII	Silt loam	7.3	0.9	0.087	0.096	Flufenacet
	Hoefchen im Tal	Silt loam	5.8	2.4	0.051	0.051	Flufenacet
Arithmetic mean (n = 3)						0.069	Flufenacet

Conclusion:

As a result of the evaluation presented above RMS determined the normalised geomean **DT₅₀ = 72.57 days**, value for FOE Methylsulfone, recommended to be used in GW (and SW) model exposure assessment. Also the median normalised **DT₅₀ = 81.70 days** was calculated, which can be alternatively used for the same purpose.

The kinetic formation fraction recommended to be used in GW model exposure assessment is ***ff* = 0.069**.

e) The kinetic endpoints determined for FOE Thiadone:

The data on the persistence of FOE Thiadone in soil were obtained in three studies with Flufenacet applied as parent compound and FOE Thiadone forming as one of the primary major degradation products – [Pangilinan and Smith; 1994a], [Hein; 2012] and [Hein; 2012a], as well as in one additional study in which FOE Thiadone was applied to soil as a parent compound – [Lentz and Bloomberg; 1999]. The results of the study by [Pangilinan and Smith; 1994a] were kinetically examined and the outcome presented in the study report [Reinken and Partsch; 2014d], those obtained in the studies by [Hein; 2012] and [Hein; 2012a] in the study report by [Reinken and Partsch; 2014c] and finally those obtained in the study by [Lentz and Bloomberg; 1999] in the study report by [Reinken and Partsch; 2014g].

That analysis resulted in the set of seven persistence kinetic endpoint determined in eight test soils. No reliable kinetic endpoint could be determined in soil Howe, Indiana (study by [Pangilinan and Smith; 1994a]) due to the poor results of the fitting. RMS however was able to derive the reliable persistence kinetic endpoint for that soil

as well, using the top-down approach. The summary table presenting the persistence and modelling kinetic endpoints for FOE Thiadone is given below as table B.8.1.1.2.1.1._CA-300.

Table B.8.1.1.2.1.1._CA-300: The persistence and modelling kinetic endpoints – DT_{50} and DT_{90} values, determined for FOE Thiadone.

Study	Test soil data				Persistence kinetic endpoints			Kinetic endpoints recommended for modelling
	Soil name	Soil type (USDA)	Key soil properties		Kinetic model	DT_{50} [days]	DT_{90} [days]	DT_{50} [days]
			pH	OC [%]				
<i>Lentz and Bloomberg; 1999</i>	Iowa	Loamy sand	7.2	1.91	SFO	1.98	6.59	1.27
	Indiana	Sandy loam	6.5	1.28	SFO	1.40	4.66	0.90
	Nebraska	Silt loam	7.7	1.66	SFO	2.93	9.74	2.29
<i>Pangilinan and Smith; 1994a</i>	Howe, Indiana	Sandy loam	6.2	0.35	SFO	15.9	52.9	10.32
<i>Hein; 2012</i>	Hoefchen am Hohenseh 4a	Silt loam	6.7	2.5	SFO	1.13	3.77	1.10
<i>Hein; 2012a</i>	Laacherhof AXXa	Loamy sand	6.1	2.4	SFO	1.36	4.53	1.33
	Dollendorf II	Clay loam	7.2	5.3	SFO	2.84	9.45	2.70
	Lacherhof Wurmweise	Loam	5.4	2.2	SFO	1.99	6.60	1.95
Geomean (n = 8)						2.41	8.00	1.95
Median (n = 8)						1.99	6.60	1.64

The study report also provided the kinetic formation fractions determined for FOE Thiadone. These are presented, together with the respective values considered reliable by the RMS, below in the table B.8.1.1.2.1.1._CA-301.

Table B.8.1.1.2.1.1._CA-301: The kinetic formation fraction values – ff , determined by the Applicant and verified by the RMS.

Study	Test soil data				Kinetic formation fractions - ff		
	Soil name	Soil type (USDA)	Key soil properties		Value proposed by the Applicant	Value accepted by RMS	Precursor
			pH	OC [%]			
<i>Hein; 2012</i>	Hoefchen am Hohenseh 4a	Silt loam	6.7	2.5	0.913	0.913	Flufenacet
<i>Hein; 2012a</i>	Laacherhof AXXa	Loamy sand	6.1	2.4	0.524	0.524	Flufenacet
	Dollendorf II	Clay loam	7.2	5.3	0.438	0.438	Flufenacet
	Lacherhof Wurmweise	Loam	5.4	2.2	0.405	0.404	Flufenacet
Arithmetic mean (n = 4)						0.570	Flufenacet

Conclusion:

As a result of the evaluation presented above RMS determined the normalised geomean $DT_{50} = 1.95$ days, value for FOE Thiadone, recommended to be used in GW (and SW) model exposure assessment. Also the median normalised $DT_{50} = 1.64$ days was calculated, which can be alternatively used for the same purpose.

The kinetic formation fraction recommended to be used in GW model exposure assessment is $ff = 0.570$.

- f) The kinetic endpoints determined for FOE 5043-Trifluoroethanesulfonic acid (TFESA):

The data on the persistence of FOE 5043-Trifluoroethanesulfonic acid in soil were obtained in two studies with Flufenacet applied as parent compound and FOE 5043-Trifluoroethanesulfonic acid forming as a secondary major degradation products – [Hein; 2012] and [Hein; 2012a]. The results of these studies were kinetically examined and the outcome presented in the study report by [Reinken and Partsch; 2014c].

That analysis resulted in the set of four persistence kinetic endpoint determined in four test soils. It shall be noted that in case of two test soils – Dollendorf II Clay loam soil and Laacherhof Wurmweise Loam soil the Applicant's and RMS's values are significantly different. That was due to the fact that, because of the poor

fitting results RMS repeated the analysis using the top-down approach. The summary table presenting the persistence and modelling kinetic endpoints for FOE 5043-Trifluoroethanesulfonic acid (TFESA) is given below as table B.8.1.1.2.1.1._CA-302.

Table B.8.1.1.2.1.1._CA-302: The persistence and modelling kinetic endpoints – DT_{50} and DT_{90} values, determined for FOE 5043-Trifluoroethanesulfonic acid (TFESA).

Study	Test soil data				Persistence kinetic endpoints			Kinetic endpoints recommended for modelling
	Soil name	Soil type (USDA)	Key soil properties		Kinetic model	DT_{50} [days]	DT_{90} [days]	DT_{50} [days]
			pH	OC [%]				
<i>Hein; 2012</i>	Hoefchen am Hohenseh 4a	Silt loam	6.7	2.5	SFO	9.10	30.23	8.83
<i>Hein; 2012a</i>	Laacherhof AXXa	Loamy sand	6.1	2.4	SFO	4.48	14.87	4.39
	Dollendorf II	Clay loam	7.2	5.3	SFO	20.9	69.5	19.87
	Laacherhof Wurmweise	Loam	5.4	2.2	SFO	2.24	7.45	2.19
Geomean (n = 4)						6.61	21.96	6.41

The study report also provided the kinetic formation fractions determined for FOE 5043-Trifluoroethanesulfonic acid (TFESA). These are presented, together with the respective values considered reliable by the RMS, below in the table B.8.1.1.2.1.1._CA-303.

Table B.8.1.1.2.1.1._CA-303: The kinetic formation fraction values – ff , determined by the Applicant and verified by the RMS.

Study	Test soil data				Kinetic formation fractions - ff		
	Soil name	Soil type (USDA)	Key soil properties		Value proposed by the Applicant	Value accepted by RMS	Precursor
			pH	OC [%]			
<i>Hein; 2012</i>	Hoefchen am Hohenseh 4a	Silt loam	6.7	2.5	0.264	0.264	FOE Thiadone
<i>Hein; 2012a</i>	Laacherhof AXXa	Loamy sand	6.1	2.4	0.534	0.534	FOE Thiadone
	Dollendorf II	Clay loam	7.2	5.3	0.422	0.422	FOE Thiadone
	Laacherhof Wurmweise	Loam	5.4	2.2	0.655	0.655	FOE Thiadone
Arithmetic mean (n = 4)						0.469	FOE Thiadone

Conclusion:

As a result of the evaluation presented above RMS determined the normalised geomean $DT_{50} = 6.41$ days, value for FOE 5043-Trifluoroethanesulfonic acid (TFESA), recommended to be used in GW (and SW) model exposure assessment.

The kinetic formation fraction recommended to be used in GW model exposure assessment is $ff = 0.469$.

g) The kinetic endpoints determined for Trifluoroacetic acid (TFA):

The data on the persistence of Trifluoroacetic acid – TFA, were obtained in two studies Flufenacet applied as parent compound and TFA forming as secondary and ternary major degradation product – [Hein; 2012] and [Hein; 2012a], as well as in one additional study in which TFA was applied to soil as a parent compound – [Eckermann; 2012]. The results of the studies by [Hein; 2012] and [Hein; 2012a] were kinetically examined and the outcome presented in the study report [Reinken and Partsch; 2014c]. The kinetic analysis of the data obtained in the study by [Eckermann; 2012] was found incomplete by RMS, therefore repeated and the hence the reliable persistence kinetic endpoints reported here are those determined by the RMS. The results showed that no degradation was observed, so the default values were set to represent the persistence of TFA in soil. These are: $DT_{50} = 10000$ days and $DT_{90} = 10000$ days.

The values as default require no normalisation. Therefore the value recommended for modelling should be **DT₅₀ = 10000 days**, but because the FOCUS models do not accept such value, the normalised value proposed for modelling is **DT₅₀ = 1000 days**.

The study report also provided the kinetic formation fractions determined for TFA. These are presented, together with the respective values considered reliable by the RMS, below in the table B.8.1.1.2.1.1._CA-304.

Table B.8.1.1.2.1.1._CA-304: The kinetic formation fraction values –*ff*, determined by the Applicant and verified by the RMS.

Study	Test soil data				Kinetic formation fractions - <i>ff</i>		
	Soil name	Soil type (USDA)	Key soil properties		Value proposed by the Applicant	Value accepted by RMS	Precursor
			pH	OC [%]			
Hein; 2012	Hoefchen am Hohenseh 4a	Silt loam	6.7	2.5	0.087	0.087	Flufenacet
					0.736	0.736	FOE Thiadone
Hein; 2012a	Laacherhof AXXa	Loamy sand	6.1	2.4	0.476	0.476	Flufenacet
					0.466	0.466	FOE Thiadone
	Dollendorf II	Clay loam	7.2	5.3	0.562	0.562	Flufenacet
					0.578	0.578	FOE Thiadone
	Lacherhof Wurmweise	Loam	5.4	2.2	0.596	0.596	Flufenacet
					0.345	0.345	FOE Thiadone
Arithmetic mean (n = 4)						0.430	Flufenacet
						0.531	FOE Thiadone

Conclusion:

As a result of the evaluation presented above RMS proposed to use the default **DT₅₀ = 1000 days**, as a value for Trifluoroacetic acid (TFA) recommended to be used in GW (and SW) model exposure assessment. The kinetic formation fraction values recommended to be used in GW model exposure assessment are ***ff* = 0.430** for the compound formed from Flufenacet and ***ff* = 0.531** for the compound formed from FOE Thiadone.

Study 25:

Report: Reinken G. Porschewski R., (2014): “Flufenacet Core PEC_{sw} FOCUS EU: Modelling Core Info Document for Standard FOCUS 1-2 and STEP 3-4 Surface Water Exposure Assessment in Europe.”; Bayer CropScienceAG, Environmental Safety, Alfred-Nobel-Straße 50, 40789 Monheim, Germany, unpublished Report No. EnSa-13-1008; 2014. 02. 25; study reference number: M-478438-01-1;

Guidelines: Not specified, it was stated however that the assessment of the kinetic endpoints for Flufenacet and its major soil degradation products to select those suitable for calculating PEC_{SW} and PEC_{SED} values was performed to comply with the recommendations for modelling input selection given by the EU Commission, FOCUS and EFSA.

GLP: No, not applicable, modelling study

RMS comments: The study was performed as a supportive study to the main study presenting the results of the model exposure assessment for the surface water compartment performed by the Applicant for Flufenacet and its major soil degradation products. It provides for each compound of interest the list of determined reliable soil and aquatic (water and sediment) DT₅₀ values as well as adsorption parameters (K_f, K_{foc} and 1/n values), the analysis of the data sets aimed on the identification of potential outliers and identification, with justification, of the endpoints considered suitable in calculation of PEC_{SW} and PEC_{SED} values.

RMS evaluated the study and found it acceptable, although some of the conclusions drawn by the Applicant had to be modified as a result of the repeated kinetic analysis performed by the RMS. The study was intended by the Applicant to be supportive for model risk assessment for the surface water compartment. It shall be pointed out that in the area of the determination of soil DT₅₀ values appropriate for modelling the study overlaps with the preceding study (**Study 24**). For that reason, in order not to overburden the report, RMS decided not to provide its summary.

Additionally the search of the open literature resulted in identifying two papers containing the data relevant for the determination of the rate of degradation of Flufenacet in soil.

Study 26:

Report: Gupta S., Gajbhiye V. T., Agnihotri N. P. (2001): “Adsorption-Desorption, Persistence and Leaching Behavior of Flufenacet in Alluvial Soil of India.”; Division of Agricultural Chemicals, Indian Agricultural Research Institute, New Delhi 110 012, India; published study - published in: “Bulletin of Environmental Contamination and Toxicology”, vol 66, 2001, pp 9-16.

Guidelines: : None declared as this is an open-source study, therefore not submitted for the regulatory purposes.

GLP: no, not applicable – peer-reviewed scientific paper

RMS comments: The paper presents the results of the examination of soil equilibrium sorption (determination of Freundlich sorption isotherms), mobility in soil profile (column leaching experiment) and persistence in aerobic and anaerobic soil, for Flufenacet. The experiments were performed using one test soil. Although in the paper it was not indicated that the experiments were performed in line with any relevant guidelines, it can be stated that the study protocol generally complied with the OECD 307 guideline for soil persistence, OECD 106 Guideline for examining batch sorption and OECD 312 for column leaching. The level of details was sufficient to evaluate the study for its validity. The study may be considered valid, and therefore is summarised below, in this section of the Assessment Report for its part examining the persistence of Flufenacet in soil under laboratory conditions. However, RMS is of the opinion that the results it provides may be regarded only as supplementary and conformatory to the endpoints provided by the regulatory studies submitted by the Applicant, and should not be used as a source of regulatory endpoints.

Summary:

The Editor has not provided the abstract for that publication. However the paper contained the introduction, clearly outlining the aims and scope of the research activity described in it, which may be considered a summary of the study. Due to the copyright restrictions, RMS could not present it here and the readers are kindly asked to consult the relevant document. Instead, below is presented the extended summary prepared by the RMS.

Extended summary prepared by RMS:

The aim of the study was to examine the mobility and persistence of Flufenacet in soil. The test soil used in the experiment was an agricultural soil, of the type of inceptisol, having the following physicochemical properties:

- **particle size distribution:** 64.7% sand, 15.6% silt and 19.7% clay;
- **soil texture class:** Sandy loam;
- **pH:** 7.1;
- **OC:** 0.34%;
- **Moisture content at FC (field capacity):** 20%.

The soil used in the experiment was freshly sampled from the top 15-cm layer of the fields of Indian Agricultural Research Institute in New Delhi, India. It was then air-dried and sieved through 2-mm mesh screen before being used.

The test compound was analytical grade Flufenacet, having a purity of > 99.5%, provided by M/s Bayer India Ltd. It was applied to the test soil in form of aqueous solution in 0.01 N CaCl₂, prepared from the stock solution of Flufenacet in acetone, having a concentration of 0.5 mg/mL.

The persistence of Flufenacet in aerobic soil was examined for two application doses – 1 µg Flufenacet/g soil (d. w.) and 10 µg Flufenacet/g soil (d. w.). To obtain that level, initially 200-g portions of the dry test soil were treated with the test compound at the level 100 µg Flufenacet/g soil (d. w.). Next the treated soil was mixed thoroughly with the appropriate amount of untreated soil to obtain the target application level of either 1 µg Flufenacet/g soil (d. w.) or 10 µg Flufenacet/g soil (d. w.). The 20-g portions of so prepared test soil were weighed to beakers and brought to the designated level of moisture content (FC) by addition of the appropriate

amount of distilled water. That level of soil moisture was maintained throughout the study by daily controlling and adjusting it, when necessary.

The samples were incubated for up to 90 days at constant temperature $T = 25 \pm 1^\circ\text{C}$. At designated time points: DAT (Days After Treatment) 0, 3, 6, 10, 14, 29, 45, 60 and 90, triplicate samples were taken for the analysis.

Alongside treated samples the non-treated control samples were set and maintained in the same way as treated samples.

Additionally the experiment was performed on submerged soil treated at the level $10\ \mu\text{g}$ Flufenacet/g soil (d. w.). The test soil samples were treated in the same way as described above for the experiment with aerobic samplers. Next, before being placed in incubation chamber, the samples were flooded with water added to each beaker in such amount to give 3-cm layer above the soil surface. That level was maintained throughout the whole incubation period, lasting also up to 90 days. The sampling points were the same as for aerobic samples. Although it was not called so, in RMS's opinion that variant of the experiment represents the examination of persistence of flufenacet in anaerobic soil.

At sampling soil samples incubated under aerobic conditions were air-dried at room temperature, mixed with 0.2 mL of liquid NH_3 and left for ~3 hours. After that period 0.5-g portions of activated florisil and charcoal were mixed with each soil sample, the so prepared mixture dry-packed into the 50-cm long glass column having a diameter of 2.5 cm, containing at the bottom 2-cm layer of anhydrous Na_2SO_4 . The so prepared columns were eluted using 125 mL of acetone-hexane (1:9) mixture. Extract was concentrated to dryness, residues reconstituted in n-hexane and analysed using GLC-ECD chromatography. The LOD of the analytical method was $0.005\ \mu\text{g/L}$.

The submerged samples were processed by extracting them repeatedly with acetone. After extraction the organic solvent was evaporated and the remaining aqueous phase extracted with three 30-mL portions of dichloromethane. The organic phase was collected, remnants of water removed by passing the whole volume through anhydrous Na_2SO_4 , and evaporated to dryness. The residue was reconstituted in n-hexane and analysed using GLC-ECD. The LOD of the analytical method was $0.005\ \mu\text{g/g}$.

The results of the analysis – the concentration of the test compound in soil as a function of time, given in $\mu\text{g/g}$ and as a % decrease of DAT-0 level, for each variant of the experiment are presented below in the table B.8.1.1.2.1.1._CA-305.

Table B.8.1.1.2.1.1._CA-305: The numerical results of the experiment

Time point – DAT (Days After Treatment)	Results obtained for:					
	Aerobic soil treated at the level $1\ \mu\text{g}$ Flufenacet/g soil		Aerobic soil treated at the level $10\ \mu\text{g}$ Flufenacet/g soil		Submerged (anaerobic) soil treated at the level $10\ \mu\text{g}$ Flufenacet/g soil	
	Concentration of flufenacet [$\mu\text{g/g}$]	% decrease of concentration comparing to DAT 0 amount	Concentration of flufenacet [$\mu\text{g/g}$]	% decrease of concentration comparing to DAT 0 amount	Concentration of flufenacet [$\mu\text{g/g}$]	% decrease of concentration comparing to DAT 0 amount
0	0.87	0.0	8.13	0.0	8.13	0.0
3	0.67	23.7	7.67	6.8	6.49	20.0
6	0.58	34.0	6.49	20.1	4.79	41.1
10	0.50	42.7	5.80	28.7	4.03	50.4
14	0.46	47.7	5.40	33.6	3.77	53.6
29	0.16	81.4	2.76	66.0	3.09	62.0
45	0.05	94.2	0.99	87.8	1.88	76.9
60	0.01	98.6	0.23	97.2	1.20	85.2
90	<LOD	not given	0.09	98.8	0.37	95.5

The obtained results were subjected to the kinetic analysis using linear-regression-1st order kinetics model. The obtained kinetic curves were not presented in the paper, instead the regression equations were given together with the calculated half-lives.

The parameters of the kinetic curves were as follows:

- for aerobic soil treated at the level $1\ \mu\text{g}$ Flufenacet/g soil the regression equation was $Y = 0.019 - 0.0323 X$, with correlation coefficient $r = 0.99$;
- for aerobic soil treated at the level $10\ \mu\text{g}$ Flufenacet/g soil the regression equation was $Y = 0.979 - 0.0231 X$, with correlation coefficient $r = 0.99$;
- for submerged (anaerobic) soil treated at the level $10\ \mu\text{g}$ Flufenacet/g soil the regression equation was $Y = 0.626 - 0.134 X$, with correlation coefficient $r = 0.99$.

The calculated half-lives, for convenience marked as DT_{50} were following:

- for aerobic soil treated at the level $1\ \mu\text{g}$ Flufenacet/g soil the $\text{DT}_{50} = 9.3$ days;
- for aerobic soil treated at the level $10\ \mu\text{g}$ Flufenacet/g soil the $\text{DT}_{50} = 13.0$ days;
- for submerged (anaerobic) soil treated at the level $10\ \mu\text{g}$ Flufenacet/g soil the $\text{DT}_{50} = 22.5$ days.

The authors stated that the rate of degradation in aerobic soil treated at different fortification levels was initially slower than in anaerobic soil, but later that trend reversed, what was postulated to be due to the strong sorption of the test compound to alluvial soil.

RMS noted that the kinetic endpoints were determined for the incubation temperature higher than the standard recommended $T = 20^{\circ}\text{C}$. Therefore for the comparative purpose the kinetic endpoints were normalised to standard conditions. The normalisation for soil moisture content was not performed as in case of aerobic soils they were incubated at the reference level – FC level, while for anaerobic/submerged soils such procedure is not necessary.

The results of the normalisation are presented below:

- for aerobic soil treated at the level 1 μg Flufenacet/g soil the $\text{DT}_{50} = 14.3$ days;
- for aerobic soil treated at the level 10 μg Flufenacet/g soil the $\text{DT}_{50} = 20.4$ days;
- for submerged (anaerobic) soil treated at the level 10 μg Flufenacet/g soil the $\text{DT}_{50} = 35.3$ days.

RMS comments:

The obtained kinetic endpoints are within the range of the values obtained for Flufenacet in regulatory studies. However, because of the method of their derivation, as well as due to the fact that the test soil is a non-EU soil, nor it is representative for the EU agricultural soils, they shall be considered only as indicative and not used as regulatory endpoints.

Study 27:

Report: Suman Gupta, Vijay T. Gajbhiye (2002): “Effect of concentration, moisture and soil type on the dissipation of flufenacet from soil.”; Division of Agricultural Chemicals, Indian Agricultural Research Institute, New Delhi 110012, India; published study - published in: “Chemosphere”, vol 47, 2002, pp 901 - 906.

Guidelines: None declared as this is an open-source study, therefore not submitted for the regulatory purposes.

GLP: no, not applicable – peer-reviewed scientific paper;

RMS comments: The paper presents the results of the examination of persistence of Flufenacet in soil under various experimental conditions. The experiment was performed on three Indian agricultural soils, incubated under either aerobic or anaerobic (submerged) conditions. In case of aerobic soil rate of degradation was examined for two fortification levels. Although in the paper it was not indicated that the experiments were performed in line with any relevant guidelines, it can be stated that the study protocol generally complied with the OECD 307 Guideline. The level of detail was sufficient to evaluate the study for its validity. The study may be considered valid, and therefore is summarised below. However, RMS is of the opinion that the results it provides may be regarded only as supplementary and conformatory to the endpoints provided by the regulatory studies submitted by the Applicant and should not be used as a source of regulatory endpoints.

Summary:

The paper contains an abstract, outlining the aims of the experiment and its key results, which was made available on-line. However, due to the copyright restrictions RMS could not present it here and the readers are kindly asked to consult the relevant document. Instead, below is presented the extended summary prepared by the RMS.

Extended summary prepared by RMS:

The aim of the study was to examine the persistence of Flufenacet in agricultural soils incubated in the laboratory, either under aerobic or anaerobic conditions. The examination was performed on three soils, representing different regions of India. Their characteristic is provided below in the table B.8.1.1.2.1.1._CA-306. They were freshly sampled from the top 15-cm layer of the cultivated of the three locations: Dehli, Ranchi and Nagpur. After sampling they were air-dried, ground, sieved through 2-mm sieve and stored in plastic containers until being used.

Table B.8.1.1.2.1.1._CA-306: The characteristic of the test soils used in the experiment

Parameter		Soil		
		<i>Delhi</i>	<i>Ranchi</i>	<i>Nagpur</i>
Soil type		Inceptisol	Ultisol	Vertisol
Soil textural type (reported in the study)		Sandy loam	Sandy loam	Clayley
Soil type (USDA; determined by RMS)		US Loamy sand	US Sandy clay loam	US Clay
Particle size distribution	Sand [%]	77.5	60.0	40.0
	Silt [%]	17.5	8.7	16.3
	Clay [%]	5.0	31.3	43.7
pH value (medium not specified)		7.69	5.54	8.25
Organic carbon content (OC) [%]		0.501	0.042	0.399
Organic matter content (OM) [%]		0.864	0.072	0.688
Cation Exchange Capacity – CEC [mEq/100g]		6.95	3.86	13.69
Water holding capacity	a Field Capacity (FC) [%]	20	17	30

The test compound was a non-radiolabelled Flufenacet, having a chemical purity of > 99.5%, supplied by Bayer India Ltd. It was used in form of a stock solution in acetone, having a concentration 1.0 mg/mL, if necessary further diluted using distilled hexane.

The persistence of Flufenacet in aerobic soil was examined for two application doses – 1 µg Flufenacet/g soil (d.w.) and 10 µg Flufenacet/g soil (d. w.). To obtain that level, initially 200-g portions of the dry test soils were treated with the test compound at the level 100 µg Flufenacet/g soil (d. w.). Next the treated soils were mixed thoroughly with the appropriate amount of adequate untreated soils to obtain the target application level of either 1 µg Flufenacet/g soil (d. w.) or 10 µg Flufenacet/g soil (d. w.). The 10-g portions of so prepared test soils were weighed into beakers and brought to the designated level of moisture content (FC) by addition of the appropriate amount of distilled water. That level of soil moisture was maintained throughout the study by daily controlling and adjusting it, when necessary.

The samples were incubated for up to 90 days at constant temperature $T = 25 \pm 1^\circ\text{C}$. The sampling dates used in the experiment were not specified, but as the paper refers on several instances to the earlier study by the same authors, summarised above, it is possible that they were the same.

Alongside treated samples the non-treated control samples were set and maintained it the same way as treated samples.

Additionally the experiment was performed on submerged soil treated at the level 10 µg Flufenacet/g soil (d. w.). The samples of the test soils were treated in the same way as described above for the experiment with aerobic soils. Next, before being placed in incubation chamber, samples were flooded with water added to each beaker in such amount to give 3-cm layer above the soil surface. That level was maintained throughout the whole incubation period, lasting also up to 90 days. The sampling points were the same as for aerobic samples. Although it was not called so, in RMS's opinion that variant of the experiment represents the examination of persistence of flufenacet in anaerobic soil.

At sampling soil samples incubated under aerobic conditions were air-dried at room temperature, mixed with 0.2 mL of liquid NH_3 and left for ~3 hours. After that period 0.5-g portions of activated florasil and charcoal were mixed with each soil sample, the so prepared mixture dry-packed into the 50-cm long glass column having a diameter of 2.5 cm, containing at the bottom 2-cm layer of anhydrous Na_2SO_4 . The so prepared columns were eluted using 150 mL of acetone-hexane (1:9) mixture. Extract was concentrated to dryness, residues reconstituted n-hexane and analysed using GC-ECD chromatography.

The submerged samples were processed by extracting them repeatedly with acetone. After extraction the organic solvent was evaporated and the remaining aqueous phase extracted with three 30-mL portions of dichloromethane. The organic phase was collected, remnants of water removed by passing the whole volume through anhydrous Na_2SO_4 and evaporated to dryness. The residue was reconstituted in n-hexane and analysed using GC-ECD.

The detailed numerical results of the study were not provided. Instead they were given in graphical form. In the study it was stated that the recovery levels were acceptable, all above 80% on DAT 0, so the residue data were not corrected for the recovery. In samples treated at the level 1 µg Flufenacet/g soil the initial recovery was on the level 81 – 87% and in samples treated at the level of 10 µg Flufenacet/g soil 89 – 102%.

Therefore the initial concentration measured in three test soils treated at the level of 1 µg Flufenacet/g soil were in range 0.793 – 0.905 µg/g soil and in case of soils treated at the level of 10 µg Flufenacet/g soil they were in range 7.53 – 8.13 µg/g soil.

The dissipation followed 1st order kinetics. It was stated that it was concentration-dependent: in soils treated at the level of 1 µg Flufenacet/g soil on day 60th after treatment 96 – 100% of the initial dose disappeared from three

test soils, while for the treatment level of 10 µg Flufenacet/g soil for the same time period that value was lower – 65 – 97%. The influence of aerobic or anaerobic conditions (in paper referred to as influence of soil moisture) on the rate of dissipation of Flufenacet from the test soils was less pronounced. Finally it was stated that the physicochemical properties of test soils had a substantial influence on the rate of degradation of Flufenacet in soil. It was stated that the positive correlation was observed between the determined DT_{50} values and soil clay content, what in turn was attributed to higher adsorption capacity. No significant correlation was observed between the determined DT_{50} and both soil pH and OM content. However, in case of that last parameter RMS noted that in all test soils the OC/OM content was low, lower than that recommended in the relevant guidelines.

The obtained results were subjected to the kinetic analysis using linear-regression 1st order kinetics model. The obtained kinetic curves were not presented in the paper, instead the regression equations were given together with the calculated half-lives.

For Delhi test soil the parameters of the kinetic curves were as follows:

- for aerobic soil treated at the level 1 µg Flufenacet/g soil the regression equation was **$Y = -0.0143 - 0.0299 X$** , with correlation coefficient **$r = 0.99$** ;
- for aerobic soil treated at the level 10 µg Flufenacet/g soil the regression equation was **$Y = 0.9792 - 0.0231 X$** , with correlation coefficient **$r = 0.99$** ;
- for submerged (anaerobic) soil treated at the level 10 µg Flufenacet/g soil the regression equation was **$Y = 0.8302 - 0.0135 X$** , with correlation coefficient **$r = 0.99$** ;

The calculated half-lives, for convenience marked as DT_{50} , were following:

- for aerobic soil treated at the level 1 µg Flufenacet/g soil the **$DT_{50} = 10.1$ days**;
- for aerobic soil treated at the level 10 µg Flufenacet/g soil the **$DT_{50} = 13.0$ days**;
- for submerged (anaerobic) soil treated at the level 10 µg Flufenacet/g soil the **$DT_{50} = 22.3$ days**.

For Ranchi test soil the parameters of the kinetic curves were as follows:

- for aerobic soil treated at the level 1 µg Flufenacet/g soil the regression equation was **$Y = -0.1353 - 0.0286 X$** , with correlation coefficient **$r = 0.99$** ;
- for aerobic soil treated at the level 10 µg Flufenacet/g soil the regression equation was **$Y = 0.8537 - 0.0141 X$** , with correlation coefficient **$r = 0.99$** ;
- for submerged (anaerobic) soil treated at the level 10 µg Flufenacet/g soil the regression equation was **$Y = 0.8414 - 0.0125 X$** , with correlation coefficient **$r = 0.99$** ;

The calculated half-lives, for convenience marked as DT_{50} , were following:

- for aerobic soil treated at the level 1 µg Flufenacet/g soil the **$DT_{50} = 10.5$ days**;
- for aerobic soil treated at the level 10 µg Flufenacet/g soil the **$DT_{50} = 21.3$ days**;
- for submerged (anaerobic) soil treated at the level 10 µg Flufenacet/g soil the **$DT_{50} = 24.1$ days**.

For Nagpur test soil the parameters of the kinetic curves were as follows:

- for aerobic soil treated at the level 1 µg Flufenacet/g soil the regression equation was **$Y = -0.1651 - 0.0097 X$** , with correlation coefficient **$r = 0.99$** ;
- for aerobic soil treated at the level 10 µg Flufenacet/g soil the regression equation was **$Y = 0.8451 - 0.0103 X$** , with correlation coefficient **$r = 0.94$** ;
- for submerged (anaerobic) soil treated at the level 10 µg Flufenacet/g soil the regression equation was **$Y = 0.8633 - 0.0100 X$** , with correlation coefficient **$r = 0.93$** ;

The calculated half-lives, for convenience marked as DT_{50} , were following:

- for aerobic soil treated at the level 1 µg Flufenacet/g soil the **$DT_{50} = 31.0$ days**;
- for aerobic soil treated at the level 10 µg Flufenacet/g soil the **$DT_{50} = 29.2$ days**;
- for submerged (anaerobic) soil treated at the level 10 µg Flufenacet/g soil the **$DT_{50} = 30.1$ days**.

RMS noted that the kinetic endpoints were determined for the incubation temperature higher than the standard recommended $T = 20^{\circ}\text{C}$. Therefore for the comparative purpose the kinetic endpoints were normalised to standard conditions. The normalisation for soil moisture content was not performed as in case of aerobic soils they were incubated at the reference level – FC level, while for anaerobic/submerged soils such procedure is not necessary.

The results of the normalisation in Delhi soil were following:

- for aerobic soil treated at the level 1 µg Flufenacet/g soil the **$DT_{50} = 15.8$ days**;
- for aerobic soil treated at the level 10 µg Flufenacet/g soil the **$DT_{50} = 20.4$ days**;
- for submerged (anaerobic) soil treated at the level 10 µg Flufenacet/g soil the **$DT_{50} = 35.0$ days**.

The results of the normalisation in Ranchi soil were following:

- for aerobic soil treated at the level 1 µg Flufenacet/g soil the **DT₅₀ = 16.5 days**;
- for aerobic soil treated at the level 10 µg Flufenacet/g soil the **DT₅₀ = 33.4 days**;
- for submerged (anaerobic) soil treated at the level 10 µg Flufenacet/g soil the **DT₅₀ = 37.8 days**.

The results of the normalisation in Nagpur soil were following:

- for aerobic soil treated at the level 1 µg Flufenacet/g soil the **DT₅₀ = 48.6 days**;
- for aerobic soil treated at the level 10 µg Flufenacet/g soil the **DT₅₀ = 45.8 days**;
- for submerged (anaerobic) soil treated at the level 10 µg Flufenacet/g soil the **DT₅₀ = 47.2 days**.

RMS comments:

The obtained kinetic endpoints are within the range of the values obtained for Flufenacet in regulatory studies. However, because of the method of their derivation, as well as due to the fact that the test soils are the non-EU soils or representative for the EU agricultural conditions, they shall be considered only as indicative and not used as regulatory endpoints.

Summary – Rate of degradation of Flufenacet and its degradation products in aerobic soil:

The degradation kinetics of Flufenacet in aerobic soil was extensively examined by the Applicant and its results presented in 26 study reports, of which 24 were found by the RMS acceptable and relevant for the current assessment. Additionally two literature studies were identified by the RMS which also provided the data on the degradation kinetics of Flufenacet in aerobic soils. These reports were found by the RMS relevant as supplementary source of data, however not suitable for deriving the regulatory endpoints.

The key results for each of the evaluated compounds are presented below, in tabularised form, individually for each of the test compounds.

Additionally RMS presented the obtained data in form of the tables recommended in the current template for the List of End Points.

a) Kinetic endpoints determined for Flufenacet:

The degradation kinetics of Flufenacet in aerobic soil was examined in ten trials using nine soils. One of the test soils – Howe, Indiana, Sandy loam soil, was used in two trials in which was used Flufenacet differently radiolabelled (either in phenyl ring or in C2 position of thiadiazole moiety), but the resulting kinetic endpoints cannot be averaged prior to calculating the overall geomean because they were derived in two separate studies, significantly differing in sample processing method.

The persistence (best-fit) kinetic endpoints obtained for Flufenacet are presented below in the table B.8.1.1.2.1.1._CA-307. The modelling endpoints are given in the table B.8.1.1.2.1.1._CA-308.

Table B.8.1.1.2.1.1._CA-307: The persistence kinetic endpoints determined for Flufenacet in aerobic soil.

Soil		Soil properties		Incubation conditions	Kinetic model	Evaluation of the fit		Kinetic parameters		Kinetic endpoints	
Soil name	Soil type (USDA)	OC	pH			χ^2 error	Visual fit ¹⁾ /R ²	Param.	Value	DT ₅₀ [days]	DT ₉₀ [days]
BBA 2.2; [Phenyl-U- ¹⁴ C] label	Loamy sand	2.58	6.2 ²⁾	20°C; 40% MWHC	SFO	8.53	A/ 0.974	k	0.0217	31.9	106.1
Laacherhof; [Phenyl-U- ¹⁴ C] label	Silt loam	0.9	6.2 ²⁾	20°C; 40% MWHC	SFO	11.0	G/0.978	k	0.0411	16.9	56
Höfchen im Tal; [Phenyl-U- ¹⁴ C] label	Silt loam	2.40	6.2 ²⁾	20°C; 40% MWHC	SFO	5.47	G/ 0.990	k	0.0339	20.4	67.9
Howe, Indiana; [Phenyl-U- ¹⁴ C] label	Sandy loam	0.35	6.2 ³⁾	21°C; 75% of ½ bar	SFO	2.36	G/ 0.981	k	0.0215	32.2	107.0
Laacherhof AXXa; [Phenyl-U- ¹⁴ C] label	Sandy loam	1.41	6.1 ⁴⁾	20°C; 50% MWHC	SFO	11.23	A/ 0.975	k	0.0943	7.35	24.4
Hoefchen Am Hohenseh 4a; [Thiadiazole-5- ¹⁴ C] label	Silt loam	2.5	6.7 ⁴⁾	19.1°C; 55% MWHC	SFO	4.88	G/ 0.995	k	0.0438	15.8	52.6
Laacherhof AXXa; [Thiadiazole-5- ¹⁴ C] label	Loamy sand	2.4	6.1 ⁴⁾	19.9°C; 55% MWHC	SFO	3.03	G/ 0.997	k	0.0349	19.85	65.9
Dollendorf II; [Thiadiazole-5- ¹⁴ C] label	Clay loam	5.3	7.2 ⁴⁾	19.9°C; 55% MWHC	SFO	4.67	G/ 0.994	k	0.0425	16.3	54.2
Laacherhof Wurmweise; [Thiadiazole-5- ¹⁴ C] label	Loam	2.2	5.4 ⁴⁾	19.9°C; 55% MWHC	SFO	4.27	G/ 0.994	k	0.0465	14.9	49.5
Howe, Indiana; [Thiadiazole-2- ¹⁴ C] label	Sandy loam	0.35	6.2 ³⁾	21°C; 75% of ½ bar	SFO	2.80	A/ 0.940	k	0.0120	57.6	191.42

Footnotes to the table:

- 1) The abbreviations used to describe the visual fit: G. – good, A. – acceptable, P. – poor;
- 2) Declared to be measured in CaCl₂/Water;
- 3) Measured in distilled water;
- 4) Measured in CaCl₂

The $DT_{50} = 57.6$ days value, determined in Howe, Indiana Sandy loam soil treated with [Thiadiazole-2- ^{14}C] Flufenacet was identified as appropriate input parameter for soil exposure assessment.

Table B.8.1.1.2.1.1_CA-308: The modelling kinetic endpoints determined for Flufenacet in aerobic soil.

Soil		Soil properties		Incubation conditions	Kinetic model	Evaluation of the fit		Kinetic parameters		Kinetic endpoints	
Soil name	Soil type (USDA)	OC	pH			χ^2 error	Visual fit ¹⁾ /R ²	Param.	Value	DT_{50} [days]	DT_{90} [days]
BBA 2.2; [Phenyl- U - ^{14}C] label	Loamy sand	2.58	6.2 ²⁾	20°C; 40% MWHC	SFO	8.53	A/ 0.974	k	0.0217	31.9	106.1
Laacherhof; [Phenyl- U - ^{14}C] label	Silt loam	0.9	6.2 ²⁾	20°C; 40% MWHC	SFO	11.0	G/0.978	k	0.0500	13.86	45.92
Höfchen im Tal; [Phenyl- U - ^{14}C] label	Silt loam	2.40	6.2 ²⁾	20°C; 40% MWHC	SFO	5.47	G/ 0.990	k	0.0339	20.44	67.9
Howe, Indiana; [Phenyl- U - ^{14}C] label	Sandy loam	0.35	6.2 ³⁾	21°C; 75% of 1/3 bar	SFO	2.36	G/ 0.981	k	0.0332	20.90	69.44
Laacherhof AXXa; [Phenyl- U - ^{14}C] label	Sandy loam	1.41	6.1 ⁴⁾	20°C; 50% MWHC	SFO	11.23	A/ 0.975	k	0.0985	7.04	23.37
Hoefchen Am Hohenseh 4a; [Thiadiazole-5- ^{14}C] label	Silt loam	2.5	6.7 ⁴⁾	19.1°C; 55% MWHC	SFO	4.88	G/ 0.995	k	0.0451	15.36	51.02
Laacherhof AXXa; [Thiadiazole-5- ^{14}C] label	Loamy sand	2.4	6.1 ⁴⁾	19.9°C; 55% MWHC	SFO	3.03	G/ 0.997	k	0.0356	19.45	64.58
Dollendorf II; [Thiadiazole-5- ^{14}C] label	Clay loam	5.3	7.2 ⁴⁾	19.9°C; 55% MWHC	SFO	4.67	G/ 0.994	k	0.0447	15.49	51.52
Laacherhof Wurmweise; [Thiadiazole-5- ^{14}C] label	Loam	2.2	5.4 ⁴⁾	19.9°C; 55% MWHC	SFO	4.27	G/ 0.994	k	0.0474	14.61	48.51
Howe, Indiana; [Thiadiazole-2- ^{14}C] label	Sandy loam	0.35	6.2 ³⁾	21°C; 75% of 1/3 bar	SFO	2.80	A/ 0.940	k	0.0185	37.40	124.23
Geometric mean (n = 10)									0.0387	17.89	59.42
Median (n = 10)									0.0402	17.47	58.05

Footnotes to the table:

- 1) The abbreviations used to describe the visual fit: G. – good, A. – acceptable, P. – poor;
- 2) Declared to be measured in $CaCl_2$ /Water;
- 3) Measured in distilled water;
- 4) Measured in $CaCl_2$

For GW and SW model exposure assessment the **geomean $DT_{50} = 17.89$ days** and **geomean $k = 0.0387$ [days⁻¹]** are the kinetic endpoints recommended as input parameters.

b) Kinetic endpoints determined for FOE Sulfonic acid:

The degradation kinetics of FOE Sulfonic acid in aerobic soil was examined in seventeen trials on the same number of the test soils. The experiments were performed in two variants – four trials with soils treated with Flufenacet (active substance) and the remaining thirteen trials with soils treated with FOE Sulfonic acid.

The performed kinetic analysis resulted in a data base consisting of twelve reliable kinetic endpoints, all determined in trials in which the test soils were treated with FOE Sulfonic acid. In case of the experiments on soils treated with Flufenacet it was not possible to obtain reliable kinetic endpoints characterising degradation of FOE Sulfonic acid in soil because decline of that compound was not observed. As a result, the default values – $DT_{50} = 1000$ days and $DT_{90} > 1000$ days, were proposed for these trials. These values, due to their nature and uncertainty related to them, were not used either as input parameters in soil exposure assessment or to calculate

normalised mean values used subsequently in GW/SW exposure assessment. They are however provided in the table presenting the persistence endpoints, as with them are associated reliable kinetic formation fractions for FOE Sulfonic acid, recommended to be used in GW exposure assessment. RMS however decided not to provide them in the table presenting the kinetic endpoints recommended for modelling.

In case of the kinetic analysis of the data obtained in Laacherhof IIIA Silt loam soil in the study by [Hellpointner; 1996], it was not possible to obtain a reliable kinetic fit and hence kinetic endpoints. For that reason the trial was removed from both summary table presenting persistence and modelling endpoints.

The persistence (best-fit) kinetic endpoints obtained for FOE Sulfonic acid are presented below in the table B.8.1.1.2.1.1._CA-309. The modelling endpoints are given in the table B.8.1.1.2.1.1._CA-310.

Table B.8.1.1.2.1.1._CA-309: The persistence kinetic endpoints determined for FOE Sulfonic acid in aerobic soil.

Soil		Soil properties		Incubation conditions	Kinetic model	Evaluation of the fit		Kinetic parameters		Kinetic endpoints		
Soil name	Soil type (USDA)	OC	pH ¹⁾			χ^2 error	Vis. fit ²⁾	Par.	Value	DT ₅₀ [days]	DT ₉₀ [days]	Kinetic formation fraction ff
BBA 2.2	Loamy sand	2.58	6.2 ^{a)}	20 ⁰ C; 40% MWHC	SFO	15.4	G	k	n. d. ³⁾	1000	>1000	0.257
Laacherhof	Silt loam	0.9	7.3 ^{a)}	20 ⁰ C; 40% MWHC	SFO	8.42	G	k	n. d. ³⁾	1000	>1000	0.272
Höfchen im Tal	Silt loam	2.40	5.8 ^{a)}	20 ⁰ C; 40% MWHC	SFO	6.56	G	k	n. d. ³⁾	1000	>1000	0.143
Howe, Indiana;	Sandy loam	0.35	6.2 ^{b)}	21 ⁰ C; 75% of 1/3 bar	SFO	6.28	G	k	n. d. ³⁾	1000	>1000	0.108
BBA 2.1	Sand	0.57	5.3 ^{c)}	20 ± 2 ⁰ C; 75% of 1/3 bar	SFO	1.78	G	k	2.18 E-3	318	1060	n. a. ⁴⁾
BBA 2.2	Loamy sand	2.48	6.3 ^{c)}	20 ± 2 ⁰ C; 75% of 1/3 bar	SFO	1.88	G	k	3.28 E-3	211	701	n. a. ⁴⁾
Laacherhof AXXa	Sandy loam	1.47	6.3 ^{c)}	20 ± 2 ⁰ C; 40% MWHC	SFO	3.05	G	k	0.0111	62.31	206.99	n. a. ⁴⁾
Laacherhof AIII	Silt loam	0.88	6.8 ^{c)}	20 ± 2 ⁰ C; 40% MWHC	SFO	3.03	G	k	0.0115	60.26	200.18	n. a. ⁴⁾
Laacherhof AXXa	Loamy sand	1.7	6.2 ^{c)}	19.6 ⁰ C; 55% MWHC	SFO	1.28	G	k	9.45 E-3	73.38	243.77	n. a. ⁴⁾
Dollendorf II	Loam	4.6	7.0 ^{c)}	19.6 ⁰ C; 55% MWHC	SFO	5.59	G	k	0.1033	6.71	22.30	n. a. ⁴⁾
Hoefchen Am Hohenseh 4a;	Silt loam	2.0	6.1 ^{c)}	19.6 ⁰ C; 55% MWHC	SFO	7.68	G	k	0.0242	28.58	94.95	n. a. ⁴⁾
Wurm-wiese	Sandy loam	1.8	5.0 ^{c)}	19.6 ⁰ C; 55% MWHC	SFO	3.66	G	k	0.0139	49.77	165.32	n. a. ⁴⁾
Hanscheider Hof	Loam	2.8	5.6 ^{c)}	19.9 ⁰ C; 55% MWHC	SFO	3.25	G	k	0.02539	27.30	90.70	n. a. ⁴⁾
Frankenforst	Silt loam	1.8	6.8 ^{c)}	19.9 ⁰ C; 55% MWHC	SFO	6.41	G	k	0.03181	21.79	72.39	n. a. ⁴⁾
LUFA 2.3	Sandy loam	1.1	6.8 ^{c)}	19.9 ⁰ C; 55% MWHC	SFO	1.45	G	k	0.0108	63.87	212.16	n. a. ⁴⁾
LUFA 6S	Clay	1.9	7.0 ^{c)}	19.9 ⁰ C; 55% MWHC	SFO	6.49	G	k	0.01838	37.71	125.28	n. a. ⁴⁾
Arithmetic mean for ff (n = 4)												0.195

Footnotes to the table:

- 1) Measured in:
 - CaCl₂/water for values marked a);
 - distilled water for results marked b);
 - 0.01M CaCl₂ for results marked c);
- 2) The abbreviations used to describe the visual fit: G. – good, A. – acceptable, P. – poor;
- 3) Value not determined – the decline phase not reached;
- 4) Value not available – the test compound applied as parent.

The DT₅₀ = **318 days** value, determined in BBA 2.1 Sand soil treated with FOE Sulfonic acid was identified as appropriate input parameter for soil exposure assessment.

Table B.8.1.1.2.1.1_CA-310: The modelling kinetic endpoints determined for FOE Sulfonic acid in aerobic soil.

Soil		Soil properties		Incubation conditions	Kinetic model	Evaluation of the fit		Kinetic parameters		Kinetic endpoints		
Soil name	Soil type (USDA)	OC	pH ¹⁾			χ^2 error	Vis. fit ²⁾	Par.	Value	DT ₅₀ [days]	DT ₉₀ [days]	Kinetic formation fraction ff
BBA 2.2	Loamy sand	2.58	6.2 ^{a)}	20 ⁰ C; 40% MWHC	SFO	15.4	G	k	n. d. ³⁾	n. d. ³⁾	n. d. ³⁾	0.257
Laacherhof	Silt loam	0.9	7.3 ^{a)}	20 ⁰ C; 40% MWHC	SFO	8.42	G	k	n. d. ³⁾	n. d. ³⁾	n. d. ³⁾	0.272
Höfchen im Tal	Silt loam	2.40	5.8 ^{a)}	20 ⁰ C; 40% MWHC	SFO	6.56	G	k	n. d. ³⁾	n. d. ³⁾	n. d. ³⁾	0.143
Howe, Indiana;	Sandy loam	0.35	6.2 ^{b)}	21 ⁰ C; 75% of 1/3 bar	SFO	6.28	G	k	n. d. ³⁾	n. d. ³⁾	n. d. ³⁾	0.108
BBA 2.1	Sand	0.57	5.3 ^{c)}	20 ± 2 ⁰ C; 75% of 1/3 bar	SFO	1.78	G	k	2.66 E-3	260.76	869.2	n. a. ⁴⁾
BBA 2.2	Loamy sand	2.48	6.3 ^{c)}	20 ± 2 ⁰ C; 75% of 1/3 bar	SFO	1.88	G	k	3.28 E-3	211.00	701	n. a. ⁴⁾
Laacherhof AXXa	Sandy loam	1.47	6.3 ^{c)}	20 ± 2 ⁰ C; 40% MWHC	SFO	3.05	G	k	0.0139	49.85	165.59	n. a. ⁴⁾
Laacherhof AIII	Silt loam	0.88	6.8 ^{c)}	20 ± 2 ⁰ C; 40% MWHC	SFO	3.03	G	k	0.0172	40.37	134.12	n. a. ⁴⁾
Laacherhof AXXa	Loamy sand	1.7	6.2 ^{c)}	19.6 ⁰ C; 55% MWHC	SFO	1.28	G	k	9.84 E-3	70.44	234.02	n. a. ⁴⁾
Dollendorf II	Loam	4.6	7.0 ^{c)}	19.6 ⁰ C; 55% MWHC	SFO	5.59	G	k	0.1109	6.25	20.77	n. a. ⁴⁾
Hoefchen Am Hohenseh 4a;	Silt loam	2.0	6.1 ^{c)}	19.6 ⁰ C; 55% MWHC	SFO	7.68	G	k	0.0269	25.79	85.68	n. a. ⁴⁾
Wurm-wiese	Sandy loam	1.8	5.0 ^{c)}	19.6 ⁰ C; 55% MWHC	SFO	3.66	G	k	0.0145	47.78	158.71	n. a. ⁴⁾
Hanscheider Hof	Loam	2.8	5.6 ^{c)}	19.9 ⁰ C; 55% MWHC	SFO	3.25	G	k	0.0256	27.03	89.79	n. a. ⁴⁾
Frankenforst	Silt loam	1.8	6.8 ^{c)}	19.9 ⁰ C; 55% MWHC	SFO	6.41	G	k	0.0321	21.57	70.68	n. a. ⁴⁾
LUFA 2.3	Sandy loam	1.1	6.8 ^{c)}	19.9 ⁰ C; 55% MWHC	SFO	1.45	G	k	0.0110	63.23	210.04	n. a. ⁴⁾
LUFA 6S	Clay	1.9	7.0 ^{c)}	19.9 ⁰ C; 55% MWHC	SFO	6.49	G	k	0.02158	32.11	106.60	n. a. ⁴⁾
Geometric mean (n = 12)									0.0154	45.11	149.74	----
Median (n = 12)									0.0159	44.08	146.42	----
Arithmetic mean for ff (n = 4)												0.195

Footnotes to the table:

- 1) Measured in:
 - CaCl₂/water for values marked a);
 - distilled water for results marked b);
 - (0.01M) CaCl₂ for results marked c);
- 2) The abbreviations used to describe the visual fit: G. – good, A. – acceptable, P. – poor;
- 3) Value not determined – the decline phase not reached;
- 4) Value not available – the test compound applied as parent.

For GW and SW model exposure assessment the **geomean DT₅₀ = 45.11 days** and **geomean k = 0.0154 [days⁻¹]** are the kinetic endpoints recommended as input parameters. The corresponding recommended **ff** value is **ff = 0.195** (arithmetic mean) for Flufenacet as a precursor.

c) Kinetic endpoints determined for FOE Oxalate:

The degradation kinetics of FOE Oxalate in aerobic soil was examined in four trials on the same number of the test soils. The experiments were performed with soils treated with Flufenacet (active substance).

The performed kinetic analysis resulted in a data base consisting of three reliable kinetic endpoints. In case of the experiment in Howe, Indiana, Sandy loam soil it was not possible to obtain reliable kinetic endpoints characterising degradation of FOE Oxalate because the decline of that compound was not observed. As a result,

the default values – $DT_{50} = 1000$ days and $DT_{90} > 1000$ days, were proposed for that trial. These values, due to their nature and uncertainty related to them, were not used either as input parameters in soil exposure assessment or to calculate normalised mean values used subsequently in GW/SW exposure assessment. They are however provided in the table presenting the persistence endpoints, as with them are associated reliable kinetic formation fraction for FOE Oxalate, recommended to be used in GW exposure assessment. RMS however decided not to provide them in the table presenting the kinetic endpoints recommended for modelling.

The persistence (best-fit) kinetic endpoints obtained for FOE Oxalate are presented below in the table B.8.1.1.2.1.1._CA-311. The modelling endpoints are given in the table B.8.1.1.2.1.1._CA-312.

Table B.8.1.1.2.1.1._CA-311: The persistence kinetic endpoints determined for FOE Oxalate in aerobic soil.

Soil		Soil properties		Incubation conditions	Kinetic model	Evaluation of the fit		Kinetic parameters		Kinetic endpoints		
Soil name	Soil type (USDA)	OC	pH ¹⁾			χ^2 error	Vis. fit ²⁾	Par.	Value	DT ₅₀ [days]	DT ₉₀ [days]	Kinetic formation fraction ff
BBA 2.2	Loamy sand	2.58	6.2 ^{a)}	20°C; 40% MWHC	SFO	25.2	A	k	0.1011	6.9	22.8	0.448
Laacherhof	Silt loam	0.9	7.3 ^{a)}	20°C; 40% MWHC	SFO	12.7	G	k	0.0366	18.9	62.9	0.422
Höfchen im Tal	Silt loam	2.40	5.8 ^{a)}	20°C; 40% MWHC	SFO	10.5	G	k	0.0530	13.09	43.48	0.350
Howe, Indiana;	Sandy loam	0.35	6.2 ^{b)}	21°C; 75% of 1/3 bar	SFO	3.99	G	k	n. d. ³⁾	1000	>1000	0.484
Arithmetic mean for ff (n = 4)												0.426

Footnotes to the table:

- 1) Measured in:
- CaCl₂/water for values marked a);
- distilled water for results marked b);
- 2) The abbreviations used to describe the visual fit: G. – good, A. – acceptable, P. – poor;
- 3) Value not determined – the decline phase not reached;

The **DT₅₀ = 18.9 days** value, determined in Laacherhof Silt loam soil was identified as appropriate input parameter for soil exposure assessment.

Table B.8.1.1.2.1.1._CA-312: The modelling kinetic endpoints determined for FOE Oxalate in aerobic soil.

Soil		Soil properties		Incubation conditions	Kinetic model	Evaluation of the fit		Kinetic parameters		Kinetic endpoints		
Soil name	Soil type (USDA)	OC	pH ¹⁾			χ^2 error	Vis. fit ²⁾	Par.	Value	DT ₅₀ [days]	DT ₉₀ [days]	Kinetic formation fraction ff
BBA 2.2	Loamy sand	2.58	6.2 ^{a)}	20°C; 40% MWHC	SFO	25.2	A	k	0.1011	6.7	22.8	0.448
Laacherhof	Silt loam	0.9	7.3 ^{a)}	20°C; 40% MWHC	SFO	12.7	G	k	0.0447	15.5	51.58	0.422
Höfchen im Tal	Silt loam	2.40	5.8 ^{a)}	20°C; 40% MWHC	SFO	10.5	G	k	0.0530	13.09	43.48	0.350
Howe, Indiana;	Sandy loam	0.35	6.2 ^{b)}	21°C; 75% of 1/3 bar	SFO	3.99	G	k	n. d. ³⁾	n. d. ³⁾	n. d. ³⁾	0.484
Geometric mean (n = 3)									0.0639	11.08	37.12	----
Arithmetic mean for ff (n = 4)												0.426

Footnotes to the table:

- 1) Measured in:
- CaCl₂/water for values marked a);
- distilled water for results marked b);
- 2) The abbreviations used to describe the visual fit: G. – good, A. – acceptable, P. – poor;
- 3) Value not determined – the decline phase not reached;

For GW and SW model exposure assessment the **geomean DT₅₀ = 11.08 days** and **geomean k = 0.0639 [days⁻¹]** are the kinetic endpoints recommended as input parameters. The corresponding recommended **ff** value is **ff = 0.426** (arithmetic mean) for Flufenacet as a precursor.

d) Kinetic endpoints determined for FOE Methylsulfone:

The degradation kinetics of FOE Methylsulfone in aerobic soil was examined in eleven trials using the same number of the test soils. The experiments were performed in two variants – three trials with soils treated with Flufenacet (active substance) and the remaining eight trials with soils treated with FOE Methylsulfone.

The performed kinetic analysis resulted in a data base consisting of nine reliable kinetic endpoints, one with soil treated with Flufenacet as a precursor of FOE Methylsulfone and remaining eight with soils treated with FOE Methylsulfone. In case of two trials on soils treated with Flufenacet – BBA 2.2 Loamy sand soil and Hoefchen im Tal Silt loam soil, it was not possible to obtain reliable kinetic endpoints characterising degradation of FOE Methylsulfone in soil, because decline of that compound was not observed. As a result, the default values – $DT_{50} = 1000$ days and $DT_{90} > 1000$ days, were proposed for these trials. These values, due to their nature and uncertainty related to them, were not used either as input parameters in soil exposure assessment or to calculate normalised mean values used subsequently in GW/SW exposure assessment. They are however provided in the table presenting the persistence endpoints, as with them are associated reliable kinetic formation fractions for FOE Methylsulfone, recommended to be used in GW exposure assessment. RMS however decided not to provide them in the table presenting the kinetic endpoints recommended for modelling.

The persistence (best-fit) kinetic endpoints obtained for FOE Methylsulfone are presented below in the table B.8.1.1.2.1.1._CA-313. The modelling endpoints are given in the table B.8.1.1.2.1.1._CA-314.

Table B.8.1.1.2.1.1._CA-313: The persistence kinetic endpoints determined for FOE Methylsulfone in aerobic soil.

Soil		Soil properties		Incubation conditions	Kinetic model	Evaluation of the fit		Kinetic parameters		Kinetic endpoints		
Soil name	Soil type (USDA)	OC	pH ¹⁾			χ^2 error	Vis. fit ²⁾	Par.	Value	DT ₅₀ [days]	DT ₉₀ [days]	Kinetic formation fraction ff
BBA 2.2	Loamy sand	2.58	6.2 ^{a)}	20°C; 40% MWHC	SFO	28.5	G	k	n. d. ³⁾	1000	>1000	0.061
Laacherhof	Silt loam	0.9	7.3 ^{a)}	20°C; 40% MWHC	SFO	14.4	G	k	3.99 E-3	174	576	0.096
Höfchen im Tal	Silt loam	2.40	5.8 ^{a)}	20°C; 40% MWHC	SFO	17.3	G	k	n. d. ³⁾	1000	>1000	0.052
Laacherhof AXXa	Loamy sand	1.7	6.2 ^{b)}	19.6°C; 55% MWHC	SFO	3.37	G	k	1.61 E-2	43.14	143.32	n. a. ⁴⁾
Dollendorf II	Loam	4.6	7.0 ^{b)}	19.6°C; 55% MWHC	SFO	3.04	G	k	2.98 E-2	23.30	77.41	n. a. ⁴⁾
Hoefchen Am Hohenseh 4a;	Silt loam	2.0	6.1 ^{b)}	19.6°C; 55% MWHC	SFO	3.58	G	k	1.58 E-2	43.84	145.64	n. a. ⁴⁾
Wurm-wiese	Sandy loam	1.8	5.0 ^{b)}	19.6°C; 55% MWHC	SFO	3.32	G	k	7.21 E-3	96.13	319.32	n. a. ⁴⁾
Hanscheider Hof	Loam	2.8	5.6 ^{b)}	19.9°C; 55% MWHC	SFO	2.11	G	k	8.40 E-3	82.53	274.14	n. a. ⁴⁾
Frankenforst	Silt loam	1.8	6.8 ^{b)}	19.9°C; 55% MWHC	SFO	2.88	G	k	0.01083	63.98	212.53	n. a. ⁴⁾
LUFA 2.3	Sandy loam	1.1	6.8 ^{b)}	19.9°C; 55% MWHC	SFO	2.10	G	k	4.72 E-3	146.78	487.60	n. a. ⁴⁾
LUFA 6S	Clay	1.9	7.0 ^{b)}	19.9°C; 55% MWHC	SFO	1.70	G	k	4.25 E-3	163.06	541.68	n. a. ⁴⁾
Arithmetic mean for ff (n = 3)												0.070

Footnotes to the table:

- 1) Measured in:
- CaCl₂/water for values marked a);
- (0.01M) CaCl₂ for results marked b);
- 2) The abbreviations used to describe the visual fit: G. – good, A. – acceptable, P. – poor;
- 3) Value not determined – the decline phase not reached;
- 4) Value not available – the test compound applied as parent.

The **DT₅₀ = 174 days** value, determined in Laacherhof Silt loam soil was identified as appropriate input parameter for soil exposure assessment.

Table B.8.1.1.2.1.1._CA-314: The modelling kinetic endpoints determined for FOE Methylsulfone in aerobic soil.

Soil		Soil properties		Incubation conditions	Kinetic model	Evaluation of the fit		Kinetic parameters		Kinetic endpoints		
Soil name	Soil type (USDA)	OC	pH ¹⁾			χ^2 error	Vis. fit ²⁾	Par.	Value	DT ₅₀ [days]	DT ₉₀ [days]	Kinetic formation fraction <i>ff</i>
BBA 2.2	Loamy sand	2.58	6.2 ^{a)}	20 ⁰ C; 40% MWHC	SFO	28.5	G	<i>k</i>	n. d. ³⁾	n. d. ³⁾	n. d. ³⁾	0.061
Laacherhof	Silt loam	0.9	7.3 ^{a)}	20 ⁰ C; 40% MWHC	SFO	14.4	G	<i>k</i>	4.86 E-3	142.68	472.32	0.096
Höfchen im Tal	Silt loam	2.40	5.8 ^{a)}	20 ⁰ C; 40% MWHC	SFO	17.3	G	<i>k</i>	n. d. ³⁾	n. d. ³⁾	n. d. ³⁾	0.052
Laacherhof AXXa	Loamy sand	1.7	6.2 ^{b)}	19.6 ⁰ C; 55% MWHC	SFO	3.37	G	<i>k</i>	1.66 E-2	41.85	139.00	n. a. ⁴⁾
Dollendorf II	Loam	4.6	7.0 ^{b)}	19.6 ⁰ C; 55% MWHC	SFO	3.04	G	<i>k</i>	3.07 E-2	22.60	75.09	n. a. ⁴⁾
Hoefchen Am Hohensch 4a;	Silt loam	2.0	6.1 ^{b)}	19.6 ⁰ C; 55% MWHC	SFO	3.58	G	<i>k</i>	1.63 E-2	42.52	141.23	n. a. ⁴⁾
Wurm-wiese	Sandy loam	1.8	5.0 ^{b)}	19.6 ⁰ C; 55% MWHC	SFO	3.32	G	<i>k</i>	7.43 E-3	93.25	309.74	n. a. ⁴⁾
Hanscheider Hof	Loam	2.8	5.6 ^{b)}	19.9 ⁰ C; 55% MWHC	SFO	2.11	G	<i>k</i>	8.48 E-3	81.70	271.40	n. a. ⁴⁾
Frankenforst	Silt loam	1.8	6.8 ^{b)}	19.9 ⁰ C; 55% MWHC	SFO	2.88	G	<i>k</i>	1.09 E-2	63.34	210.40	n. a. ⁴⁾
LUFA 2.3	Sandy loam	1.1	6.8 ^{b)}	19.9 ⁰ C; 55% MWHC	SFO	2.10	G	<i>k</i>	4.77 E-3	145.31	482.72	n. a. ⁴⁾
LUFA 6S	Clay	1.9	7.0 ^{b)}	19.9 ⁰ C; 55% MWHC	SFO	1.70	G	<i>k</i>	4.99 E-3	138.83	461.19	n. a. ⁴⁾
Geometric mean (n = 9)									9.55 E-3	72.57	240.99	----
Median (n = 9)									8.48 E-3	81.70	271.40	----
Arithmetic mean for <i>ff</i> (n = 3)												0.070

Footnotes to the table:

- 1) Measured in:
 - CaCl₂/water for values marked a);
 - (0.01M) CaCl₂ for results marked b);
- 2) The abbreviations used to describe the visual fit: G. – good, A. – acceptable, P. – poor;
- 3) Value not determined – the decline phase not reached;
- 4) Value not available – the test compound applied as parent.

For GW and SW model exposure assessment the **median DT₅₀ = 81.70 days** and **median *k* = 0.00848 [days⁻¹]** are the kinetic endpoints recommended as input parameters. The corresponding recommended *ff* value is ***ff* = 0.070** (arithmetic mean) for Flufenacet as a precursor.

e) Kinetic endpoints determined for FOE Thiadone:

The degradation kinetics of FOE Thiadone in aerobic soil was examined in eight trials using the equal number of the test soils. The experiments were performed in two variants – five trials with soils treated with Flufenacet (active substance) and the remaining eight trials with soils treated with FOE Methylsulfone.

The performed kinetic analysis resulted in a data base consisting of eight reliable kinetic endpoints, four with soil treated with Flufenacet as a precursor of FOE Thiadone and three with soils treated with FOE Thiadone. In case of one trial on soil treated with Flufenacet – Howe, Indiana Sandy loam soil, it was not possible to obtain reliable fit for FOE Thiadone in combination with the parent compound. Such fit however was obtained when the data were kinetically analysed for FOE Thiadone alone using the top-down approach. That solution however implied that no reliable value for kinetic formation fraction in that trial could be obtained and reported. RMS decided not to report the default value $ff = 1.00$, proposed by the Applicant. The persistence (best-fit) kinetic endpoints obtained for FOE Thiadone are presented below in the table B.8.1.1.2.1.1_CA-315. The modelling endpoints are given in the table B.8.1.1.2.1.1_CA-316.

Table B.8.1.1.2.1.1_CA-315: The persistence kinetic endpoints determined for FOE Thiadone in aerobic soil.

Soil		Soil properties		Incubation conditions	Kinetic model	Evaluation of the fit		Kinetic parameters		Kinetic endpoints		
Soil name	Soil type (USDA)	OC	pH			χ^2 error	Vis. fit ¹⁾	Par.	Value	DT ₅₀ [days]	DT ₉₀ [days]	Kinetic formation fraction ff
Hoefchen Am Hohenseh 4a;	Silt loam	2.5	6.7 ²⁾	19.1 ⁰ C; 55% MWHC	SFO	16.42	G	k	0.6110	1.13	3.77	0.913
Laacherhof AXXa;	Loamy sand	2.4	6.1 ²⁾	19.9 ⁰ C; 55% MWHC	SFO	15.65	G	k	0.5087	1.36	4.53	0.524
Dollendorf II;	Clay loam	5.3	7.2 ²⁾	19.9 ⁰ C; 55% MWHC	SFO	16.36	G	k	0.2438	2.84	9.45	0.438
Laacherhof Wurm-wiese;	Loam	2.2	5.4 ²⁾	19.9 ⁰ C; 55% MWHC	SFO	14.73	G	k	0.3490	1.99	6.60	0.404
Howe, Indiana;	Sandy loam	0.35	6.2 ³⁾	21 ⁰ C; 75% of 1/3 bar	SFO	4.95	G	k	0.0435	15.9	52.9	n. d. ⁵⁾
Iowa	Loamy sand	1.91	7.2 ⁴⁾	20 ⁰ C; 75% of 1/3 bar	SFO	6.72	A	k	0.3494	1.98	6.59	n. d. ⁶⁾
Indiana	Sandy loam	1.28	6.5 ⁴⁾	20 ⁰ C; 75% of 1/3 bar	SFO	5.67	A	k	0.4945	1.40	4.66	n. d. ⁶⁾
Nebraska	Silt loam	1.66	7.7 ⁴⁾	20 ⁰ C; 75% of 1/3 bar	SFO	3.71	A	k	0.2363	2.93	9.74	n. d. ⁶⁾
Arithmetic mean for ff (n = 3)												0.570

Footnotes to the table:

- 1) The abbreviations used to describe the visual fit: G. – good, A. – acceptable, P. – poor;
- 2) Measured in 0.01M CaCl₂;
- 3) Measured in distilled water;
- 4) Medium for measuring pH not given;
- 5) Value not available – kinetic endpoints determined using the top-down approach;
- 6) Value not available – the test compound applied as parent.

The DT₅₀ = **15.9 days** value, determined in Howe, Indiana Sandy loam soil was identified as appropriate input parameter for soil exposure assessment.

Table B.8.1.1.2.1.1_CA-316: The modelling kinetic endpoints determined for FOE Thiadone in aerobic soil.

Soil		Soil properties		Incubation conditions	Kinetic model	Evaluation of the fit		Kinetic parameters		Kinetic endpoints		
Soil name	Soil type (USDA)	OC	pH			χ^2 error	Vis. fit ¹⁾	Par.	Value	DT ₅₀ [days]	DT ₉₀ [days]	Kinetic formation fraction <i>ff</i>
<i>Hoefchen Am Hohenseh 4a;</i>	Silt loam	2.5	6.7 ²⁾	19.1 ⁰ C; 55% MWHC	SFO	16.42	G	<i>k</i>	0.6301	1.10	3.66	0.913
<i>Laacherhof AXa;</i>	Loamy sand	2.4	6.1 ²⁾	19.9 ⁰ C; 55% MWHC	SFO	15.65	G	<i>k</i>	0.5212	1.33	4.44	0.524
<i>Dollendorf II;</i>	Clay loam	5.3	7.2 ²⁾	19.9 ⁰ C; 55% MWHC	SFO	16.36	G	<i>k</i>	0.2567	2.70	8.98	0.438
<i>Laacherhof Wurm-wiese;</i>	Loam	2.2	5.4 ²⁾	19.9 ⁰ C; 55% MWHC	SFO	14.73	G	<i>k</i>	0.3555	1.95	6.47	0.404
<i>Howe, Indiana;</i>	Sandy loam	0.35	6.2 ³⁾	21 ⁰ C; 75% of 1/3 bar	SFO	4.95	G	<i>k</i>	0.0672	10.32	34.33	n. d. ⁵⁾
<i>Iowa</i>	Loamy sand	1.91	7.2 ⁴⁾	20 ⁰ C; 75% of 1/3 bar	SFO	6.72	A	<i>k</i>	0.5458	1.27	4.22	n. d. ⁶⁾
<i>Indiana</i>	Sandy loam	1.28	6.5 ⁴⁾	20 ⁰ C; 75% of 1/3 bar	SFO	5.67	A	<i>k</i>	0.7702	0.90	2.98	n. d. ⁶⁾
<i>Nebraska</i>	Silt loam	1.66	7.7 ⁴⁾	20 ⁰ C; 75% of 1/3 bar	SFO	3.71	A	<i>k</i>	0.3027	2.29	7.60	n. d. ⁶⁾
Geometric mean (n = 8)									0.3557	1.95	6.48	----
Median (n = 8)									0.4384	1.64	5.46	----
Arithmetic mean for <i>ff</i> (n = 3)												0.570

Footnotes to the table:

- 1) The abbreviations used to describe the visual fit: G. – good, A. – acceptable, P. – poor;
- 2) Measured in 0.01M CaCl₂;
- 3) Measured in distilled water;
- 4) Medium for measuring pH not given;
- 5) Value not available – kinetic endpoints determined using the top-down approach;
- 6) Value not available – the test compound applied as parent.

For GW and SW model exposure assessment the **geomean DT₅₀ = 1.95 days** and **geomean *k* = 0.3557 [days⁻¹]** are the kinetic endpoints recommended as input parameters. The corresponding recommended *ff* value is ***ff* = 0.570** (arithmetic mean) for Flufenacet as a precursor.

f) Kinetic endpoints determined for FOE 5043-Trifluoroethanesulfonic acid (TFESA):

The degradation kinetics of FOE 5043-Trifluoroethanesulfonic acid (TFESA) in aerobic soil was examined in four trials using the equal number of the test soils. The experiments were performed with soils treated with Flufenacet (active substance).

The performed kinetic analysis resulted in a data base consisting of four reliable kinetic endpoints. In case of two trials – on the Dollendorf II Clay loam soil and Laacherhof Wurm-wiese Loam soil it was not possible to obtain reliable kinetic fits for the whole transformation scheme, therefore the top-down approach was used. RMS however decided to keep the determined values of kinetic formation fraction *ff*. The persistence (best-fit) kinetic endpoints obtained for FOE 5043-Trifluoroethanesulfonic acid (TFESA) are presented below in the table B.8.1.1.2.1.1_CA-317. The modelling endpoints are given in the table B.8.1.1.2.1.1_CA-318.

Table B.8.1.1.2.1.1_CA-317: The persistence kinetic endpoints determined for FOE 5043-Trifluoroethanesulfonic acid in aerobic soil.

Soil		Soil properties		Incubation conditions	Kinetic model	Evaluation of the fit		Kinetic parameters		Kinetic endpoints		
Soil name	Soil type (USDA)	OC	pH ¹⁾			χ^2 error	Vis. fit ²⁾	Par.	Value	DT ₅₀ [days]	DT ₉₀ [days]	Kinetic formation fraction ff
Hoefchen Am Hohenseh 4a;	Silt loam	2.5	6.7	19.1 ⁰ C; 55% MWHC	SFO	5.85	G	k	0.0761	9.10	30.23	0.264
Laacherhof AXXa;	Loamy sand	2.4	6.1	19.9 ⁰ C; 55% MWHC	SFO	18.25	G	k	0.1548	4.48	14.87	0.534
Dollendorf II;	Clay loam	5.3	7.2	19.9 ⁰ C; 55% MWHC	SFO	4.31	G	k	0.0331	20.9	69.5	0.422
Laacherhof Wurm-wiese;	Loam	2.2	5.4	19.9 ⁰ C; 55% MWHC	SFO	12.3	G	k	0.3090	2.24	7.45	0.655
Arithmetic mean for ff (n = 3)												0.469

Footnotes to the table:

- 1) Measured in 0.01M CaCl₂;
 2) The abbreviations used to describe the visual fit: G. – good, A. – acceptable, P. – poor;

The DT₅₀ = **20.9 days** value, determined in Dollendorf II Clay loam soil was identified as appropriate input parameter for soil exposure assessment.

Table B.8.1.1.2.1.1_CA-318: The modelling kinetic endpoints determined for FOE 5043-Trifluoroethanesulfonic acid in aerobic soil.

Soil		Soil properties		Incubation conditions	Kinetic model	Evaluation of the fit		Kinetic parameters		Kinetic endpoints		
Soil name	Soil type (USDA)	OC	pH ¹⁾			χ^2 error	Vis. fit ²⁾	Par.	Value	DT ₅₀ [days]	DT ₉₀ [days]	Kinetic formation fraction ff
Hoefchen Am Hohenseh 4a;	Silt loam	2.5	6.7	19.1 ⁰ C; 55% MWHC	SFO	5.85	G	k	0.0785	8.83	29.32	0.264
Laacherhof AXXa;	Loamy sand	2.4	6.1	19.9 ⁰ C; 55% MWHC	SFO	18.25	G	k	0.1579	4.39	14.57	0.534
Dollendorf II;	Clay loam	5.3	7.2	19.9 ⁰ C; 55% MWHC	SFO	4.31	G	k	0.0349	19.87	66.01	0.422
Laacherhof Wurm-wiese;	Loam	2.2	5.4	19.9 ⁰ C; 55% MWHC	SFO	12.3	G	k	0.3165	2.19	7.30	0.655
Geometric mean (n = 4)									0.1082	6.41	21.30	----
Arithmetic mean for ff (n = 3)												0.469

Footnotes to the table:

- 1) Measured in 0.01M CaCl₂;
 2) The abbreviations used to describe the visual fit: G. – good, A. – acceptable, P. – poor;

For GW and SW model exposure assessment the **geomean DT₅₀ = 6.41 days** and **geomean k = 0.1082 [days⁻¹]** are the kinetic endpoints recommended as input parameters. The corresponding recommended ff value is **ff = 0.469** (arithmetic mean) for FOE Thiadone as a precursor.

g) Kinetic endpoints determined for Trifluoroacetic acid (TFA):

The degradation kinetics of Trifluoroacetic acid (TFA) in aerobic soil was examined in eight trials using the equal number of the test soils. The experiments were performed in two variants – four trials with soils treated with Flufenacet (active substance) and the remaining four trials with soils treated with TFA.

Due to the high persistence of the test compound – TFA, in none of the test soils it was possible to obtain the reliable kinetic endpoints. For that reason the default values were proposed.

Due to the difference between the modelling tools, for the persistence endpoints two sets of the default values were provided. For trials on test soils treated with Flufenacet as precursor of TFA, where the analysis performed by the Applicant was accepted, the default kinetic endpoints were: **DT₅₀ = 1000 days** and **DT₉₀ > 1000 days**. In case however of the trials with TFA applied as parent compound, for which RMS had to repeat the kinetic analysis, the kinetic endpoints were: **DT₅₀ = 10000 days** and **DT₉₀ > 10000 days** – the values returned by the applied tool. RMS considers these defaults to be representative for the persistence of TFA in soil, as that indicated the results of the examination of the fate of TFA in environment presented in the open-source literature.

However for modelling the recommended input value is **DT₅₀ = 1000 days**, because of the constraints of the current modelling tools. It shall be noted that due to the nature of the determined endpoint – a default value, its normalisation was not performed as not necessary.

For TFA a set for two kinetic formation fraction values were determined – one for formation of TFA from Flufenacet and the second for its formation from FOE Thiadone.

The persistence (best-fit) kinetic endpoints obtained for TFA are presented below in the table B.8.1.1.2.1.1._CA-319. The modelling endpoints are given in the table B.8.1.1.2.1.1._CA-320.

Table B.8.1.1.2.1.1._CA-319: The persistence kinetic endpoints determined for Trifluoroacetic acid (TFA) in aerobic soil.

Soil		Soil properties		Incubation conditions	Kinetic model	Evaluation of the fit		Kinetic parameters		Kinetic endpoints		
Soil name	Soil type (USDA)	OC	pH ¹⁾			χ^2 error	Vis. fit ¹⁾	Par.	Value	DT ₅₀ [days]	DT ₉₀ [days]	Kinetic formation fraction <i>ff</i> ⁴⁾
Hoefchen Am Hohenseh 4a;	Silt loam	2.5	6.7	19.1 ⁰ C; 55% MWHC	SFO	10.49	G	k	n. d. ³⁾	1000	>1000	<i>ff</i> ₁ = 0.087 <i>ff</i> ₂ = 0.736
Laacherhof AXXa;	Loamy sand	2.4	6.1	19.9 ⁰ C; 55% MWHC	SFO	10.34	G	k	n. d. ³⁾	1000	>1000	<i>ff</i> ₁ = 0.476 <i>ff</i> ₂ = 0.466
Dollendorf II;	Clay loam	5.3	7.2	19.9 ⁰ C; 55% MWHC	SFO	9.45	G	k	n. d. ³⁾	1000	>1000	<i>ff</i> ₁ = 0.562 <i>ff</i> ₂ = 0.578
Laacherhof Wurm-wiese;	Loam	2.2	5.4	19.9 ⁰ C; 55% MWHC	SFO	9.44	G	k	n. d. ³⁾	1000	>1000	<i>ff</i> ₁ = 0.596 <i>ff</i> ₂ = 0.345
Hanscheider Hof	Loam	2.8	5.6	19.9 ⁰ C; 55% MWHC	SFO	4.95	G	k	n. d. ³⁾	10000	>10000	n. d. ³⁾
Frankenfirst	Silt loam	1.8	6.8	19.9 ⁰ C; 55% MWHC	SFO	6.72	A	k	n. d. ³⁾	10000	>10000	n. d. ³⁾
LUFA 2.3	Sandy loam	1.1	6.8	19.9 ⁰ C; 55% MWHC	SFO	5.67	A	k	n. d. ³⁾	10000	>10000	n. d. ³⁾
LUFA 6S	Clay	1.9	7.0	19.9 ⁰ C; 55% MWHC	SFO	3.71	A	k	n. d. ³⁾	10000	>10000	n. d. ³⁾
Arithmetic mean for <i>ff</i> (n = 4)												<i>ff</i> ₁ = 0.430 <i>ff</i> ₂ = 0.531

Footnotes to the table:

- 1) Measured in 0.01M CaCl₂;
- 2) The abbreviations used to describe the visual fit: G. – good, A. – acceptable, P. – poor;
- 3) n. d. – not determined
- 4) *ff*₁ – kinetic formation fraction for formation of TFA from Flufenacet; *ff*₂ – kinetic formation fraction for formation of TFA from FOE Thiadone.

The default **DT₅₀ = 10000 days** value was identified as appropriate input parameter for soil exposure assessment.

Table B.8.1.1.2.1.1_CA-320: The modelling kinetic endpoints determined for Trifluoroacetic acid (TFA) in aerobic soil.

Soil		Soil properties		Incubation conditions	Kinetic model	Evaluation of the fit		Kinetic parameters		Kinetic endpoints		
Soil name	Soil type (USDA)	OC	pH ¹⁾			χ^2 error	Vis. fit ¹⁾	Par.	Value	DT ₅₀ [days]	DT ₉₀ [days]	Kinetic formation fraction $ff^{4)}$
Hoefchen Am Hohenseh 4a;	Silt loam	2.5	6.7	19.1°C; 55% MWHC	SFO	10.49	G	k	n. d. ³⁾	1000	>1000	$ff_1 = 0.087$ $ff_2 = 0.736$
Laacherhof AXXa;	Loamy sand	2.4	6.1	19.9°C; 55% MWHC	SFO	10.34	G	k	n. d. ³⁾	1000	>1000	$ff_1 = 0.476$ $ff_2 = 0.466$
Dollendorf II;	Clay loam	5.3	7.2	19.9°C; 55% MWHC	SFO	9.45	G	k	n. d. ³⁾	1000	>1000	$ff_1 = 0.562$ $ff_2 = 0.578$
Laacherhof Wurm-wiese;	Loam	2.2	5.4	19.9°C; 55% MWHC	SFO	9.44	G	k	n. d. ³⁾	1000	>1000	$ff_1 = 0.596$ $ff_2 = 0.345$
Hanscheider Hof	Loam	2.8	5.6	19.9°C; 55% MWHC	SFO	4.95	G	k	n. d. ³⁾	1000	>1000	n. d. ³⁾
Frankenfirst	Silt loam	1.8	6.8	19.9°C; 55% MWHC	SFO	6.72	A	k	n. d. ³⁾	1000	>1000	n. d. ³⁾
LUFA 2.3	Sandy loam	1.1	6.8	19.9°C; 55% MWHC	SFO	5.67	A	k	n. d. ³⁾	1000	>1000	n. d. ³⁾
LUFA 6S	Clay	1.9	7.0	19.9°C; 55% MWHC	SFO	3.71	A	k	n. d. ³⁾	1000	>1000	n. d. ³⁾
Geometric mean (n = 8)										1000	>1000	----
Arithmetic mean for ff (n = 4)												$ff_1 = 0.430$ $ff_2 = 0.531$

Footnotes to the table:

- 1) Measured in 0.01M CaCl₂;
- 2) The abbreviations used to describe the visual fit: G. – good, A. – acceptable, P. – poor;
- 3) n. d. – not determined
- 4) ff_1 – kinetic formation fraction for formation of TFA from Flufenacet; ff_2 – kinetic formation fraction for formation of TFA from FOE Thiadone.

For GW and SW model exposure assessment the default **DT₅₀ = 1000 days** is a kinetic endpoint recommended as input parameter. The corresponding recommended ff values are $ff_1 = 0.430$ (arithmetic mean) for Flufenacet as a precursor and $ff_2 = 0.531$ (arithmetic mean) for FOE Thiadone as a precursor.

The kinetic endpoints identified by RMS as appropriate to be used in model exposure assessment for soil, groundwater and surface water compartments are summarised below in the table B.8.1.1.2.1.1_CA-321. For completeness also the maximum concentrations observed in soils are provided. That table will be directly transferred to the List of EndPoints.

Table B.8.1.1.2.1.1._CA-321: The kinetic endpoints determined in laboratory studies on aerobic soils, recommended to be used in model exposure assessment for soil, groundwater and surface water compartments.

Compound	Compartment	Recommended endpoints					
		Maximum observed in soil		Kinetic formation fraction - <i>ff</i>		Persistence in soil – <i>DT</i> ₅₀ value	
		Observed soil maximum [%]	Remark	<i>ff</i>	Remark	<i>DT</i> ₅₀ [days]	Remark
Flufenacet	Soil	Not applicable	Not applicable – parent compound	----	Not applicable – parent compound	57.6	Longest not normalised lab value
	Groundwater			----		17.89	Normalised lab geomean value
	Surface Water			----		17.89	Normalised lab geomean value
FOE Sulfonic acid	Soil	26.5	Recommended for simple modelling ¹⁾	0.272	Precursor: flufenacet; highest <i>ff</i> , to be used in complex modelling ²⁾	318	Longest not normalised lab value
	Groundwater	----	Not applicable	0.195	Precursor: flufenacet;	45.11	Normalised lab geomean value
	Surface Water	26.5	To be used in calculations at Steps 1 and 2	0.195	Precursor: flufenacet; to be used in Step 3-4 assessment	45.11	Normalised lab geomean value
FOE Oxalate	Soil	26.3	Recommended for simple modelling ¹⁾	0.484	Precursor: flufenacet; highest <i>ff</i> , to be used in complex modelling ²⁾	18.9	Longest not normalised lab value
	Groundwater	----	Not applicable	0.426	Precursor: flufenacet;	11.08	Normalised lab geomean value
	Surface Water	26.3	To be used in calculations at Steps 1 and 2	0.426	Precursor: flufenacet; to be used in Step 3-4 assessment	11.08	Normalised lab geomean value
FOE Methylsulfone	Soil	6.6	Recommended for simple modelling ¹⁾	0.096	Precursor: flufenacet; highest <i>ff</i> , to be used in complex modelling ²⁾	174	Longest not normalised lab value
	Groundwater	----	Not applicable	0.070	Precursor: flufenacet;	81.70	Normalised lab median value
	Surface Water	6.6	To be used in calculations at Steps 1 and 2	0.070	Precursor: flufenacet; to be used in Step 3-4 assessment	81.70	Normalised lab median value
FOE Thiadone	Soil	5.8	Recommended for simple modelling ¹⁾	0.913	Precursor: flufenacet; highest <i>ff</i> , to be used in complex modelling ²⁾	15.9	Longest not normalised lab value
	Groundwater	----	Not applicable	0.570	Precursor: flufenacet;	1.95	Normalised lab geomean value
	Surface Water	5.8	To be used in calculations at Steps 1 and 2	0.570	Precursor: flufenacet; to be used in Step 3-4 assessment	1.95	Normalised lab geomean value
FOE 5043-Trifluoroethane-sulfonic acid	Soil	6.0	Recommended for simple modelling ¹⁾	0.655	Precursor: Thiadone; highest <i>ff</i> , to be used in complex modelling ²⁾	20.9	Longest not normalised lab value
	Groundwater	----	Not applicable	0.469	Precursor: Thiadone;	6.41	Normalised lab geomean value
	Surface Water	6.0	To be used in calculations at Steps 1 and 2	0.469	Precursor: Thiadone; to be used in Step 3-4 assessment	6.41	Normalised lab geomean value
Trifluoroacetic acid (TFA)	Soil	81.5	Recommended for simple modelling ¹⁾	0.430	Precursor: flufenacet; average <i>ff</i> , to be used in complex modelling ^{2, 3)}	10000	Longest lab value (default)
				0.531	Precursor: Thiadone; average <i>ff</i> , to be used in complex modelling ^{2, 3)}		
	Groundwater	----	Not applicable	0.430	Precursor: flufenacet;	1000	FOCUS default for non-degrading compounds
				0.531	Precursor: Thiadone;		
	Surface Water	81.5	To be used in calculations at Steps 1 and 2	0.430	Precursor: flufenacet; to be used in Step 3-4 assessment	1000	FOCUS default for non-degrading compounds
				0.531	Precursor: Thiadone; to be used in Step 3-4 assessment		

Footnotes to the table:

- 1) By the term “simple modelling” are understood calculations performed using simple models with metabolites applied as parent;
- 2) The term “complex models” concerns calculations performed using more sophisticated tools, e.g. ESCAPE, in which metabolites are calculated as formed from their precursor (parent compound or preceding degradation product);
- 3) For that compound, due to the complex formation scheme, average *ff* values are proposed to be used in complex soil exposure assessment with the average *ff* for Thiadone to be used in case it becomes necessary to recalculate the value to obtain the bet formation of TFA in that process (as if from parent).

Additionally all kinetic endpoints determined in laboratory studies for aerobic soil are given below in format recommended for presenting the data in the current EU List of EndPoints.

Rate of degradation in soil (aerobic) laboratory studies active substance (Regulation (EU) N° 283/2013, Annex Part A, point 7.1.2.1.1 and Regulation (EU) N° 284/2013, Annex Part A, point 9.1.1.1)

Parent - Flufenacet	Dark aerobic conditions						
	Soil type	OC [%]	pH ^{a)}	t. °C / % MWHC	DT ₅₀ /DT ₉₀ (d)	DT ₅₀ (d) 20 °C pF2/10kPa ^{b)}	St. (X ²) Method of calculation
	Loamy sand	2.58	6.2 ¹⁾	20°C; 40% MWHC	31.9/ 106.1	31.9	8.53 SFO
	Silt loam	0.9	7.3 ¹⁾	20°C; 40% MWHC	16.9/ 56.0	13.86	11.0 SFO
	Silt loam	2.40	5.8 ¹⁾	20°C; 40% MWHC	20.4/ 67.9	20.44	5.47 SFO
	Sandy loam	0.35	6.2 ²⁾	21°C; 75% of ½ bar	32.2/ 107.0	20.90	2.36 SFO
	Sandy loam	1.41	6.1 ³⁾	20°C; 50% MWHC	7.35/ 24.4	7.04	11.23 SFO
	Silt loam	2.5	6.7 ³⁾	19.1°C; 55% MWHC	15.8/ 52.6	15.36	4.88 SFO
	Loamy sand	2.4	6.1 ³⁾	19.9°C; 55% MWHC	19.85/ 65.9	19.45	3.03 SFO
	Clay loam	5.3	7.2 ³⁾	19.9°C; 55% MWHC	16.3/ 54.2	15.49	4.67 SFO
	Loam	2.2	5.4 ³⁾	19.9°C; 55% MWHC	14.9/ 49.5	14.61	4.27 SFO
	Sandy loam	0.35	6.2 ²⁾	21°C; 75% of ½ bar	57.6/ 191.42	37.40	2.80 SFO
	Geometric mean (if not pH dependent) <i>n</i> = 10				20.22/ 67.19	17.89	---- SFO
	Median <i>n</i> = 10				18.38/ 60.95	17.47	---- SFO
	pH dependence, <i>Yes or No</i>				No		

^{a)} Measured in: CaCl₂/water for results marked ¹⁾, distilled water for results marked ²⁾ and 0.01M CaCl₂ for results marked ³⁾;

^{b)} Normalised using a Q10 of 2.58 and Walker equation coefficient of 0.7

Rate of degradation in soil (aerobic) laboratory studies transformation products (Regulation (EU) N° 283/2013, Annex Part A, point 7.1.2.1.2 and Regulation (EU) N° 284/2013, Annex Part A, point 9.1.1.1)

FOE Oxalate (FOE OXA)	Dark aerobic conditions; Precursor from which the f.f. was derived was <i>Flufenacet</i>							
	Soil type	OC [%]	pH ^{a)}	t. °C / % MWHC	DT ₅₀ / DT ₉₀ (d)	f. f. k _f / k _{dp}	DT ₅₀ (d) 20 °C pF2/10kPa ^{b)}	St. (X ²) Method of calculation
	Loamy sand	2.58	6.2 ¹⁾	20°C; 40% MWHC	6.9/ 22.8	0.448	6.7	25.2 SFO; Flufenacet as parent
	Silt loam	0.9	7.3 ¹⁾	20°C; 40% MWHC	18.9/ 62.9	0.422	15.5	12.7 SFO; Flufenacet as parent
	Silt loam	2.40	5.8 ¹⁾	20°C; 40% MWHC	13.09/ 43.48	0.350	13.09	10.5 SFO; Flufenacet as parent
	Sandy loam	0.35	6.2 ²⁾	21°C; 75% of ½ bar	1000/ >1000 ^{c)}	0.484	Not determined	3.99 SFO; Flufenacet as parent
	Geometric mean (if not pH dependent) <i>n</i> = 3				11.95/ 39.65	----	11.08	---- SFO
	Arithmetic mean (for ff) <i>n</i> = 4				----	0.426	----	---- SFO
	pH dependence, <i>Yes or No</i>				No			

^{a)} Measured in: CaCl₂/water for results marked ¹⁾, distilled water for results marked ²⁾ and 0.01M CaCl₂ for results marked ³⁾;

^{b)} Normalised using a Q10 of 2.58 and Walker equation coefficient of 0.7;

^{c)} Default values presented for completeness and not used in calculation of mean values nor in exposure assessment;

FOE Sulfonic acid (FOE SA)	Dark aerobic conditions; Metabolite as parent dosed in test soils marked ²⁾; the precursor from which the f.f. was derived was <i>Flufenacet</i> in test soils marked ¹⁾							
Soil type ^{a)}	OC [%]	pH ^{b)}	t. °C / % MWHC	DT ₅₀ / DT ₉₀ (d)	f. f. k _f / k _{dp}	DT ₅₀ (d) 20 °C pF2/10kPa ^{c)}	St. (x ²)	Method of calculation
Loamy sand ¹⁾	2.58	6.2 ¹⁾	20°C; 40% MWHC	1000/ >1000 ^{d)}	0.257	Not determined	15.4	SFO; Flufenacet as parent
Silt loam ¹⁾	0.9	7.3 ¹⁾	20°C; 40% MWHC	1000/ >1000 ^{d)}	0.272	Not determined	8.42	SFO; Flufenacet as parent
Silt loam ¹⁾	2.40	5.8 ¹⁾	20°C; 40% MWHC	1000/ >1000 ^{d)}	0.143	Not determined	6.56	SFO; Flufenacet as parent
Sandy loam ¹⁾	0.35	6.2 ²⁾	21°C; 75% of 1/3 bar	1000/ >1000 ^{d)}	0.108	Not determined	6.28	SFO; Flufenacet as parent
Sand ²⁾	0.57	5.3 ³⁾	20°C; 75% of 1/3 bar	318/1060	----	260.76	1.78	SFO; FOE SA as parent
Loamy sand ²⁾	2.48	6.3 ³⁾	20°C; 75% of 1/3 bar	211/701	----	211.00	1.88	SFO; FOE SA as parent
Sandy loam ²⁾	1.47	6.3 ³⁾	20°C; 40% MWHC	62.31/ 206.99	----	49.85	3.05	SFO; FOE SA as parent
Silt loam ²⁾	0.88	6.8 ³⁾	20°C; 40% MWHC	60.26/ 200.18	----	40.37	3.03	SFO; FOE SA as parent
Loamy sand ²⁾	1.7	6.2 ³⁾	19.6°C; 55% MWHC	73.38/ 243.77	----	70.44	1.28	SFO; FOE SA as parent
Loam ²⁾	4.6	7.0 ³⁾	19.6°C; 55% MWHC	6.71/ 22.30	----	6.25	5.59	SFO; FOE SA as parent
Silt loam ²⁾	2.0	6.1 ³⁾	19.6°C; 55% MWHC	28.58/ 94.95	----	25.79	7.68	SFO; FOE SA as parent
Sandy loam ²⁾	1.8	5.0 ³⁾	19.6°C; 55% MWHC	49.77/ 165.32	----	47.78	3.66	SFO; FOE SA as parent
Loam ²⁾	2.8	5.6 ³⁾	19.9°C; 55% MWHC	27.30/ 90.70	----	27.03	3.25	SFO; FOE SA as parent
Silt loam ²⁾	1.8	6.8 ³⁾	19.9°C; 55% MWHC	21.79/ 72.39	----	21.57	6.41	SFO; FOE SA as parent
Sandy loam ²⁾	1.1	6.8 ³⁾	19.9°C; 55% MWHC	63.87/ 212.16	----	63.23	1.45	SFO; FOE SA as parent
Clay ²⁾	1.9	7.0 ³⁾	19.9°C; 55% MWHC	11.86/ 39.39	----	10.10	6.49	SFO; FOE SA as parent
Geometric mean (if not pH dependent) <i>n</i> = 12				45.54/ 151.32	----	40.97	----	SFO
Median <i>n</i> = 12				55.02/ 182.75	----	44.08	----	SFO
Arithmetic mean (for <i>ff</i>) <i>n</i> = 4				----	0.195	----	----	
pH dependence, <i>Yes or No</i>						No		

^{a)} For soils marked ¹⁾ experiment performed with Flufenacet dosed as parent; for soils marked ²⁾ experiment performed with FOE sulfonic acid applied as parent;

^{b)} Measured in: CaCl₂/water for results marked ¹⁾, distilled water for results marked ²⁾ and in (0.01M) CaCl₂ for results marked ³⁾;

^{c)} Normalised using a Q10 of 2.58 and Walker equation coefficient of 0.7;

^{d)} Default values presented for completeness and not used in calculation of mean values nor in exposure assessment;

FOE Methylsulfone (FOE MET)	Dark aerobic conditions; Metabolite as parent dosed in test soils marked ²⁾ ; the precursor from which the f.f. was derived was <i>Flufenacet</i> in test soils marked ¹⁾							
Soil type ^{a)}	OC [%]	pH ^{b)}	t. °C / % MWHC	DT ₅₀ / DT ₉₀ (d)	f. f. k _f / k _{dp}	DT ₅₀ (d) 20 °C pF2/10kPa ^{c)}	St. (x ²)	Method of calculation
Loamy sand ¹⁾	2.58	6.2 ¹⁾	20°C; 40% MWHC	1000/ >1000 ^{d)}	0.061	Not determined	28.5	SFO; Flufenacet as parent
Silt loam ¹⁾	0.9	7.3 ¹⁾	20°C; 40% MWHC	174/ 576	0.096	142.68	14.4	SFO; Flufenacet as parent
Silt loam ¹⁾	2.40	5.8 ¹⁾	20°C; 40% MWHC	1000/ >1000 ^{d)}	0.052	Not determined	17.3	SFO; Flufenacet as parent
Loamy sand ²⁾	1.7	6.2 ²⁾	19.6°C; 55% MWHC	43.14/ 143.32	----	41.85	3.37	SFO; FOE MET as parent
Loam ²⁾	4.6	7.0 ²⁾	19.6°C; 55% MWHC	23.30/ 77.41	----	22.60	3.04	SFO; FOE MET as parent
Silt loam ²⁾	2.0	6.1 ²⁾	19.6°C; 55% MWHC	43.84/ 145.64	----	42.52	3.58	SFO; FOE MET as parent
Sandy loam ²⁾	1.8	5.0 ²⁾	19.6°C; 55% MWHC	96.13/ 319.32	----	93.25	3.32	SFO; FOE MET as parent
Loam ²⁾	2.8	5.6 ²⁾	19.9°C; 55% MWHC	82.53/ 274.14	----	81.70	2.11	SFO; FOE MET as parent
Silt loam ²⁾	1.8	6.8 ²⁾	19.9°C; 55% MWHC	63.98/ 212.53	----	63.34	2.88	SFO; FOE MET as parent
Sandy loam ²⁾	1.1	6.8 ²⁾	19.9°C; 55% MWHC	146.78/ 487.60	----	145.31	2.10	SFO; FOE MET as parent
Clay ²⁾	1.9	7.0 ²⁾	19.9°C; 55% MWHC	163.06/ 541.68	----	138.83	1.70	SFO; FOE MET as parent
Geometric mean (if not pH dependent) <i>n</i> = 9				76/82/ 255.09	----	72.57	----	SFO
Median <i>n</i> = 9				82.53/ 274.14	----	81.70	----	SFO
Arithmetic mean (for <i>ff</i>) <i>n</i> = 3					0.070		----	SFO
pH dependence, <i>Yes or No</i>						No		

^{a)} For soils marked ¹⁾ experiment performed with Flufenacet dosed as parent; for soils marked ²⁾ experiment performed with FOE Methylsulfone applied as parent;

^{b)} Measured in: CaCl₂/water for results marked ¹⁾ and in (0.01M) CaCl₂ for results marked ²⁾

^{c)} Normalised using a Q10 of 2.58 and Walker equation coefficient of 0.7;

^{d)} Default values presented for completeness and not used in calculation of mean values nor in exposure assessment.

FOE Thiadone (FOE THIA)		Dark aerobic conditions; Metabolite as parent dosed in test soils marked ²⁾; the precursor from which the f.f. was derived was <i>Flufenacet</i> in test soils marked ¹⁾						
Soil type ^{a)}	OC [%]	pH ^{b)}	t. °C / % MWHC	DT ₅₀ / DT ₉₀ (d)	f. f. k _f / k _{dp}	DT ₅₀ (d) 20 °C pF2/10kPa ^{c)}	St. (x ²)	Method of calculation
Silt loam ¹⁾	2.5	6.7 ¹⁾	19.1 ⁰ C; 55% MWHC	1.13/ 3.77	0.913	1.10	16.42	SFO; Flufenacet as parent
Loamy sand ¹⁾	2.4	6.1 ¹⁾	19.9 ⁰ C; 55% MWHC	1.36/ 4.53	0.524	1.33	15.65	SFO; Flufenacet as parent
Clay loam ¹⁾	5.3	7.2 ¹⁾	19.9 ⁰ C; 55% MWHC	2.84/ 9.45	0.438	2.70	16.36	SFO; Flufenacet as parent
Loam ¹⁾	2.2	5.4 ¹⁾	19.9 ⁰ C; 55% MWHC	1.99/ 6.60	0.404	1.95	14.73	SFO; Flufenacet as parent
Sandy loam ¹⁾	0.35	6.2 ²⁾	21 ⁰ C; 75% of 1/3 bar	15.9/ 52.9	----	10.32	4.95	SFO; top-down approach
Loamy sand ²⁾	1.91	7.2 ³⁾	20 ⁰ C; 75% of 1/3 bar	1.98/ 6.59	----	1.27	6.72	SFO; FOE THIA as parent
Sandy loam ²⁾	1.28	6.5 ³⁾	20 ⁰ C; 75% of 1/3 bar	1.40/ 4.66	----	0.90	5.67	SFO; FOE THIA as parent
Silt loam ²⁾	1.66	7.7 ³⁾	20 ⁰ C; 75% of 1/3 bar	2.93/ 9.74	----	2.29	3.71	SFO; FOE THIA as parent
Geometric mean (if not pH dependent) <i>n</i> = 8				2.41/ 8.00	----	1.95	----	SFO
Median <i>n</i> = 8				1.99/ 6.60	----	1.64	----	SFO
Arithmetic mean (for <i>ff</i>) <i>n</i> = 4					0.570	-----	----	SFO
pH dependence, <i>Yes or No</i>						No		

^{a)} For soils marked ¹⁾ experiment performed with Flufenacet dosed as parent; for soils marked ²⁾ experiment performed with FOE Thiadone applied as parent;

^{b)} Measured in: 0.01 M CaCl₂ for results marked ¹⁾, distilled water for results marked ²⁾ and in not specified medium for results marked ³⁾;

^{c)} Normalised using a Q10 of 2.58 and Walker equation coefficient of 0.7.

FOE 5043-Trifluoroethane-sulfonic acid (FOE TFESA)		Dark aerobic conditions; Precursor from which the f.f. was derived was <i>FOE Thiadone</i> and soils were treated with <i>Flufenacet</i>						
Soil type ^{a)}	OC [%]	pH ^{b)}	t. °C / % MWHC	DT ₅₀ / DT ₉₀ (d)	f. f. k _f / k _{dp}	DT ₅₀ (d) 20 °C pF2/10kPa ^{c)}	St. (x ²)	Method of calculation
Silt loam	2.5	6.7	19.1 ⁰ C; 55% MWHC	9.10/ 30.23	0.264	8.83	5.85	SFO; Flufenacet as parent; FOE TFESA formed from FOE Thiadone
Loamy sand	2.4	6.1	19.9 ⁰ C; 55% MWHC	4.48/ 14.87	0.534	4.39	18.25	SFO; Flufenacet as parent; FOE TFESA formed from FOE Thiadone
Clay loam	5.3	7.2	19.9 ⁰ C; 55% MWHC	20.9/ 69.5	0.422	19.87	4.31	SFO; top-down approach
Loam	2.2	5.4	19.9 ⁰ C; 55% MWHC	2.24/ 7.45	0.655	2.19	12.3	SFO; top-down approach
Geometric mean (if not pH dependent) <i>n</i> = 4				6.61/ 21.96	----	6.41	----	
Arithmetic mean (for <i>ff</i>) <i>n</i> = 4				----	0.469	----	----	
pH dependence, <i>Yes or No</i>						No		

^{a)} For all test soils experiment performed with Flufenacet dosed as parent;

^{b)} Measured in 0.01 M CaCl₂;

^{c)} Normalised using a Q10 of 2.58 and Walker equation coefficient of 0.7.

Trifluoroacetic acid (TFA)	Dark aerobic conditions; Metabolite as parent dosed in test soils marked ²⁾ ; the precursors from which the f.f. was derived were <i>Flufenacet</i> ¹⁾ and <i>FOE Thiadone</i> ²⁾ in test soils treated with <i>Flufenacet</i> and marked ¹⁾							
Soil type ^{a)}	OC [%]	pH ^{b)}	t. °C / % MWHC	DT ₅₀ / DT ₉₀ (d)	f. f. k _f / k _{dp} ^{c)}	DT ₅₀ (d) 20 °C pF2/10kPa ^{d)}	St. (X ²)	Method of calculation
Silt loam ¹⁾	2.5	6.7	19.1 ⁰ C; 55% MWHC	1000/ >1000 ^{e)}	0.087 ¹⁾ 0.736 ²⁾	1000 ^{f)}	10.49	SFO; Flufenacet as parent; TFA formed from Flufenacet and FOE Thiadone
Loamy sand ¹⁾	2.4	6.1	19.9 ⁰ C; 55% MWHC	1000/ >1000 ^{e)}	0.476 ¹⁾ 0.466 ²⁾	1000 ^{f)}	10.34	SFO; Flufenacet as parent; TFA formed from Flufenacet and FOE Thiadone
Clay loam ¹⁾	5.3	7.2	19.9 ⁰ C; 55% MWHC	1000/ >1000 ^{e)}	0.562 ¹⁾ 0.578 ²⁾	1000 ^{f)}	9.45	SFO; Flufenacet as parent; TFA formed from Flufenacet and FOE Thiadone
Loam ¹⁾	2.2	5.4	19.9 ⁰ C; 55% MWHC	1000/ >1000 ^{e)}	0.596 ¹⁾ 0.345 ²⁾	1000 ^{f)}	9.44	SFO; Flufenacet as parent; TFA formed from Flufenacet and FOE Thiadone
Loam ²⁾	2.8	5.6	19.9 ⁰ C; 55% MWHC	10000/ >10000 ^{e)}	----	1000 ^{f)}	4.95	SFO; TFA as parent
Silt loam ²⁾	1.8	6.8	19.9 ⁰ C; 55% MWHC	10000/ >10000 ^{e)}	----	1000 ^{f)}	6.72	SFO; TFA as parent
Sandy loam ²⁾	1.1	6.8	19.9 ⁰ C; 55% MWHC	10000/ >10000 ^{e)}	----	1000 ^{f)}	5.67	SFO; TFA as parent
Clay ²⁾	1.9	7.0	19.9 ⁰ C; 55% MWHC	10000/ >10000 ^{e)}	----	1000 ^{f)}	3.71	SFO; TFA as parent
Geometric mean (if not pH dependent)				----		1000 ^{f)}	----	SFO
Arithmetic mean				----	0.430 ¹⁾ 0.531 ²⁾	----	----	SFO
pH dependence, <i>Yes or No</i>						No		

^{a)} For soils marked ¹⁾ experiment performed with Flufenacet dosed as parent; for soils marked ²⁾ experiment performed with TFA applied as parent;

^{b)} Measured in 0.01 M CaCl₂;

^{c)} The values marked ¹⁾ are for TFA forming from Flufenacet and the values marked ²⁾ are for TFA forming from FOE Thiadone;

^{d)} Normalised using a Q10 of 2.58 and Walker equation coefficient of 0.7;

^{e)} Default values reported by the used modelling tools; the averages not calculated;

^{f)} Maximum FOCUS default value accepted by the current GW/SW modelling tools;

Finally, the key results of the two literature studies examining the rate of degradation of Flufenacet in aerobic soil incubated under controlled – laboratory, conditions are presented below in the table B.8.1.1.2.1.1._CA-322. As already indicated, these results may be considered only as indicative and were not used to derive the regulatory endpoints.

Table B.8.1.1.2.1.1_CA-322: The key results of the relevant publications examining the rate of degradation of Flufenacet in aerobic soils.

Study	Test soil	Key soil properties			Incubation conditions		Fortification level [µg a. s./g soil]	Kinetic endpoints – DT ₅₀ [days]		Method of calculation
		Soil type (USDA)	pH	OC [%]	T [°C]	Soil moisture		T=25°C; FC	T=20°C; FC	
<i>Gupta, Gajbhiye, Agnihotri [2001]</i>	Sandy loam	Sandy loam	7.1	0.34	25	FC	1	9.3	13.4	1 st order, linear regression, r =0.99
							10	13.0	20.4	1 st order, linear regression, r =0.99
<i>Gupta, Gajbhiye, [2002]</i>	Dehli sandy loam	US Loamy sand	7.69	0.50	25	FC	1	10.1	15.8	1 st order, linear regression, r =0.99
							10	13.0	20.4	1 st order, linear regression, r =0.99
	Ranchi sandy loam	US Sandy clay loam	5.54	0.04	25	FC	1	10.5	16.5	1 st order, linear regression, r =0.99
							10	21.3	33.4	1 st order, linear regression, r =0.99
	Nagpur clayey soil	US Clay	8.25	0.40	25	FC	1	31.0	48.6	1 st order, linear regression, r =0.99
							10	29.2	45.8	1 st order, linear regression, r =0.94

B.8.1.1.2.1.2. – Anaerobic degradation

Degradation of Flufenacet in soil under anaerobic conditions was examined in two newly submitted studies, both summarised under the point B.8.1.1.2. of this report as **Study 1** and **Study 2**.

Study 1, [Pangilinan and Smith; 1995], examined the degradation of [Phenyl-U-¹⁴C]Flufenacet in one soil incubated under anaerobic conditions. The study report contained the results of the kinetic analysis of the data for Flufenacet, performed however not in line with the recommendations of the FOCUS Kinetics Work Group [FOCUS; 2006] – the fitting was done using linear regression and the statistical evaluation of the fit, except r^2 value, was not provided. For that reason RMS decided not to present them in the Renewal Assessment Report.

Study 2, [Heinemann; 2012], examined the degradation of [Thiadiazole-5-¹⁴C]Flufenacet in two soils incubated under anaerobic conditions. The study report also contained the results of the kinetic evaluation of the data obtained for Flufenacet. The kinetic analysis was performed in line with the recommendations of the FOCUS Kinetics Work Group [FOCUS; 2006]. The study report contains however only results of the fitting obtained using DFOP kinetic model, most probably returning the best fit. As such, the results of the kinetic examination of the data cannot be considered complete. Therefore RMS decided not to present them, moreover because more detailed kinetic analysis of the same data is available in the new study report, specifically aimed on the kinetic examination of the data obtained in the studies listed above, summarised below as **Study 1**.

Additionally two open-source literature reports provided additional data on the degradation kinetics of Flufenacet in anaerobic soil. The studies were summarised under the preceeding point – B.8.1.1.2.1.1. as **Study 27** and **Study 28**, therefore the RMS decided not to provide their summaries in this section. The results will however be provided in the part summarising the results of the degradation of Flufenacet in soil under anaerobic conditions.

Study 1:

Report: Reinken G., Partsch S., Bolekhan A., (2014): “Kinetic evaluation of the Degradation of Flufenacet and its Degradation Products under Anaerobic Soil Conditions in Laboratory According to FOCUS Kinetics Using the KinGUI 2 Tool.”; Bayer CropScience AG, Environmental Safety, Alfred-Nobel-Strasse 50, 40789 Monheim, Germany; unpublished study Report No. EnSa-13-0971; 2014. 02. 28; study reference number: M-478213-02-1;.

Guidelines: the study was declared to be performed following the guidance of the FOCUS Kinetics Work Group given in:

- FOCUS, 2006: “Guidance Document on Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration.”; Report of the FOCUS Work Group on Degradation Kinetics, EC Document Reference Sanco/10058/2005 version 2.0, 434 pp.;
- FOCUS, 2011: “Generic Guidance for Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration.” Version 1.0, Nov. 23, 2011.

No deviations were stated.

GLP: No, not required, as the study is a modelling study.

RMS comments: The study was verified and it was found acceptable. It is summarised below.

Summary:

The aim of the study was the kinetic analysis, performed in line with recommendations of FOCUS Kinetics Work Group, of the data obtained in two studies examining the degradation of Flufenacet in soil under anaerobic conditions in order to:

- a) determine the persistence of Flufenacet and its degradation products by deriving the appropriate kinetic endpoints;
- b) derive the kinetic endpoints – DT₅₀ values, suitable for use in model calculations.

The data used in this study came from two studies examining the degradation of Flufenacet in soil under anaerobic conditions – [Pangilinan and Smith; 1995] (**Study 1**) and [Heinemann; 2012] (**Study 2**), summarised in details under the point B.8.1.1.2. of this report. The examination was performed using three soils, the characteristic of which is provided below in the table B.8.1.1.2.1.2._CA-1.

Table B.8.1.1.2.1.2._CA-1: The characteristic of soil used in examination of the degradation of Flufenacet in soil under anaerobic conditions.

Parameter	Study/test soil		
	Pangilinan & Smith; 1995	Heinemann; 2012	
	Howe	Hoefchen am Hohenseh 4a	Dollendorf II
Soil origin	Indiana, USA	Burscheid, Germany	Blankenheim, Germany
Soil type (USDA)	Sandy loam	Silt loam	Loam
Particle size distribution	Sand [%]	73.5	22
	Silt [%]	19.1	62
	Clay [%]	7.5	16
pH value (in H ₂ O, 1:1)	6.2	6.3	7.1
pH value (in CaCl ₂)	5.6	6.1	7.0
Organic carbon content (C _{org}) [%]	0.35	2.0	4.6
Cation Exchange Capacity – CEC [mEq/100g]	6.5	11.1	19.5
Water holding capacity at ½ bar	13.1 %	20.9 g H ₂ O/100 g soil	35.1 g H ₂ O/100 g soil
Bulk density (disturbed) [g/cm ³]	1.37	1.09	1.03

The test substance used in the study by [Pangilinan and Smith; 1995] was [Phenyl-U-¹⁴C]Flufenacet applied to soil at a rate of 1.03 mg/kg soil. The treated soil samples were incubated in the dark at T = 21 ± 1 °C, firstly for 30 days under aerobic conditions, followed by 180-days incubation under anaerobic conditions. The test soil was demonstrated to be fully biologically viable throughout both aerobic and anaerobic incubation phases.

For the purpose of the kinetic evaluation only the data obtained during anaerobic phase were used. These are presented below, in the table B.8.1.1.2.1.2._CA-2. The averages of the two replicates are given, as only those were reported in the source study report.

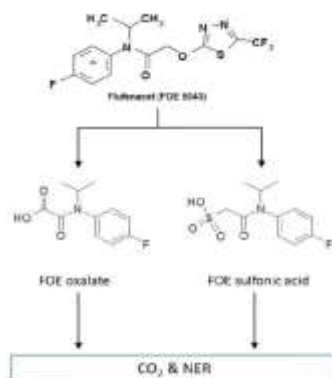
Table B.8.1.1.2.1.2._CA-2: The data obtained during anaerobic incubation period in the study by [Pangilinan and Smith; 1995].

Time point – DASF ¹⁾ [days]	Concentration in % AR of:		
	Flufenacet ²⁾	FOE Oxalate ²⁾	FOE Sulfonic acid ²⁾
0	69.0	11.2	6.6
15	60.3	12.2	6.1
30	55.6	14.5	5.3
67	52.0	10.9	4.7
123	44.2	11.4	5.0
180	39.0	9.9	4.5

Footnotes to the table:

- 1) DASF – Days after Soil Flooding;
 2) Values are averages of the two replicates.

These values were inserted, after being processed following recommendations given by FOCUS Kinetics Work Group (FOCUS; 2006, 2011), into the kinetic modelling tool – KinGUI 2 developed by Bayer. The assumed transformation pathway is shown below on figure B.8.1.1.2.1.2._CA-1.

**Figure B.8.1.1.2.1.2._CA-1:** The assumed transformation pathway of [Phenyl-U-¹⁴C] Flufenacet in anaerobic soil used in the kinetic examination of the data from the study by Pangilinan and Smith [1995] (copied from the study's report).

The test substance used in the study by [Heinemann; 2012] was [Thiadiazole-5-¹⁴C]Flufenacet applied to soil at a rate (nominal) 1.6 mg/kg soil (d. w.). The treated soil samples were incubated in the dark at $T = 20 \pm 2^{\circ}\text{C}$, firstly for 15 days under aerobic conditions, followed by 120-days incubation under anaerobic conditions. The test soils were demonstrated to be fully biologically viable throughout both aerobic and anaerobic incubation periods.

For the purpose of the kinetic evaluation only the data obtained during anaerobic phase were used. These are presented below, in the table B.8.1.1.2.1.2._CA-3.

Table B.8.1.1.2.1.2._CA-3: The data obtained during anaerobic incubation period in the study by Heinemann [2012].

Test soil	Time point – DASF ¹⁾ [days]	Concentration in % AR of:							
		Flufenacet		FOE Thiadone		FOE 5043-Trifluoroethane-sulfonic acid		Trifluoroacetic acid	
		Rep. 1 ²⁾	Rep. 2 ³⁾	Rep. 1 ²⁾	Rep. 2 ³⁾	Rep. 1 ²⁾	Rep. 2 ³⁾	Rep. 1 ²⁾	Rep. 2 ³⁾
Hoefhen am Hohenseh 4a	0	43.7	41.9	4.6	4.9	4.8	5.3	30.5	32.4
	2	38.9	38.7	8.4	8.6	4.9	5.1	33.0	32.6
	6	34.3	32.4	10.6	10.5	4.0	4.0	36.5	36.6
	14	25.4	25.6	11.7	11.4	1.1	1.8	43.1	43.9
	20	21.6	23.3	11.9	13.6	2.8	2.8	43.2	41.5
	33	19.0	17.5	13.3	12.9	4.0	4.4	41.7	42.5
	62	12.9	13.0	13.2	13.9	1.5	2.8	48.0	46.6
	90	10.2	9.3	12.2	12.1	2.0	2.4	46.0	45.9
Dollendorf II	0	34.6	36.1	6.6	7.6	3.2	3.2	40.9	39.9
	2	28.9	25.1	11.0	11.6	1.7	1.7	46.3	46.8
	6	22.8	23.7	12.1	12.8	0.7	1.4	49.3	48.0
	14	17.6	18.7	11.4	11.6	0.7	0.6	52.9	53.6
	20	17.8	13.9	12.5	11.2	< LOD	< LOD	51.4	51.1
	33	10.9	10.3	9.9	7.5	0.7	0.8	51.1	54.2
	62	3.1 ⁴⁾	12.1	15.8 ⁴⁾	7.7	0.7 ⁴⁾	0.7	114.6 ⁴⁾	47.3
	90	4.4	4.5	6.3	4.3	< LOD	< LOD	51.5	54.9
	120	3.1	3.1	2.2	3.2	1.2	1.2	49.8	53.3

Footnotes to the table:

- 1) DASF – Days After Soil Flooding;
- 2) Replicate 1;
- 3) Replicate 2;
- 4) It was indicated in the study report that mass balance in this sample was not achieved, hence the values were not considered in the kinetic analysis.

These values were inserted, after being processed following recommendations given by FOCUS Kinetics Work Group (FOCUS; 2006, 2011), into the kinetic modelling tool – KinGUI 2 developed by Bayer. The assumed transformation pathway is shown below on figure B.8.1.1.2.1.2._CA-2.

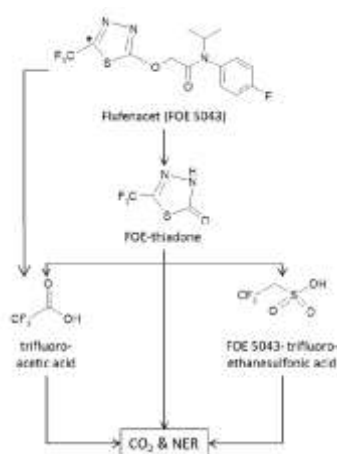


Figure B.8.1.1.2.1.2._CA-2: The assumed transformation pathway of [thiadiazole-5-¹⁴C] Flufenacet in anaerobic soil used in the kinetic examination of the data from the study by Heinemann [2012] (copied from the study's report).

The kinetic analysis of the data presented in the tables B.8.1.1.2.1.2._CA-2 and B.8.1.1.2.1.2._CA-3 consisted of the following three steps:

- **Step 1:** pre-processing of the reported soil residue values;
- **Step 2:** Kinetic evaluation of the pre-processed data using KinGUI 2 kinetic modelling tool;
- **Step 3:** Evaluation of the results of the kinetic analysis performed at **Step 2**, selection of the appropriate kinetic model and persistence kinetic endpoints as well as those recommended for modelling.

The pre-processing of data generally followed the procedure recommended by FOCUS [2006, 2011] for parent and metabolite data. Its initial step was the elimination of the data obtained during aerobic pre-incubation phase, setting the Day 0 of the anaerobic phase as the initial time point and residues measured then as initial concentration.

In case of the results of the study by [Pangilinan and Smith; 1995] the only available results were the averages of the two replicates, so these were used as input values in the kinetic analysis.

In case of the results obtained by [Heinemann; 2012] the values obtained for the individual replicates were available for both test soils. These were used singularly as input data for each time point.

The values were checked for consistency and clear outliers. Whenever lack of consistency or the fact of the data being an outlier was stated, such values were removed from the data set and that was clearly indicated. It concerned in particular one of DASF-62 replicates (Rep. 1) in Dollendorf II soil, where the mass balance was out of a Guideline recovery range of 90 – 110% AR.

Apart from the corrections listed above, the pre-processing of the data followed the procedure outlined below:

- values for day 0 after flooding (DASF-0) were set to measured value;
- values between LOD and LOQ were set to measured values;
- all samples <LOD were set to ½ LOD or after the first non-detect, to zero in case no detects appeared later on.

The pre-processed data used in the kinetic fitting are presented above in two separate tables – Table B.8.1.1.2.1.2._CA-4 for the results of the study by [Pangilinan and Smith; 1995] and B.8.1.1.2.1.2._CA-5 for those obtained by [Heinemann; 2012].

Table B.8.1.1.2.1.2._CA-4: The pre-processed data from the by [Pangilinan and Smith; 1995] used in the kinetic evaluation.

Time point – DASF ¹⁾ [days]	Concentration in % AR of:		
	<i>Flufenacet</i> ²⁾	<i>FOE Oxalate</i> ²⁾	<i>FOE Sulfonic acid</i> ²⁾
0	69.0	11.2	6.6
15	60.3	12.2	6.1
30	55.6	14.5	5.3
67	52.0	10.9	4.7
123	44.2	11.4	5.0
180	39.0	9.9	4.5

Footnotes to the table:

1) DASF – Days after Soil Flooding;

2) Values are averages of the two replicates.

Table B.8.1.1.2.1.2._CA-5: The pre-processed data from the study by [Heinemann; 2012] used in the kinetic evaluation.

Test soil	Time point – DASF ¹⁾ [days]	Concentration in % AR of:							
		<i>Flufenacet</i>		<i>FOE Thiadone</i>		<i>FOE 5043-Trifluoroethane-sulfonic acid</i>		<i>Trifluoroacetic acid</i>	
		Rep. 1 ²⁾	Rep. 2 ³⁾	Rep. 1 ²⁾	Rep. 2 ³⁾	Rep. 1 ²⁾	Rep. 2 ³⁾	Rep. 1 ²⁾	Rep. 2 ³⁾
<i>Hoefhen am Hohenseh 4a</i>	0	43.7	41.9	4.6	4.9	4.8	5.3	30.5	32.4
	2	38.9	38.7	8.4	8.6	4.9	5.1	33.0	32.6
	6	34.3	32.4	10.6	10.5	4.0	4.0	36.5	36.6
	14	25.4	25.6	11.7	11.4	1.1	1.8	43.1	43.9
	20	21.6	23.3	11.9	13.6	2.8	2.8	43.2	41.5
	33	19.0	17.5	13.3	12.9	4.0	4.4	41.7	42.5
	62	12.9	13.0	13.2	13.9	1.5	2.8	48.0	46.6
	90	10.2	9.3	12.2	12.1	2.0	2.4	46.0	45.9
<i>Dollendorf II</i>	120	6.5	6.2	10.6	10.6	1.6	3.1	47.3	48.5
	0	34.6	36.1	6.6	7.6	3.2	3.2	40.9	39.9
	2	28.9	25.1	11.0	11.6	1.7	1.7	46.3	46.8
	6	22.8	23.7	12.1	12.8	0.7	1.4	49.3	48.0
	14	17.6	18.7	11.4	11.6	0.7	0.6	52.9	53.6
	20	17.8	13.9	12.5	11.2	0.15	0.15	51.4	51.1
	33	10.9	10.3	9.9	7.5	NaN ⁴⁾	NaN ⁴⁾	51.1	54.2
	62	NaN ⁴⁾	12.1	NaN ⁴⁾	7.7	NaN ⁴⁾	NaN ⁴⁾	NaN ⁴⁾	47.3
	90	4.4	4.5	6.3	4.3	NaN ⁴⁾	NaN ⁴⁾	51.5	54.9
	120	3.1	3.1	2.2	3.2	1.2	1.2	49.8	53.3

Footnotes to the table:

- 1) DASF – Days After Soil Flooding;
- 2) Replicate 1;
- 3) Replicate 2;
- 4) NaN – “Not a Number” – KinGUI default setting when numbers are not available.

The pre-processed data were inserted into the KinGUI ver. 2 modelling tool, developed by Bayer, and kinetically analysed in a sequential procedure consisting of two steps. Firstly the data for parent compound were kinetically examined. Next those for the degradation products were added, and the whole data set kinetically re-examined using the conceptual transformation schemes presented above on figures B.8.1.1.2.1.2._CA-1 (data from [Pangilinan and Smith; 1995]) and B.8.1.1.2.1.2._CA-2 (data from [Heinemann; 2012]). For the parent compound – Flufenacet, all four available kinetic models – SFO, FOMC, DFOP and HS, were tested at first stage. At the next step, after addition of the data for the degradation products, only the model identified as returning the best fit was tested. The data for the degradation products were kinetically examined using solely SFO model. The kinetic fitting was performed using IRLS (Iteratively Reweighted Nonlinear Least Squares) algorithm as optimisation method.

The results of the kinetic analysis were evaluated for their acceptability. The following parameters were evaluated:

- visual acceptability of the fit – examination of coefficient of determination – r^2 , and residual plot;
- statistical acceptability of the fit by means of χ^2 test;
- the significance of the calculated kinetic parameters – t-test.

The 4-step procedure was applied here that followed the recommendations given by FOCUS [2006, 2011].

Results and their discussion:

The results of the kinetic analysis of the data is presented below, separately for each of the test soils used in the examination of the degradation of Flufenacet in soil under anaerobic conditions. The assessment is fully based on the results obtained by the Applicant and presented in the study report.

- 1) Results of the kinetic examination of the data obtained in soil **Howe (Indiana, USA)** for [Phenyl-U-¹⁴C] Flufenacet (study by [Pangilinan and Smith; 1995]):

The results of the kinetic examination of the data are presented below. First are presented the results of the kinetic examination of the data for parent only. The results of the kinetic examination of the data for the parent compound and degradation products are presented further down.

a) Results of the fitting of the data for parent compound only:

The obtained results are presented below in the numerical form in table B.8.1.1.2.1.2_CA-6 and in the graphical form on figure B.8.1.1.2.1.2_CA-3. For convenience the results for all kinetic models tested are presented together.

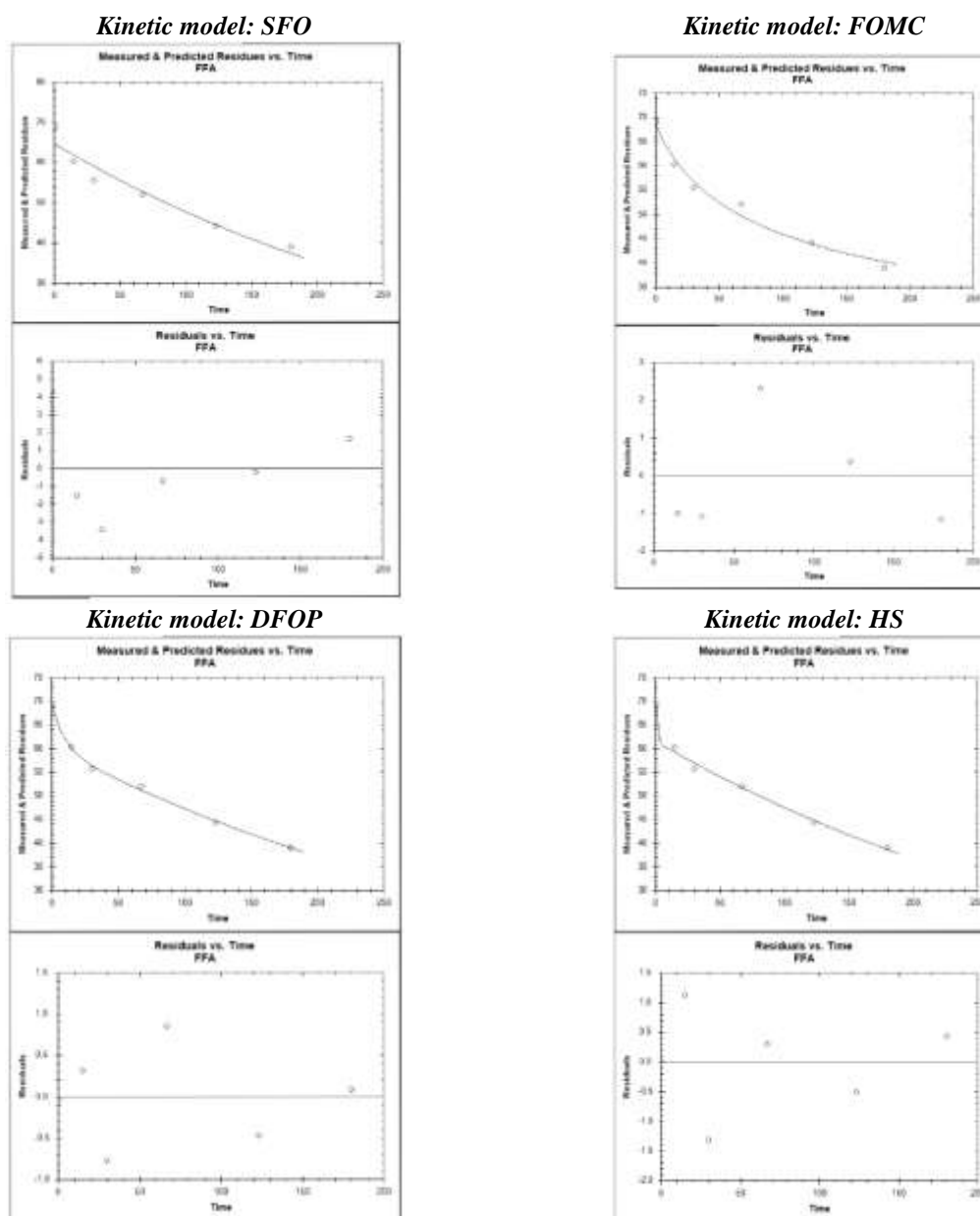


Figure B.8.1.1.2.1.2_CA-3: The graphical results of the kinetic analysis (copied from the study report).

Table B.8.1.1.2.1.2._CA-6: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment ¹⁾
				Lower	Upper			
SFO	M ₀	64.68	1.96	60.84	68.53	2.53 E-6	3.65	0.94; acceptable fit
	k	0.00305	4.245 E-4	2.221 E-3	0.004	0.00099		
FOMC	M ₀	68.41	1.81	64.86	71.97	2.05 E-5	2.05	0.98; acceptable fit
	α	0.2768	0.0912	0.0981	0.4560	0.0280		
	β	30.8332	21.5348	-11.3742	73.0410	0.1238		
DFOP	M ₀	69.04	0.84	63.39	70.69	7.43 E-5	0.98	1.00; good fit
	k ₁	0.09967	0.0398	0.02167	0.178	0.06462		
	k ₂	2.416 E-3	2.133 E-4	1.998 E-3	0.003	0.00385		
	g	0.1291	0.02323	0.08359	0.175	0.01544		
HS	M ₀	69.00	1.34	66.37	71.63	1.89 E-4	1.44	0.99; good fit
	k ₁	0.03194	8.918 E-3	0.01447	0.049	0.03494		
	k ₂	2.596 E-3	2.167 E-4	2.171 E-3	0.003	0.00345		
	t _b	3.903	0.9170	2.106	5.701	0.02550		

Footnotes to the table:

1) Visual assessment of the kinetic curve as proposed by the Applicant.

Also the kinetic endpoints – DT₅₀ and DT₉₀ values for each of the kinetic models were calculated. These are presented below in the table B.8.1.1.2.1.2._CA-7.

Table B.8.1.1.2.1.2._CA-7: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested			
		SFO	FOMC	DFOP	HS
Flufenacet	DT ₅₀ [days]	277.00	346.31	229.63	222.90
	DT ₉₀ [days]	754.09	1263.14	895.64	842.93

Evaluation:

On the basis of the obtained results the Applicant proposed to consider SFO and DFOP kinetic fits in the further analysis. That proposal was based on the fact that although SFO fit was visually and statistically acceptable, it returned worse fit than FOMC model. FOMC fit however was visually, but not statistically, acceptable (CI for β contained zero). Both DFOP and HS models returned visually and statistically acceptable fits, that for DFOP being however superior. For that reason the Applicant proposed DFOP fit as returning the best-fit results and as such should be used for deriving trigger endpoints.

RMS having examined the SFO fit stated that the decline curve was not well fitted to the experimental points, especially in its initial phase. Also the residuals were not randomly distributed and their level was higher in comparison to that observed for DFOP fit. For that reason RMS's proposal is to consider DFOP fit, visually acceptable and statistically reliable, suitable for deriving both persistence and modelling endpoints.

b) Results of the fitting of the data for parent compound and degradation products:

As a next step proposed by the Applicant the data for the parent compound were kinetically examined together with those for the degradation products using the best-fit kinetic model identified for the parent compound.

For the experiment on Sandy loam soil (Howe, Indiana, USA) with the [Phenyl-U-¹⁴C]Flufenacet, Applicant tested two options:

- SFO for parent compound (Flufenacet) and SFO for the degradation products to derive modelling endpoints – **Option 1**;
- DFOP for parent compound (Flufenacet) and SFO for the degradation products to obtain the persistence endpoints – **Option 2**.

The results of both fittings are presented below.

Option 1: SFO (Parent) – SFO (Metabolites) fitting:

The results of the fitting are presented below in graphical form on the figure B.8.1.1.2.1.2._CA-4 and in numerical form in the table B.8.1.1.2.1.2._CA-8.

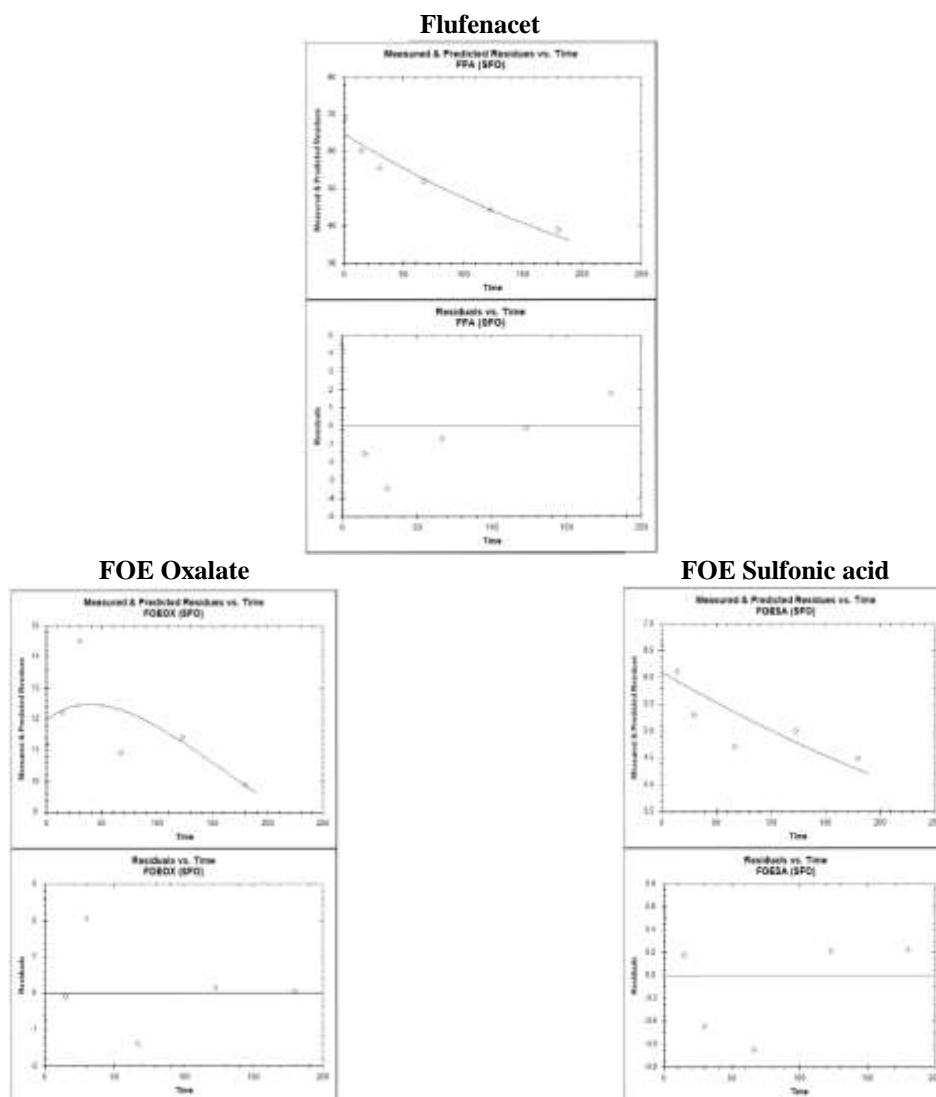


Figure B.8.1.1.2.1.2._CA-4: The graphical results of the kinetic fitting of the data for Flufenacet, FOE Oxalate and FOE Sulfonic acid using SFO for Flufenacet (copied from the study report).

Table B.8.1.1.2.1.2_CA-9: The numerical results of the kinetic fitting of the data for Flufenacet, FOE Oxalate and FOE Sulfonic acid using SFO for Flufenacet.

Compound	Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
			Value	Error	Confidence intervals		Prob. > t	χ^2 % error	Visual assessment ¹⁾
					Lower	Upper			
Flufenacet	SFO	M_0	64.78	2.13	60.61	68.96	1.71 E-11	3.65	Acceptable fit
		k	3.083 E-3	4.561 E-4	2.189 E-3	0.004	4.12 E-9		
FOE Oxalate	SFO	M_0	11.95	1.04	9.91	13.99	2.22 E-7	7.94	Poor fit
		k	1.42 E-2	2.174 E-3	9.937 E-3	0.018	3.31 E-5		
		ff	1.00	7.689 E-6	----	----	----		
FOE Sulfonic acid	SFO	M_0	6.10	0.35	5.41	6.79	4.12 E-9	6.65	Acceptable fit
		k	1.968 E-3	7.325 E-4	5.324 E-4	0.003	0.0114		
		ff	1.07 E-6	n. c. ²⁾	----	----	----		

Footnotes to the table:

- 1) Visual assessment of the kinetic curve as proposed by the Applicant;
- 2) Value not reported, not calculated by the modelling tool.

Evaluation:

The combination SFO-SFO did not return fully reliable kinetic endpoints for parent compound and its degradation products. The addition of the data for FOE Oxalate and FOE Sulfonic acid did not significantly influence the results of the fitting for the parent compound. The results of the fitting for both degradation products showed that neither for FOE Oxalate nor FOE Sulfonic acid the acceptable kinetic fit can be found. The Applicant indicated that the fit for FOE Oxalate was poor, but the fit for FOE Sulfonic acid was considered acceptable. RMS however is of the opinion that both fits are poor and as such cannot be used to derive the reliable kinetic endpoints. The distribution of the experimental points suggests that, at least for FOE Sulfonic acid the sound fit may be found, probably using the kinetic model other than SFO, when the fitting is performed applying the top-down approach. Similar solution may be applicable to FOE Oxalate.

RMS also decided not to present the kinetic endpoints resulting from that fitting.

Option 2: DFOP (Parent) – SFO (Metabolites) fitting:

The results of the fitting are presented below in graphical form on the figure B.8.1.1.2.1.2._CA-5 and in numerical form in the table B.8.1.1.2.1.2._CA-10.

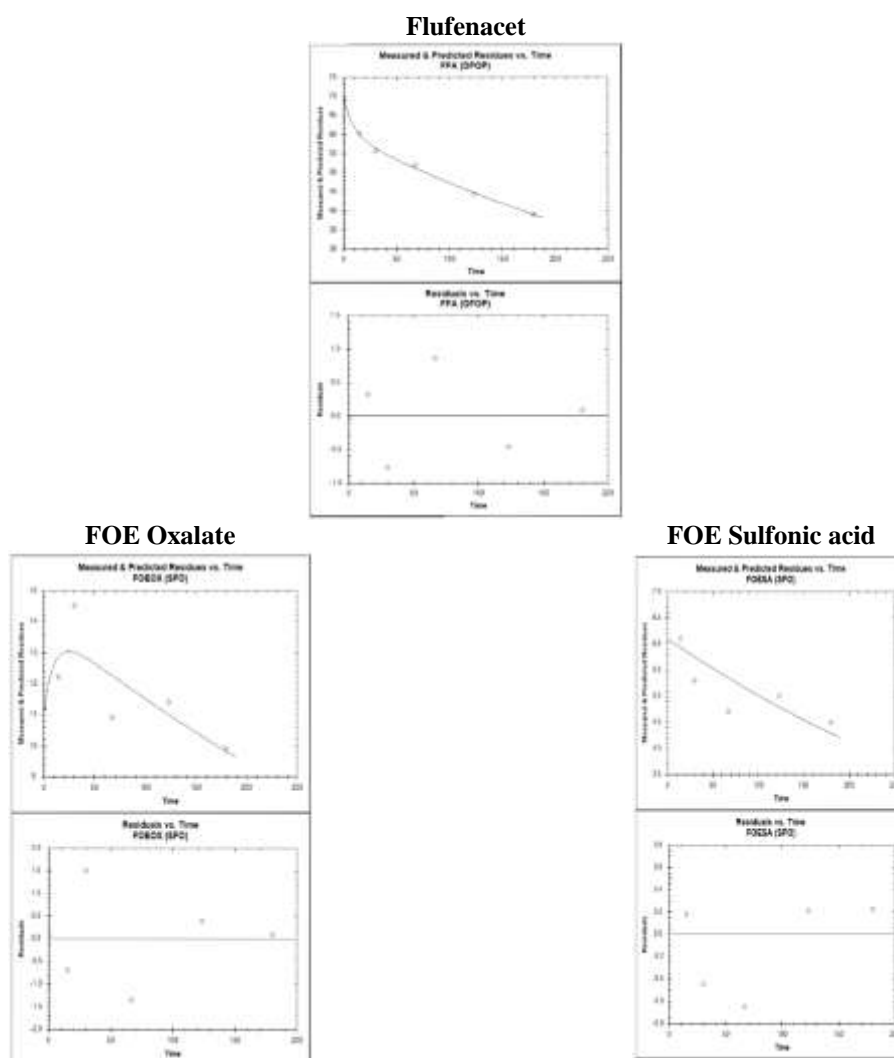


Figure B.8.1.1.2.1.2._CA-5: The graphical results of the kinetic fitting of the data for Flufenacet, FOE Oxalate and FOE Sulfonic acid using DFOP for Flufenacet (copied from the study report).

Table B.8.1.1.2.1.2_CA-10: The numerical results of the kinetic fitting of the data for Flufenacet, FOE Oxalate and FOE Acetic acid using SFO for Flufenacet.

Compound	Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
			Value	Error	Confidence intervals		Prob. > t	χ^2 % error	Visual assessment ¹⁾
					Lower	Upper			
Flufenacet	DFOP	M ₀	69.03	0.794	67.48	70.59	1.71 E-13	0.981	Good fit
		k ₁	9.958 E-2	3.577 E-2	2.985 E-2	0.169	0.0116		
		k ₂	2.417 E-3	1.803 E-4	2.063 E-3	0.003	4.60 E-7		
		g	0.1291	2.069 E-2	8.855 E-2	0.170	1.24 E-4		
FOE Oxalate	SFO	M ₀	11.13	1.39	8.41	13.85	2.16 E-5	6.66	Acceptable fit
		k	4.854 E-3	3.142 E-3	-1.30 E-3	0.011	0.0805		
		ff	0.293	0.236	----	----	----		
FOE Sulfonic acid	SFO	M ₀	6.10	0.64	4.84	7.36	6.13 E-6	6.65	Acceptable fit
		k	1.967 E-3	3.499 E-3	-4.89 E-3	0.009	0.2947		
		ff	5.03 E-8	0.161	----	----	----		

Footnotes to the table:

1) Visual assessment of the kinetic curve as proposed by the Applicant;

Evaluation:

The DFOP model returned superior fit for Flufenacet in comparison to that obtained with SFO also when the data for the degradation products were added. That conforms the conclusion drawn by the RMS during the evaluation of the fitting results for parent alone. For the degradation products the results of the kinetic fitting cannot be considered reliable. Although some improvement was observed, especially for FOE Oxalate, the fits cannot be considered acceptable – in RMS's opinion the results of their visual assessment show that they poorly represent the distribution of the data points.

However, as it has been already stated when the SFO-SFO fitting option was evaluated, the distribution of the experimental points suggests that, at least for FOE Sulfonic acid the sound fit may be found, probably using the kinetic model other than SFO, when the fitting is performed applying the top-down approach. Similar solution may be applicable to FOE Oxalate.

RMS also decided not to present the kinetic endpoints resulting from that fitting. That is due to the fact that for parent compound these do not significantly differ from the results obtained for the parent fitted alone using DFOP kinetic model, whereas the kinetic endpoints for both degradation products cannot be considered fully reliable.

Additionally RMS performed the additional kinetic analysis of the data obtained for FOE Oxalate and FOE Sulfonic acid using the top-down approach. This was done using CAKE ver. 3.1 modelling tool, developed by Tessella Inc., separately for each degradation product. To maintain the consistency with the kinetic analysis performed by the Applicant, the kinetic fitting was performed using IRLS (Iteratively Reweighted Nonlinear Least Squares) algorithm as optimisation method. The input data used in the repeated kinetic examination are presented below, in the table B.8.1.1.2.1.2_CA-11.

Table B.8.1.1.2.1.2_CA-11: The input data used in the repeated kinetic examination performed for FOE Oxalate and FOE Sulfonic acid using the top-down approach.

Data for FOE Oxalate:		Data for FOE Sulfonic acid:	
Time point	Concentration of the compound	Time point	Concentration of the compound
DASF [days]	[% AR]	DASF [days]	[% AR]
30	14.5	0	6.6
67	10.9	15	6.1
123	11.4	30	5.3
180	9.9	67	4.7
		123	5.0
		180	4.5

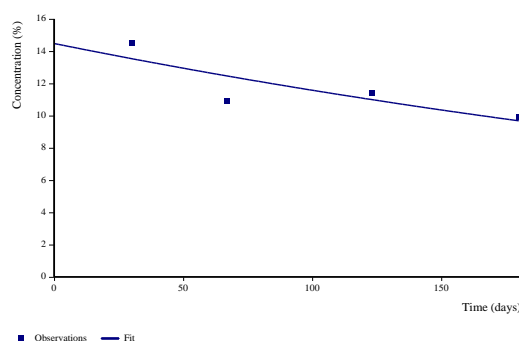
The preliminary analysis of the data showed that for FOE Oxalate, due to the limited number of data points (only four), it was possible to perform the kinetic analysis using solely SFO kinetic model. In case of FOE Sulfonic acid the number of data points was sufficient to perform the kinetic analysis using all four kinetic models. The results of the kinetic fitting are presented below.

The results of the kinetic fitting of the data for FOE Oxalate:

The results of the fitting are presented below in graphical form on the figure B.8.1.1.2.1.2._CA-6 and in numerical form in the table B.8.1.1.2.1.2._CA-12.

FOE Oxalate – SFO model

Observations and Fitted Model:



Residuals:

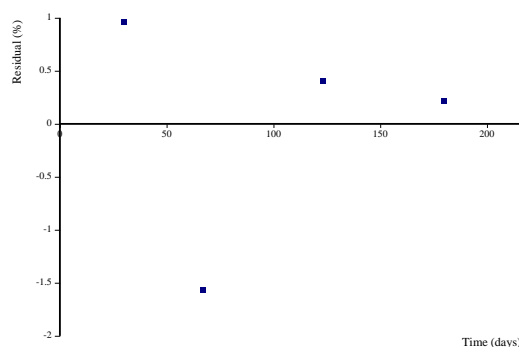


Figure B.8.1.1.2.1.2._CA-6: The graphical results of the kinetic fitting of the data for FOE Oxalate using SFO kinetic model.

Table B.8.1.1.2.1.2._CA-12: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment
				Lower	Upper			
SFO	M_0	14.48	1.55	7.82	21.13	n. c. ¹⁾	6.62	0.697 Intermediate fit
	k	0.002233	0.001049	-0.002282	0.007	0.08359		

Footnotes to the table:

1) Value not calculated by the modelling tool.

The kinetic endpoints calculated by the model are following: $DT_{50} = 310$ days, $DT_{90} = 1030$ days.

Evaluation:

The results of the kinetic re-evaluation of the data for FOE Oxalate using the top-down approach showed that no significant improvement of the kinetic fit, in comparison to the results obtained by the Applicant, was achieved. The fit, although statistically acceptable, is only intermediate according to the results of its visual assessment. It was also noticed that the calculated degradation rate constant is not fully reliable – the *Prob. > t* is higher than the recommended highest value 0.05, but lower than 0.1. Therefore the calculated kinetic endpoints – DT_{50} and DT_{90} values may be considered only as indicative with regard to the persistence of FOE Oxalate in anaerobic soil.

The results of the kinetic fitting of the data for FOE Sulfonic acid:

The obtained results are presented below in the numerical form in table B.8.1.1.2.1.2._CA-13 and in the graphical form on figure B.8.1.1.2.1.2_CA-7. For convenience the results for all kinetic models tested are presented together.

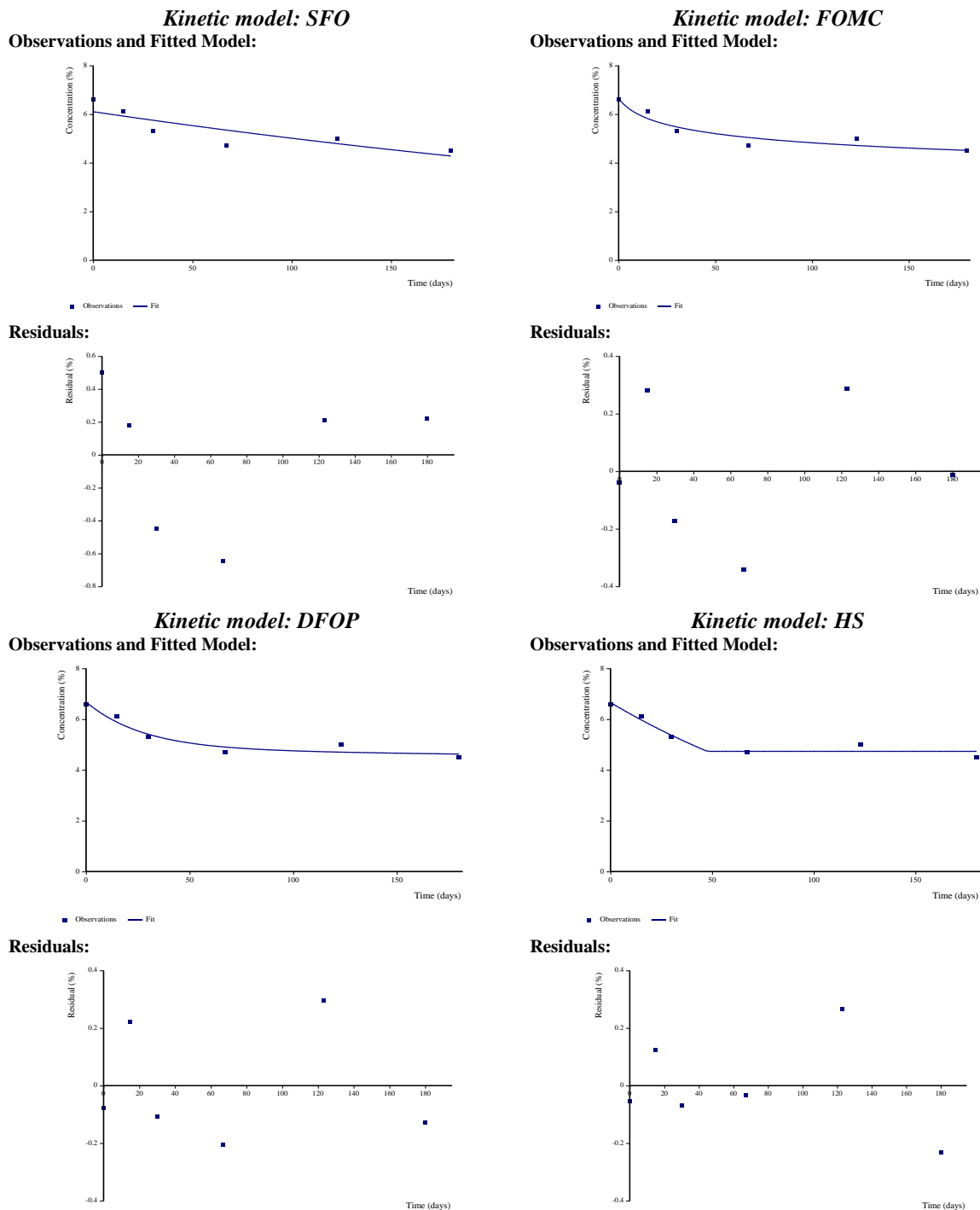


Figure B.8.1.1.2.1.2_CA-7: The graphical results of the kinetic analysis.

Table B.8.1.1.2.1.2._CA-13: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment
				Lower	Upper			
SFO	M_0	6.10	0.32	5.22	6.98	n. c. ¹⁾	6.03	0.707 Intermediate fit
	k	1.986 E-3	6.52 E-4	1.59 E-4	0.004	0.0196		
FOMC	M_0	6.64	0.31	5.66	7.62	n. c. ¹⁾	3.71	0.909 Good fit
	α	0.1202	0.05077	-0.0414	0.282	n. c. ¹⁾		
	β	7.545	9.307	-22.08	37.17	n. c. ¹⁾		
DFOP	M_0	6.68	0.32	5.30	8.05	n. c. ¹⁾	3.51	0.937 Good fit
	k_1	0.0361	0.03403	-0.1103	0.183	0.2		
	k_2	2.14 E-4	1.508 E-3	-6.277 E-3	0.007	0.4502		
	g	0.2802	0.1655	-0.4317	0.992	n. c. ¹⁾		
HS	M_0	6.66	0.25	5.56	7.75	n. c. ¹⁾	2.94	0.956 Good fit
	k_1	7.162 E-3	2.164 E-3	-3.11 E-3	0.003	0.04022		
	k_2	1.01 E-50	7.23 E-4	-3.11 E-3	0.003	0.500		
	t_b	47.58	14.27	-13.8	109.0	n. c. ¹⁾		

Footnotes to the table:

1) Value not calculated by the modelling tool.

Evaluation:

The results of the kinetic re-evaluation of the data show that the reliable fit was obtained only with SFO kinetic model. That fit, although only intermediate, as demonstrated the results of its visual inspection, was both visually and statistically acceptable. Also the calculated kinetic parameter – the rate constant k was reliable, as demonstrated the results of the t-test.

All tested bi-phasic models – FOMC, DFOP and HS, returned fits superior to that obtained with SFO, both visually and statistically, but none of them returned fully reliable kinetic parameters.

As a result, SFO model should be considered as returning the best fit and hence the determined with it kinetic endpoints – **DT₅₀ = 352 days** and **DT₉₀ = 1170 days** as representative for the determining of the persistence of that compound in anaerobic soil. However, as it has been stated for FOE Oxalate, because of the deficiencies displayed by the fit, the results should be considered as indicative.

Conclusions:

The kinetic analysis of the data for Flufenacet and its major degradation products – FOE Oxalate and FOE Sulfonic acid, obtained for Sandy loam (Howe) soil incubated under anaerobic conditions demonstrated that:

- The degradation of Flufenacet in that soil was most adequately described by DFOP kinetic model. Therefore that model should be considered as providing the kinetic endpoints describing the persistence of Flufenacet in anaerobic sandy loam soil;
- DFOP kinetic model – its slow phase, should be also considered as providing the kinetic endpoints appropriate for modelling. That conclusion is drawn by the RMS and is different from the Applicant's proposal – to consider the SFO kinetic model as a source of the kinetic endpoints appropriate for modelling. That conclusion is based on the fact that DFOP fit was superior to SFO both when the fitting was performed for the parent compound alone and for the parent and degradation products.
- It was not possible to obtain the reliable kinetic fit for either of the degradation products – FOE Oxalate and FOE Sulfonic acid kinetically examined together with parent. Slightly better results were obtained when the data for these two compounds were fitted alone using the top-down approach. In both cases SFO was identified as returning visually and statistically reliable fits with reliable parameters. RMS however is of the opinion that the kinetic endpoints derived from those fits should be considered indicative with regard to the persistence of both compounds in anaerobic sandy loam soil and cannot be further used to derive any modelling endpoints. It shall be also noted that it was not possible to derive reliable kinetic formation fractions for either FOE Oxalate or FOE Sulfonic acid.

The proposed set of the kinetic endpoints derived from that study is following:

- Flufenacet, persistence endpoints: DT₅₀ = 229.63 days, DT₉₀ = 895.64 days, DFOP model ($k_1 = 0.9976 \text{ days}^{-1}$, $k_2 = 2.416 \text{ E-3 days}^{-1}$, $g = 0.1291$);
- Flufenacet, modelling endpoints not normalised: $k = 2.416 \text{ E-3 [days}^{-1}]$, DT₅₀ = 286.90 days, DT₉₀ = 953.06 days, SFO (slow phase DFOP);
- Flufenacet, modelling endpoints normalized for temperature: $k = 2.205 \text{ E-3 [days}^{-1}]$, DT₅₀ = 314.35 days, DT₉₀ = 1044.26 days, SFO (slow phase DFOP);

-
- FOE Oxalate, persistence endpoints (indicative): $DT_{50} = 310$ days, $DT_{90} = 1030$ days, SFO model – top-down approach ($k = 0.002233 \text{ days}^{-1}$);
 - FOE Sulfonic acid, persistence endpoints (indicative): $DT_{50} = 352$ days, $DT_{90} = 1170$ days, SFO model – top-down approach ($k_I = 0.001986 \text{ days}^{-1}$).

- 2) Results of the kinetic examination of the data obtained in soil **Hoefchen am Hohenseh 4a (Germany)** for [Thiadiazole-5-¹⁴C] Flufenacet (study by [Heinemann; 2012]):

The results of the kinetic examination of the data are presented below. First are presented the results of the kinetic examination of the data for parent only. The results of the kinetic examination of the data for the parent compound and degradation products are presented further down.

- a) Results of the fitting of the data for parent compound only:

The obtained results are presented below in the numerical form in table B.8.1.1.2.1.2_CA-14 and in the graphical form on figure B.8.1.1.2.1.2_CA-8. For convenience the results for all kinetic models tested are presented together.

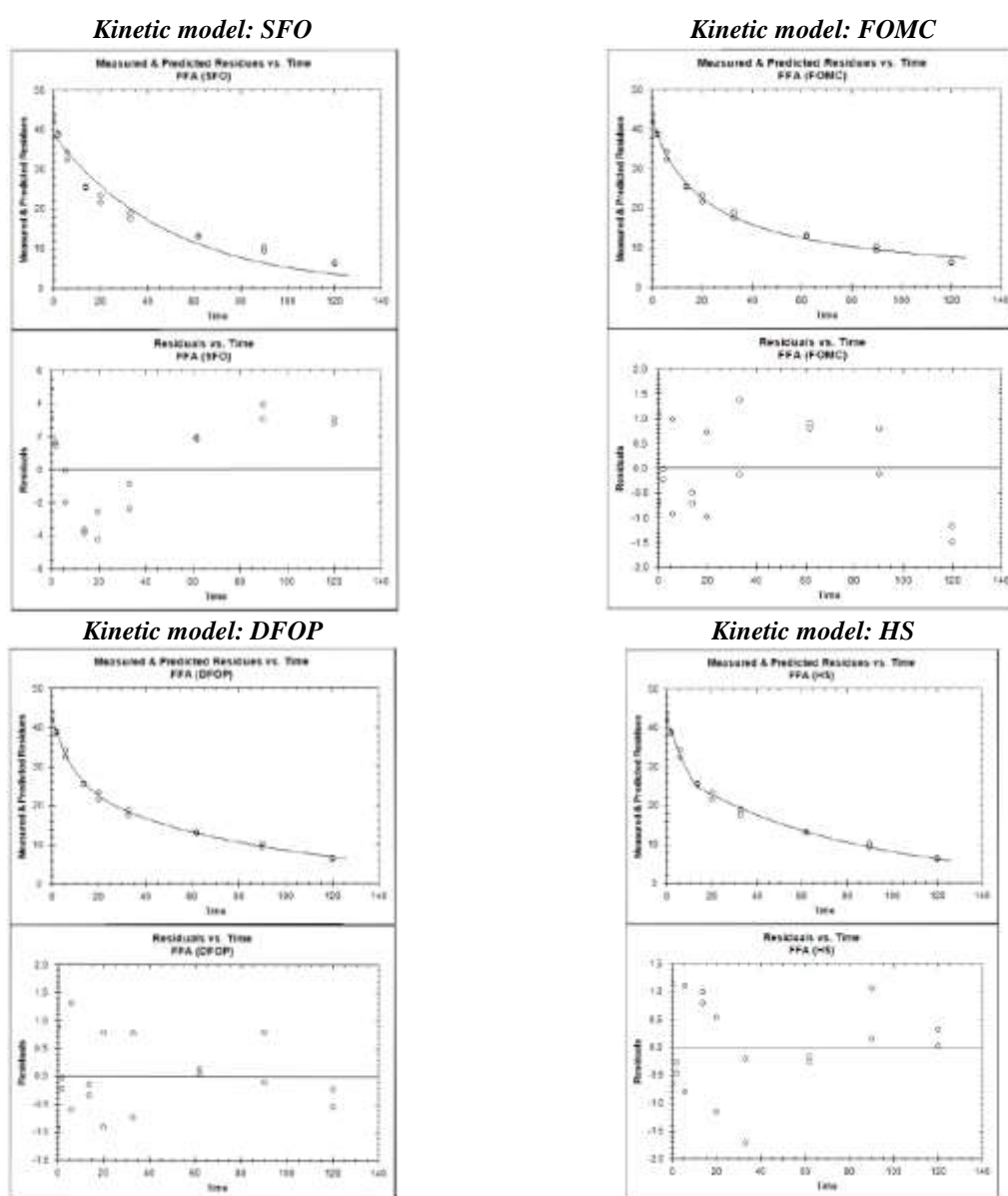


Figure B.8.1.1.2.1.2_CA-8: The graphical results of the kinetic analysis (copied from the study report).

Table B.8.1.1.2.1.2._CA-14: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment ¹⁾
				Lower	Upper			
SFO	M ₀	38.80	14.59	10.22	67.39	0.00855	9.69	0.95 Poor fit
	k	0.02025	0.0150	-0.0092	0.005	0.09846		
FOMC	M ₀	42.60	0.55	41.52	43.68	< 2.0 E-16	2.23	0.96 Acceptable fit
	α	0.8289	0.0786	0.6748	0.983	1.24 E-8		
	β	17.3844	2.9804	11.5429	23.226	1.65 E-5		
DFOP	M ₀	42.82	0.44	41.95	43.68	< 2.0 E-16	0.98	0.97 Good fit
	k ₁	0.1072	1.466 E-2	7.843 E-3	0.136	1.92 E-6		
	k ₂	1.113 E-2	8.409 E-4	9.478 E-3	0.013	1.32 E-9		
	g	0.4021	3.276 E-2	0.3397	0.466	3.50 E-9		
HS	M ₀	42.57	0.54	41.50	43.63	< 2.0 E-16	2.03	0.96 Acceptable fit
	k ₁	4.141 E-2	4.201 E-3	3.318 E-2	0.050	5.57 E-8		
	k ₂	1.303 E-2	6.325 E-4	1.179 E-2	0.014	3.60 E-12		
	t _b	12.87	1.707	9.527	16.220	1.36 E-6		

Footnotes to the table:

1) Visual assessment of the kinetic curve as proposed by the Applicant.

Also the kinetic endpoints – DT₅₀ and DT₉₀ values for each of the kinetic models were calculated. These are presented below in the table B.8.1.1.2.1.2._CA-15.

Table B.8.1.1.2.1.2._CA-15: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested			
		SFO	FOMC	DFOP	HS
Flufenacet	DT ₅₀ [days]	34.23	22.73	22.67	25.15
	DT ₉₀ [days]	113.69	262.22	160.72	148.67

Evaluation:

On the basis of the obtained results the Applicant stated that the SFO model returned statistically acceptable and reliable with regard to kinetic parameters, but visually poor fit. All tested bi-phasic models returned fits superior to SFO, both visually and statistically. In addition the kinetic parameters determined using those models were fully reliable.

Further analysis of the bi-phasic models showed that DFOP returned the best fit. Therefore the Applicant proposed to use that model for parent in kinetic examination the data set for Flufenacet and its degradation products. RMS accepted that proposal, noticing at the same time that the decline curve obtained with SFO model was rather well fitted to the experimental data, and the only problem were high and not randomly distributed residuals, the probable reason for qualifying the fit as poor by the Applicant.

b) Results of the fitting of the data for parent compound and degradation products:

As a next step proposed by the Applicant the data for the parent compound were kinetically examined together with those for the degradation products using the best-fit kinetic model identified for the parent compound.

The results of the fitting are presented below in graphical form on the figure B.8.1.1.2.1.2._CA-9 and in numerical form in the table B.8.1.1.2.1.2._CA-16.

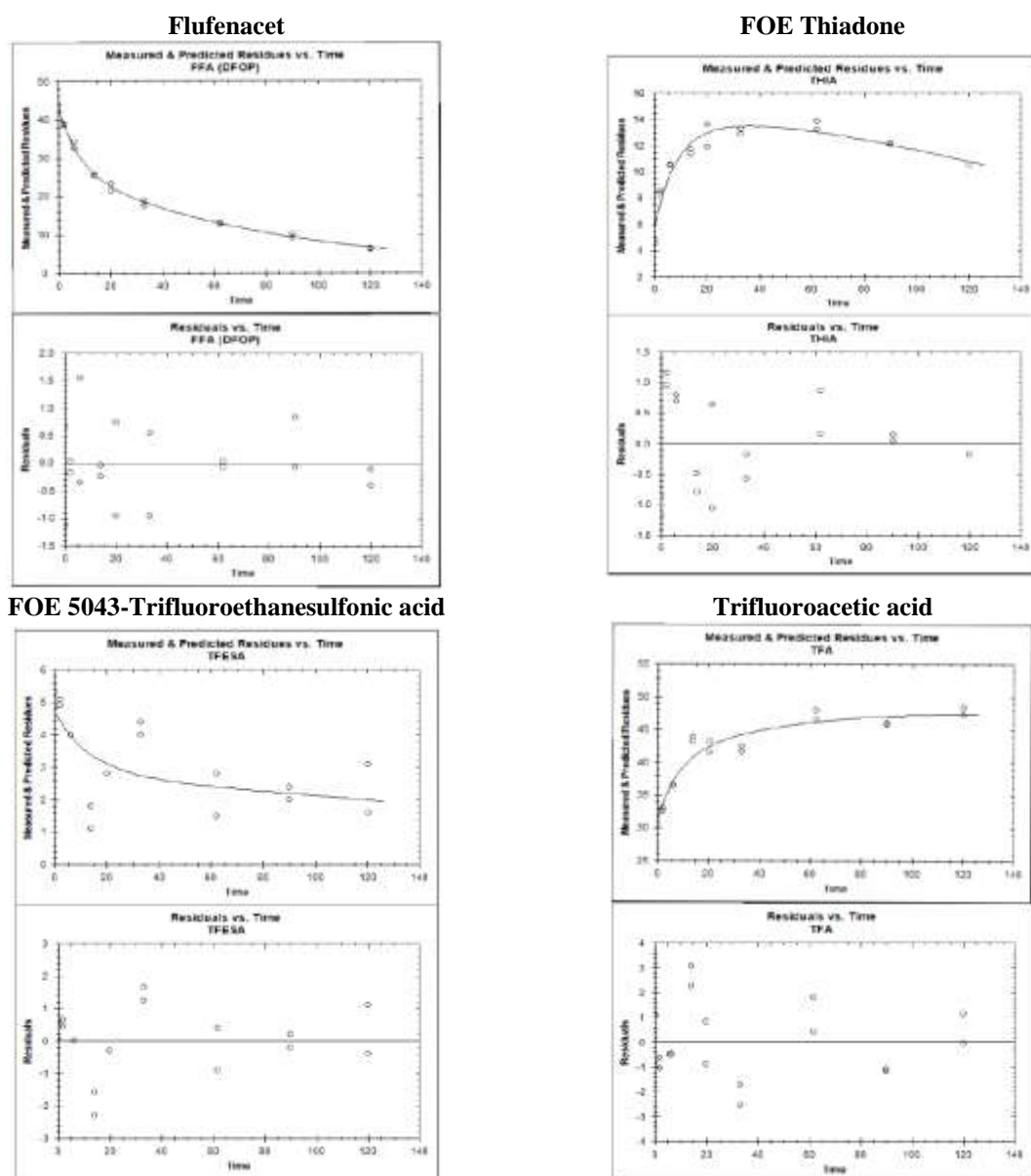


Figure B.8.1.1.2.1.2._CA-9: The graphical results of the kinetic fitting of the data for Flufenacet, FOE Thiadone, FOE 5043-Trifluoroethanesulfonic acid and Trifluoroacetic acid (copied from the study report).

Table B.8.1.1.2.1.2_CA-16: The numerical results of the kinetic fitting of the data for Flufenacet, FOE Thiadone, FOE 5043-Trifluoroethanesulfonic acid and Trifluoroacetic acid.

Compound	Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
			Value	Error	Confidence intervals		Prob. > t	χ^2 % error	Visual assessment ¹⁾
					Lower	Upper			
Flufenacet	DFOP	M ₀	43.023	0.426	42.189	43.859	< 2 E-16	1.08	Good fit
		k ₁	0.1214	0.0158	0.0905	0.152	7.98 E-11		
		k ₂	0.0116	0.00075	0.0101	0.013	< 2 E-16		
		g	0.3810	0.0275	0.3271	0.435	< 2 E-16		
FOE Thiadone	SFO	M ₀	5.776	0.403	4.987	6.565	< 2 E-16	4.95	Good fit
		k	0.0071	0.00079	0.0056	0.0090	4.21 E-13		
		ff ³⁾	0.425	0.0310	n. c. ²⁾	n. c. ²⁾	n. c. ²⁾		
FOE 5043-Trifluoroethane-sulfonic acid	SFO	M ₀	4.733	0.624	3.510	5.955	1.24 E-10	22.24	Poor fit
		k	0.0423	0.0304	-0.0173	0.102	0.0846		
		ff ⁴⁾	1.000	n. c. ²⁾	n. c. ²⁾	n. c. ²⁾	n. c. ²⁾		
Trifluoroacetic acid	SFO	M ₀	31.296	0.632	30.057	32.536	< 2 E-16	2.54	Good fit
		k	0.00091	0.0017	-0.00246	0.0040	0.2997		
		ff ^{1 5)}	0.575	0.851	n. c. ²⁾	n. c. ²⁾	n. c. ²⁾		
		ff ^{2 6)}	1.02 E-6	n. c. ²⁾	n. c. ²⁾	n. c. ²⁾	n. c. ²⁾		

Footnotes to the table:

- 1) Visual assessment of the kinetic curve as proposed by the Applicant;
- 2) Not calculated by the modelling tool;
- 3) Formed from Flufenacet;
- 4) Formed from FOE Thiadone;
- 5) Formed from Flufenacet;
- 6) Formed from FOE Thiadone.

Evaluation:

The fitting of the data for the parent compound together with those for the degradation products using the combination DFOP (parent) – SFO (metabolites) resulted in some statistical worsening of the fit for Flufenacet in comparison to the situation when this compound was fitted alone using DFOP model. It shall be pointed out however that this worsening was minimal. Applicant stated that visually and statistically good fits were obtained for FOE Thiadone and Trifluoroacetic acid, while that for FOE 5043-Trifluoroethanesulfonic acid was poor both visually and statistically.

RMS noted that there were the discrepancies in the results of the fitting reported in the main text of the study report and those presented in appendices, generated by the modelling tool. Therefore the whole assessment is based on the results presented in the source KinGUI report.

In RMS's opinion the results of the fitting show that it was possible to obtain the robust fit for Flufenacet and FOE Thiadone. For both compounds the determined kinetic parameters are reliable.

In case of Trifluoroacetic acid the obtained fit is visually and statistically acceptable, but the determined rate constant *k* is not reliable, according to the results of the t-test. That may be due to the fact that the decline phase was not achieved and it is even doubtful, from the distribution of the experimental points, that the maximum concentration was reached. As a result the kinetic endpoints – DT₅₀ and DT₉₀ values calculated by the modelling tool, bear a significant level of uncertainty. Therefore the RMS would like to propose to use, instead of the values calculated by the modelling tool, the default values – DT₅₀ = 1000 days and DT₉₀ > 1000 days.

In case of the third degradation product, for which the kinetic assessment was performed – FOE-5043 Trifluoroethanesulfonic acid, it was not possible to obtain acceptable kinetic fit and hence reliable kinetic parameters. That may be due to the fact that the concentrations of that compound recorded in the test system (soil and overlying it water) during anaerobic incubation phase were very low and scattered. That in turn may indicate that in anaerobic soil FOE-5043 Trifluoroethanesulfonic acid is a transient, rapidly degrading compound.

Conclusions:

The kinetic analysis of the data for Flufenacet and its major degradation products – FOE Thiadone, FOE-5043 Trifluoroethanesulfonic acid and Trifluoroacetic acid, obtained for Silt loam (Hoefchen am Hohenseh 4 a) soil incubated under anaerobic conditions demonstrated that:

- The degradation of Flufenacet in that soil was most adequately described by DFOP kinetic model. Therefore that model should be considered as providing the kinetic endpoints describing the persistence of Flufenacet in anaerobic Silt loam soil;

- DFOP kinetic model – its slow phase, should be also considered as providing the kinetic endpoints appropriate for modelling.
- It was possible to obtain reliable kinetic fit and kinetic endpoints for FOE Thiadone;
- Although it was possible to obtain reliable kinetic fit for Trifluoroacetic acid, the reliable kinetic parameters describing degradation of that compound could not be derived due to the fact that the decline phase was not reached. Therefore RMS proposed to use the default DT_{50} and DT_{90} values instead of those calculated by the model;
- It was not possible to obtain the reliable kinetic fit for FOE 5043-Trifluoroethanesulfonic acid, therefore for that compound no reliable kinetic endpoints are available. RMS attributed that to the low concentrations of the compound recorded in the test system and their significant scattering, what may indicate that the compound of concern is transient and rapidly degrades in anaerobic silt loam soil.

The proposed set of the kinetic endpoints derived from that study is following:

- Flufenacet, persistence endpoints: $DT_{50} = 22.66$ days, $DT_{90} = 156.90$ days, DFOP model ($k_1 = 0.1214$ days⁻¹, $k_2 = 0.01162$ days⁻¹, $g = 0.3810$);
- Flufenacet, modelling endpoints: $k = 0.01162$ [days⁻¹], $DT_{50} = 59.65$ days, $DT_{90} = 198.16$ days, SFO (slow phase DFOP), normalisation was not required as the experiment was carried out at $T = 20^{\circ}\text{C}$ and the correction for soil moisture was not necessary (soil was permanently flooded);
- FOE Thiadone, persistence and modelling endpoints: $DT_{50} = 97.04$ days, $DT_{90} = 322.30$ days, $ff = 0.425$ (from parent compound), SFO model ($k = 0.0071$ days⁻¹);
- Trifluoroacetic acid persistence endpoints (indicative): $DT_{50} = 1000$ days, $DT_{90} > 1000$ days, $ff = 0.575$ (from parent compound), SFO model;
- FOE 5043-Trifluoroethanesulfonic acid: it was not possible to derive reliable kinetic endpoints.

- 3) Results of the kinetic examination of the data obtained in soil **Dollendorf II (Germany)** for [Thiadiazole-5-¹⁴C] Flufenacet (study by [Heinemann; 2012]):

The results of the kinetic examination of the data are presented below. First are presented the results of the kinetic examination of the data for parent only. The results of the kinetic examination of the data for the parent compound and degradation products are presented further down.

- Results of the fitting of the data for parent compound only:

The obtained results are presented below in the numerical form in table B.8.1.1.2.1.2_CA-17 and in the graphical form on figure B.8.1.1.2.1.2_CA-10. For convenience the results for all kinetic models tested are presented together.

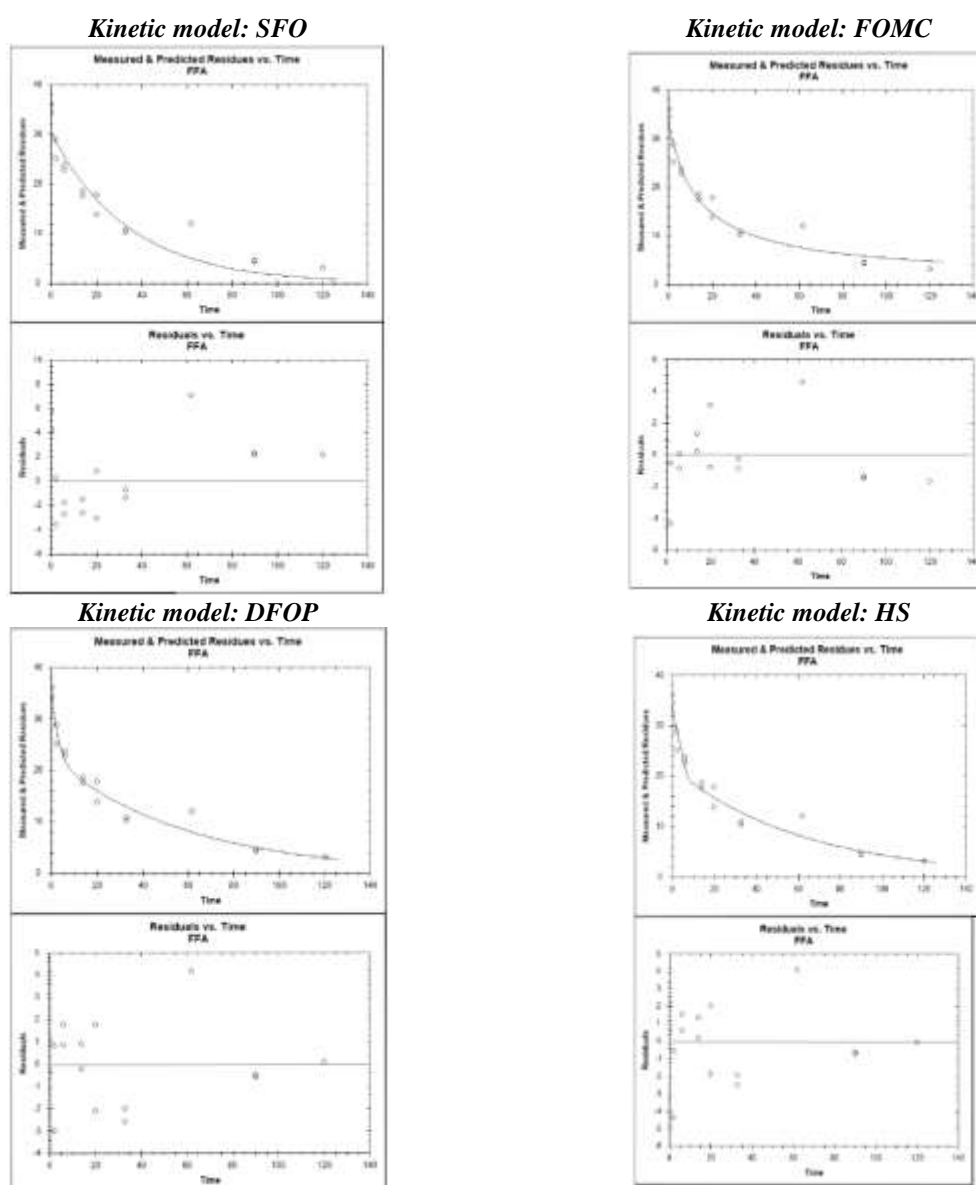


Figure B.8.1.1.2.1.2_CA-10: The graphical results of the kinetic analysis (copied from the study report).

Table B.8.1.1.2.1.2._CA-17: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment ¹⁾
				Lower	Upper			
SFO	M ₀	30.354	1.674	27.038	33.636	6.49 E-12	15.96	0.94 Poor fit
	k	0.02909	0.00491	0.01947	0.039	1.39 E-5		
FOMC	M ₀	33.759	1.525	30.770	36.748	1.35 E-12	10.25	0.96 Acceptable fit
	α	0.7654	0.2191	0.3360	1.1950	0.00179		
	β	10.1226	5.7663	-1.1791	21.4240	0.05051		
DFOP	M ₀	34.975	1.398	32.234	37.716	1.11 E-12	9.22	0.97 Good fit
	k ₁	0.3340	0.1868	-0.0321	0.700	0.0486		
	k ₂	0.0167	0.0029	0.0110	0.0220	3.43 E-5		
	g	0.3610	0.0664	0.2309	0.4910	5.68 E-5		
HS	M ₀	33.936	1.374	31.243	36.628	1.30 E-12	10.16	0.96 Acceptable fit
	k ₁	0.07097	0.0144	0.04269	0.0990	0.000140		
	k ₂	0.01613	0.0029	0.01043	0.00220	4.76 E-5		
	t _b	8.098	2.215	3.757	12.439	0.00145		

Footnotes to the table:

1) Visual assessment of the kinetic curve as proposed by the Applicant.

Also the kinetic endpoints – DT₅₀ and DT₉₀ values for each of the kinetic models were calculated. These are presented below in the table B.8.1.1.2.1.2._CA-18.

Table B.8.1.1.2.1.2._CA-18: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested			
		SFO	FOMC	DFOP	HS
Flufenacet	DT ₅₀ [days]	23.83	14.91	14.98	15.44
	DT ₉₀ [days]	79.16	194.86	111.05	115.22

Evaluation:

On the basis of the obtained results the Applicant stated that the SFO model did not return the fit statistically and visually acceptable. All tested bi-phasic models returned fits superior to SFO, both visually and statistically. However FOMC fit returned kinetic parameters that were not reliable – the CI for β passed through zero. DFOP and HS returned fits visually and statistically acceptable with reliable kinetic parameters. It was stated that DFOP was better than HS - χ^2 error was lower as well as residuals. It was determined that the distribution of residuals was very alike for both kinetic models. As a result Applicant indicated DFOP as returning the best fit for the parent and that model was used for kinetic fitting the of the data for parent when they were kinetically examined with those for the degradation products.

RMS accepted that proposal, on the basis of the overall weight of evidence, although it was noticed that the reliability of k₁ in DFOP model was rising some concerns.

- Results of the fitting of the data for parent compound and degradation products:

As a next step proposed by the Applicant the data for the parent compound were kinetically examined together with those for the degradation products using the best-fit kinetic model identified for the parent compound.

The results of the fitting are presented below in graphical form on the figure B.8.1.1.2.1.2._CA-11 and in numerical form in the table B.8.1.1.2.1.2._CA-19.

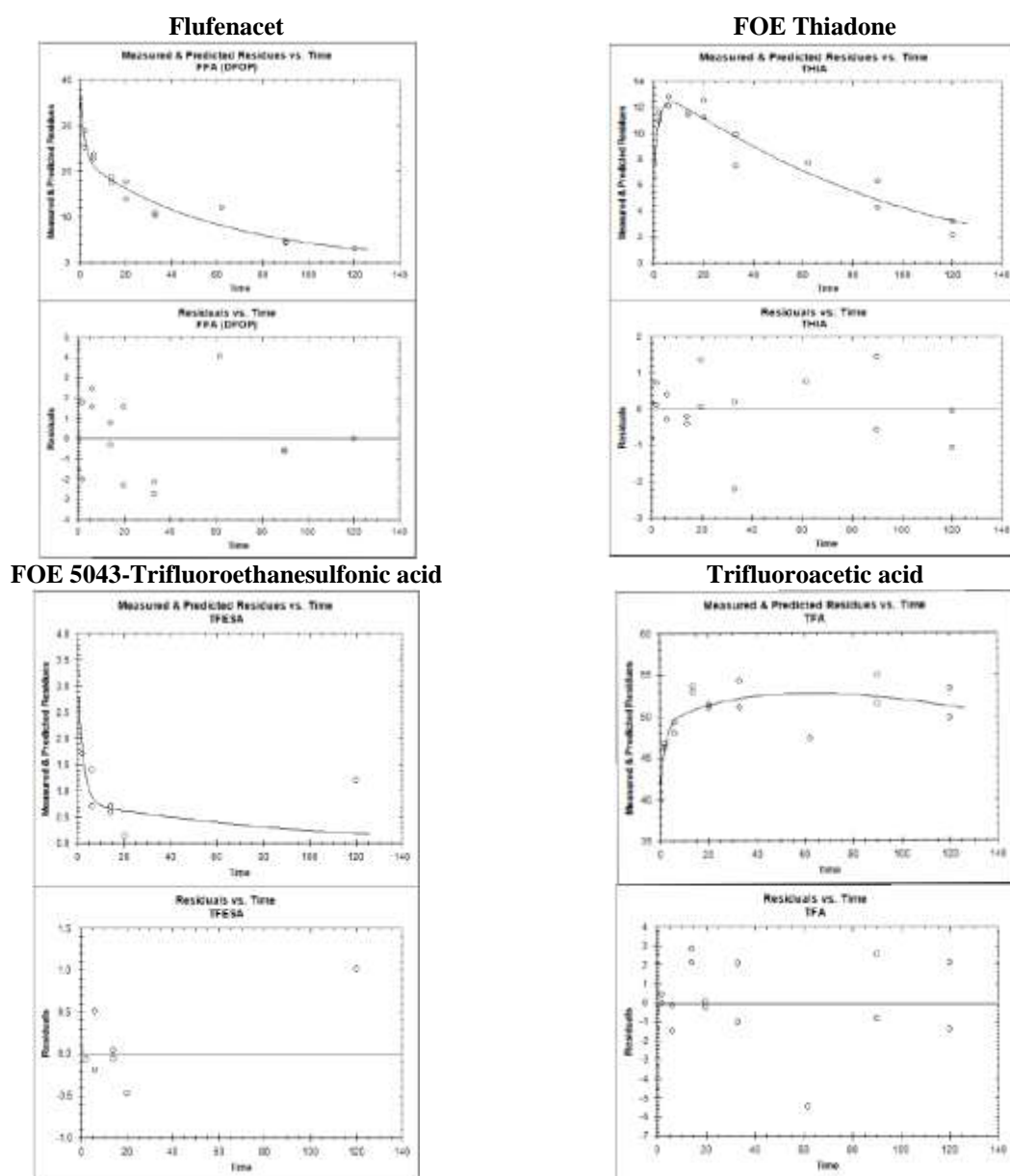


Figure B.8.1.1.2.1.2. CA-11: The graphical results of the kinetic fitting of the data for Flufenacet, FOE Thiadone, FOE-5043 Trifluoroethanesulfonic acid and Trifluoroacetic acid (copied from the study report).

Table B.8.1.1.2.1.2_CA-19: The numerical results of the kinetic fitting of the data for Flufenacet, FOE Thiadone, FOE-5043 Trifluoroethanesulfonic acid and Trifluoroacetic acid.

Compound	Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
			Value	Error	Confidence intervals		Prob. > t	χ^2 % error	Visual assessment ¹⁾
					Lower	Upper			
Flufenacet	DFOP	M ₀	36.138	1.188	33.810	38.466	< 2 E-16	9.49	Good fit
		k ₁	0.4756	0.1549	0.1720	0.7790	0.00171		
		k ₂	0.0167	0.00244	0.01188	0.0210	5.14 E-9		
		g	0.3745	0.0440	0.2883	0.4610	1.17E-11		
FOE Thiadone	SFO	M ₀	7.414	0.646	6.147	8.681	4.87 E-16	5.58	Good fit
		k	0.02045	0.00237	0.0158	0.0250	7.75 E-12		
		ff ²⁾	0.425	0.0609	n. c. ²⁾	n. c. ²⁾	n. c. ²⁾		
		ff ³⁾	0.425	0.0609	n. c. ²⁾	n. c. ²⁾	n. c. ²⁾		
FOE 5043-Trifluoroethane-sulfonic acid	SFO	M ₀	3.187	0.369	2.464	3.911	7.46 E-12	30.59	Acceptable fit
		k	0.3817	0.1274	0.1320	0.6310	0.00211		
		ff ⁴⁾	1.000	n. c. ²⁾	n. c. ²⁾	n. c. ²⁾	n. c. ²⁾		
		ff ⁵⁾	1.000	n. c. ²⁾	n. c. ²⁾	n. c. ²⁾	n. c. ²⁾		
Trifluoroacetic acid	SFO	M ₀	41.289	1.283	38.971	43.607	< 2 E-16	3.35	Acceptable fit
		k	0.00147	0.00142	-0.00131	0.0040	0.1521		
		ff ^{1 5)}	0.575	0.499	n. c. ²⁾	n. c. ²⁾	n. c. ²⁾		
		ff ^{2 6)}	2.16 E-6	n. c. ²⁾	n. c. ²⁾	n. c. ²⁾	n. c. ²⁾		

Footnotes to the table:

- 1) Visual assessment of the kinetic curve as proposed by the Applicant;
- 2) Not calculated by the modelling tool;
- 3) Formed from Flufenacet;
- 4) Formed from FOE Thiadone;
- 5) Formed from Flufenacet;
- 6) Formed from FOE Thiadone.

Evaluation:

The fitting of the data for the parent compound together with those for the degradation products using the combination DFOP (parent) – SFO (metabolites) resulted in some improvement of the fit for Flufenacet, especially in the area of the reliability of kinetic parameters derived (namely k_1). shall be pointed out however that this worsening was minimal. Applicant stated that visually and statistically good fits was obtained for FOE Thiadone. That for Trifluoroacetic acid was visually and statistically acceptable, while that for FOE 5043-Trifluoroethanesulfonic acid was visually, but not statistically, acceptable.

RMS noted that there were the discrepancies in the results of the fitting reported in the main text of the study report and those presented in appendices presenting the report generated by the modelling tool. Therefore the whole assessment is based on the results presented in the source KinGUI report.

In RMS's opinion the results of the fitting show that it was possible to obtain the robust fit for Flufenacet and FOE Thiadone. For both compounds the determined kinetic parameters are reliable.

In case of Trifluoroacetic acid the obtained fit is visually and statistically acceptable, but the determined rate constant k is not reliable, according to the results of the t-test. That may be due to the fact that although the maximum and subsequent decline phase was reached, it was very flat, indicating that the degradation may take longer than estimated by the modelling tool. Therefore the kinetic endpoints – DT₅₀ and DT₉₀ values calculated by the modelling tool bear a significant level of uncertainty. As a result the RMS would like to propose to use, instead of the values calculated by the modelling tool, the default values – DT₅₀ = 1000 days and DT₉₀ > 1000 days.

In case of the third degradation product, for which the kinetic assessment was performed – FOE-5043 Trifluoroethanesulfonic acid, it was not possible to obtain statistically acceptable kinetic fit and hence reliable kinetic parameters. That may be due to the fact that the concentrations of that compound recorded in the test system (soil and overlying it water) during anaerobic incubation phase were very low. That in turn may indicate that FOE-5043 Trifluoroethanesulfonic acid is a transient, rapidly degrading compound.

Conclusions:

The kinetic analysis of the data for Flufenacet and its major degradation products – FOE Thiadone, FOE-5043 Trifluoroethanesulfonic acid and Trifluoroacetic acid, obtained for Loam (Dollendorf II) soil incubated under anaerobic conditions demonstrated that:

- The degradation of Flufenacet in that soil was most adequately described by DFOP kinetic model. Therefore that model should be considered as providing the kinetic endpoints describing the persistence of Flufenacet in anaerobic Silt loam soil;
- DFOP kinetic model – its slow phase, should be also considered as providing the kinetic endpoints appropriate for modelling.
- It was possible to obtain reliable kinetic fit and kinetic endpoints for FOE Thiadone;
- Although it was possible to obtain reliable kinetic fit for Trifluoroacetic acid, the reliable kinetic parameters describing degradation of that compound could not be derived due to the fact that the well pronounced decline phase was not reached. Therefore RMS proposed to use the default DT_{50} and DT_{90} values instead of those calculated by the model;
- It was not possible to obtain the reliable kinetic fit for FOE 5043-Trifluoroethanesulfonic acid, therefore for that compound no reliable kinetic endpoints are available. RMS attributed that to the low concentrations of the compound recorded in the test system and their significant scattering, what may indicate that the compound of concern is transient and rapidly degrades in anaerobic silt loam soil.

The proposed set of the kinetic endpoints derived from that study is following:

- Flufenacet, persistence endpoints: $DT_{50} = 13.51$ days, $DT_{90} = 110.02$ days, DFOP model ($k_1 = 0.4756$ days⁻¹, $k_2 = 0.0167$ days⁻¹, $g = 0.3745$);
- Flufenacet, modelling endpoints not normalised: $k = 0.0167$ [days⁻¹], $DT_{50} = 41.51$ days, $DT_{90} = 137.88$ days, SFO (slow phase DFOP), normalisation was not required as the experiment was carried out at $T = 20^{\circ}\text{C}$ and the correction for soil moisture was not necessary (soil was permanently flooded);
- FOE Thiadone, persistence and modelling endpoints: $DT_{50} = 33.90$ days, $DT_{90} = 112.60$ days, $ff = 0.425$ (from parent compound), SFO model ($k = 0.0071$ days⁻¹);
- Trifluoroacetic acid persistence endpoints (indicative): $DT_{50} = 1000$ days, $DT_{90} > 1000$ days, $ff = 0.575$ (from parent compound), SFO model;
- FOE-5043 Trifluoroethanesulfonic acid: it was not possible to derive reliable kinetic endpoints.

Final conclusion of the study:

The determination of the kinetic parameters of the process of degradation of Flufenacet in anaerobic soil was performed for the results obtained in two studies, on three soils using the test compound radiolabelled in two different positions:

- uniformly in phenyl ring (one test soil);
- in C5 position of thiadiazole moiety (two test soils).

The key results are presented below, individually for each test soil.

- a) The key results obtained for Sandy loam (Howe) soil treated with [Phenyl-¹⁴C]Flufenacet (study by [Pangilinan and Smith; 1995]):

The proposed set of the kinetic endpoints derived from that study is following:

- Flufenacet, persistence endpoints: $DT_{50} = 229.63$ days, $DT_{90} = 895.64$ days, DFOP model ($k_1 = 0.9976$ days⁻¹, $k_2 = 2.416 \text{ E-}3$ days⁻¹, $g = 0.1291$);
- Flufenacet, modelling endpoints not normalised: $k = 2.416 \text{ E-}3$ [days⁻¹], $DT_{50} = 286.90$ days, $DT_{90} = 953.06$ days, SFO (slow phase DFOP);
- Flufenacet, modelling endpoints normalized for temperature: $k = 2.205 \text{ E-}3$ [days⁻¹], $DT_{50} = 314.35$ days, $DT_{90} = 1044.26$ days, SFO (slow phase DFOP);
- FOE Oxalate, persistence endpoints (indicative): $DT_{50} = 311$ days, $DT_{90} = 1030$ days, SFO model – top-down approach ($k = 0.002233$ days⁻¹);
- FOE Sulfonic acid, persistence endpoints (indicative): $DT_{50} = 352$ days, $DT_{90} = 1170$ days, SFO model – top-down approach ($k_1 = 0.001986$ days⁻¹).

- b) The key results obtained for Silt loam (Hoefchen am Hohenseh 4a) soil treated with [Thiadiazole-5-¹⁴C] Flufenacet (study by [Heinemann; 2012]):

The proposed set of the kinetic endpoints derived from that study is following:

- Flufenacet, persistence endpoints: $DT_{50} = 22.66$ days, $DT_{90} = 156.90$ days, DFOP model ($k_1 = 0.1214$ days⁻¹, $k_2 = 0.01162$ days⁻¹, $g = 0.3810$);

- Flufenacet, modelling endpoints: $k = 0.01162$ [days⁻¹], $DT_{50} = 59.65$ days, $DT_{90} = 198.16$ days, SFO (slow phase DFOP), normalisation was not required as the experiment was carried out at $T = 20^{\circ}\text{C}$ and the correction for soil moisture was not necessary (soil was permanently flooded);
 - FOE Thiadone, persistence and modelling endpoints: $DT_{50} = 97.04$ days, $DT_{90} = 322.30$ days, $ff = 0.425$ (from parent compound), SFO model ($k = 0.0071$ days⁻¹);
 - Trifluoroacetic acid persistence endpoints (indicative): $DT_{50} = 1000$ days, $DT_{90} > 1000$ days, $ff = 0.575$ (from parent compound), SFO model;
 - FOE 5043-Trifluoroethanesulfonic acid: it was not possible to derive reliable kinetic endpoints.
- c) The key results obtained for Loam (Dollendorf II) soil treated with [Thiadiazole-5-¹⁴C]Flufenacet (study by [Heinemann; 2012]):

The proposed set of the kinetic endpoints derived from that study is following:

- Flufenacet, persistence endpoints: $DT_{50} = 13.51$ days, $DT_{90} = 110.02$ days, DFOP model ($k_1 = 0.4756$ days⁻¹, $k_2 = 0.0167$ days⁻¹, $g = 0.3745$);
- Flufenacet, modelling endpoints not normalised: $k = 0.0167$ [days⁻¹], $DT_{50} = 41.51$ days, $DT_{90} = 137.88$ days, SFO (slow phase DFOP), normalisation was not required as the experiment was carried out at $T = 20^{\circ}\text{C}$ and the correction for soil moisture was not necessary (soil was permanently flooded);
- FOE Thiadone, persistence and modelling endpoints: $DT_{50} = 33.90$ days, $DT_{90} = 112.60$ days, $ff = 0.425$ (from parent compound), SFO model ($k = 0.0071$ days⁻¹);
- Trifluoroacetic acid persistence endpoints (indicative): $DT_{50} = 1000$ days, $DT_{90} > 1000$ days, $ff = 0.575$ (from parent compound), SFO model;
- FOE 5043-Trifluoroethanesulfonic acid: it was not possible to derive reliable kinetic endpoints.

These results are also presented below in format recommended currently for EU List of End Points

Rate of degradation in soil (anaerobic) laboratory studies active substance (Regulation (EU) N° 283/2013, Annex Part A, point 7.1.2.1.3 and Regulation (EU) N° 284/2013, Annex Part A, point 9.1.1.1)

Parent - Flufenacet	Dark anaerobic conditions						
Soil type	OC	pH ^{a)}	t. °C / % MWHC	DT ₅₀ / DT ₉₀ (d)	DT ₅₀ (d) 20 °C ^{b)}	St. (x ²)	Method of calculation
Sandy loam (Howe)	0.35	6.2	21/ 100% (waterlogged soil)	229.69/ 895.64	314.35	6.03	DFOP – persistence; SFO (slow phase DFOP) - modelling
Silt loam (Hoefchen am Hohenseh 4a)	2.00	6.3	20/ 100% (waterlogged soil)	22.66/ 156.90	59.65	1.08	DFOP – persistence; SFO (slow phase DFOP) - modelling
Loam (Dollendorf II)	4.6	7.0	20/ 100% (waterlogged soil)	13.51/ 110.02	41.51	9.49	DFOP – persistence; SFO (slow phase DFOP) - modelling
Geometric mean (if not pH dependent)				41.27/ 249.12	91.99	----	----

^{a)} Measured in water

^{b)} Normalised using a Q10 of 2.58

Rate of degradation in soil (anaerobic) laboratory studies transformation products (Regulation (EU) N° 283/2013, Annex Part A, point 7.1.2.1.4 and Regulation (EU) N° 284/2013, Annex Part A, point 9.1.1.1)

FOE Oxalate	Dark anaerobic conditions Precursor from which the f.f. was derived was <i>Flufenacet</i>.							
Soil type	<i>OC</i>	pH ^{a)}	t. °C / % MWHC	DT ₅₀ / DT ₉₀ (d)	f. f. k _f / k _{dp}	DT ₅₀ (d) 20°C ^{b)}	St. (χ ²)	Method of calculation
Sandy loam (Howe)	0.35	6.2	21/ 100% (waterlogged soil)	311/ 1030	0.293	----	6.62	SFO – top-down approach
Geometric mean (if not pH dependent)				----	----	----	----	----
Arithmetic mean				----	----	----	----	----

^{a)} Measured in water

^{b)} Normalised using a Q10 of 2.58

FOE Sulfonic acid	Dark anaerobic conditions Precursor from which the f.f. was derived was <i>Flufenacet</i>.							
Soil type	<i>X</i>	pH ^{a)}	t. °C / % MWHC	DT ₅₀ / DT ₉₀ (d)	f. f. k _f / k _{dp}	DT ₅₀ (d) 20°C ^{b)}	St. (χ ²)	Method of calculation
Sandy loam (Howe)	0.35	6.2	21/ 100% (waterlogged soil)	352/ 1170	----	----	6.03	SFO – top-down approach
Geometric mean (if not pH dependent)				----	----	----	----	----
Arithmetic mean				----	----	----	----	----

^{a)} Measured in water

^{b)} Normalised using a Q10 of 2.58

FOE Thiadone	Dark anaerobic conditions Precursor from which the f.f. was derived was <i>Flufenacet</i>.							
Soil type	<i>X</i>	pH ^{a)}	t. °C / % MWHC	DT ₅₀ / DT ₉₀ (d)	f. f. k _f / k _{dp}	DT ₅₀ (d) 20°C ^{b)}	St. (χ ²)	Method of calculation
Silt loam (Hoefchen am Hohenseh 4a)	2.00	6.3	20/ 100% (waterlogged soil)	97.04/ 322.30	0.425	97.04	4.95	SFO
Loam (Dollendorf II)	4.6	7.0	20/ 100% (waterlogged soil)	33.90/ 112.60	0.425	33.90	5.58	SFO
Geometric mean (if not pH dependent)				57.36/ 190.50	----	57.36	----	----
Arithmetic mean				----	0.425	----	----	----

^{a)} Measured in water

^{b)} Normalised using a Q10 of 2.58

Trichloroacetic acid	Dark anaerobic conditions Precursor from which the f.f. was derived was <i>Flufenacet</i>.							
Soil type	<i>X</i>	pH ^{a)}	t. °C / % MWHC	DT ₅₀ / DT ₉₀ (d)	f. f. k _f / k _{dp}	DT ₅₀ (d) 20°C ^{b)}	St. (χ ²)	Method of calculation
Silt loam (Hoefchen am Hohenseh 4a)	2.00	6.3	20/ 100% (waterlogged soil)	1000/ >1000	0.575	1000	2.54	SFO
Loam (Dollendorf II)	4.6	7.0	20/ 100% (waterlogged soil)	1000/ >1000	0.575	1000	3.35	SFO
Geometric mean (if not pH dependent)				1000/ >1000	----	1000	----	----
Arithmetic mean				---	0.575	----	----	----

^{a)} Measured in water

^{b)} Normalised using a Q10 of 2.58

Additionally the results of the determination of the rate of degradation of Flufenacet in anaerobic soils incubated under controlled (laboratory) conditions were provided by two literature studies, summarised under the point B.8.1.1.2.1.1. as **Study 27** and **Study 28**. Below, in the table B.8.1.1.2.1.2._CA-20 are given the key results obtained in these two studies. As already indicated, these results may be considered only as indicative and were not used to derive the regulatory endpoints.

Table B.8.1.1.2.1.2._CA-20: The key results of the relevant publications examining the rate of degradation of Flufenacet in anaerobic (submerged) soils.

Study	Test soil	Key soil properties			Incubation conditions		Fortification level [µg a. s./g soil]	Kinetic endpoints – DT ₅₀ [days]		Method of calculation
		Soil type (USDA)	pH	OC [%]	T [°C]	Soil moisture		T=25 ⁰ C; FC	T=20 ⁰ C; FC	
<i>Gupta, Gajbhiye, Agnihotri [2001]</i>	Sandy loam	Sandy loam	7.1	0.34	25	FC	10	22.5	35.3	1 st order, linear regression, r =0.99
<i>Gupta, Gajbhiye, [2002]</i>	Dehli sandy loam	US Loamy sand	7.69	0.50	25	FC	10	22.3	35.0	1 st order, linear regression, r =0.99
	Ranchi sandy loam	US Sandy clay loam	5.54	0.04	25	FC	10	24.1	37.8	1 st order, linear regression, r =0.99
	Nagpur clayey soil	US Clay	8.25	0.40	25	FC	10	30.1	47.2	1 st order, linear regression, r =0.93

B.8.1.1.2.1.3. – Soil photolysis

Two studies were submitted examining the issue of phototransformation of Flufenacet on the soil surface. One of them was aimed on the determination of route and rate of soil photolysis of Flufenacet, the other examined the phototransformation on the soil surface of FOE Thiadone – the degradation product of Flufenacet. Both studies were summarized, as **Study 1** and **Study 2** respectively, under the point B.8.1.1.1.3. of this Renewal Assessment Report. The summaries contain also the key results of the kinetic analysis of the results, performed by the RMS in line with the recommendations of FOCUS Kinetics Guidance Document (FOCUS 2006). The kinetic analysis was repeated because that presented in the study reports did not comply with the current standards set by the Guidance Document referred to above. The detailed kinetic analysis of the results is presented below, separately for each study.

Study 1 examined the photodegradation of Flufenacet, radiolabelled uniformly within the phenyl ring, on one soil. The detailed results of the kinetic evaluation of its results are presented below.

Study 1:

Report: Kasper A. M., Shadrick B. A., (1995): “Photolysis of [Phenyl- ^{14}C] FOE 5043 on Sandy Loam.”; Bayer Corporation (formerly Miles Inc.), Agriculture Division, P. O. Box 4913, Kansas City, Missouri 64120-0013, USA; study No. F3082101/F3082102 (Bayer); unpublished Miles Report No. MR 106247; 22 June 1995; study reference number: M-002145-01-1;

Guidelines: The study was performed to comply with the following Guidelines:

- US. EPA Guidelines for Pesticide Registration, Subdivision N, Section 161-3, Soil Photolysis Study.

GLP: Yes

RMS comments: The study, submitted already for the purpose of the first authorisation in the EU, was re-evaluated for the purpose of the current assessment and found acceptable for its part related to the determination of the route of degradation of Flufenacet on the soil surface when exposed to sunlight. It is summarised under the point B.8.1.1.1.3. of this Renewal Assessment Report. However, in its part dealing with rate of degradation it was stated not compliant with the provisions of the current Guidelines, namely FOCUS Kinetics Guidance document. For that reason RMS repeated the kinetic assessment of the data, the results of which are presented in the summary below.

Summary:

The aim of the study was to examine photodegradation of Flufenacet on soil surface through:

- a. determining the half-life of that compound when exposed to artificial sunlight;
- b. identifying the transformation pattern, and in particular the degradation products formed in amounts greater than 10% AR.

The analysis of the kinetic assessment of the results presented in the study report showed that:

- it was performed using linear regression method, not recommended any more by the current guidelines;
- no statistical evaluation of the fit, as recommended by FOCUS Kinetics, was provided, the only statistical parameter being correlation coefficient r ; RMS noticed that it was due to the fact that the kinetic analysis of the data, as well as a whole study, pre-dated the introduction of FOCUS Kinetics;
- for both irradiated samples and dark control samples fitting was performed using the Natural Sunlight Days as time points; the approach may be justified in case of irradiated samples as it relates the results to would-be exposure of the test compound to the sunlight on the soil surface for well defined conditions, but it is not for dark control samples, because it artificially overestimate the kinetic parameters – k , DT_{50} and DT_{90} values.

All that taken into account RMS decided to repeat the kinetic analysis. It was performed following recommendations given by FOCUS Kinetics Workgroup (FOCUS; 2006), using the KinGUI 1.1 tool developed by Bayer CropScience.

The input data used in the evaluation are presented below in the table B.8.1.1.2.1.3._CA-1. In case of irradiated samples the analysis was performed twice – firstly using the real time points from the study – Suntest

days, then using converted time points – Natural Sunlight Days. For the dark control samples the kinetic analysis was performed using solely the real time points from the study – Suntest days, for the reason given above.

Table B.8.1.1.2.1.3._CA-1: The input data used in the kinetic analysis

Irradiated sample			Dark control sample	
Time point [days]		Concentration of Flufenacet [% AR]	Time point [days]	Concentration of Flufenacet [% AR]
Suntest days (real time point)	Natural Sunlight Days (converted time point)		Suntest days (real time point)	
0.00	0.0	98.4	0.00	98.4
2.75	8.0	98.2	2.75	95.0
5.13	15.0	92.6	5.13	89.5
7.75	22.7	94.0	7.75	88.6
10.25	30.0	91.2	10.25	87.2

The results of the kinetic analysis are presented below.

- a) results of the kinetic analysis of the data for irradiated sample and real time points:

The obtained results are presented below in the numerical form in table B.8.1.1.2.1.3._CA-2 and in the graphical form on figure B.8.1.1.2.1.3_CA-1. For convenience the results for all kinetic models tested are presented together.

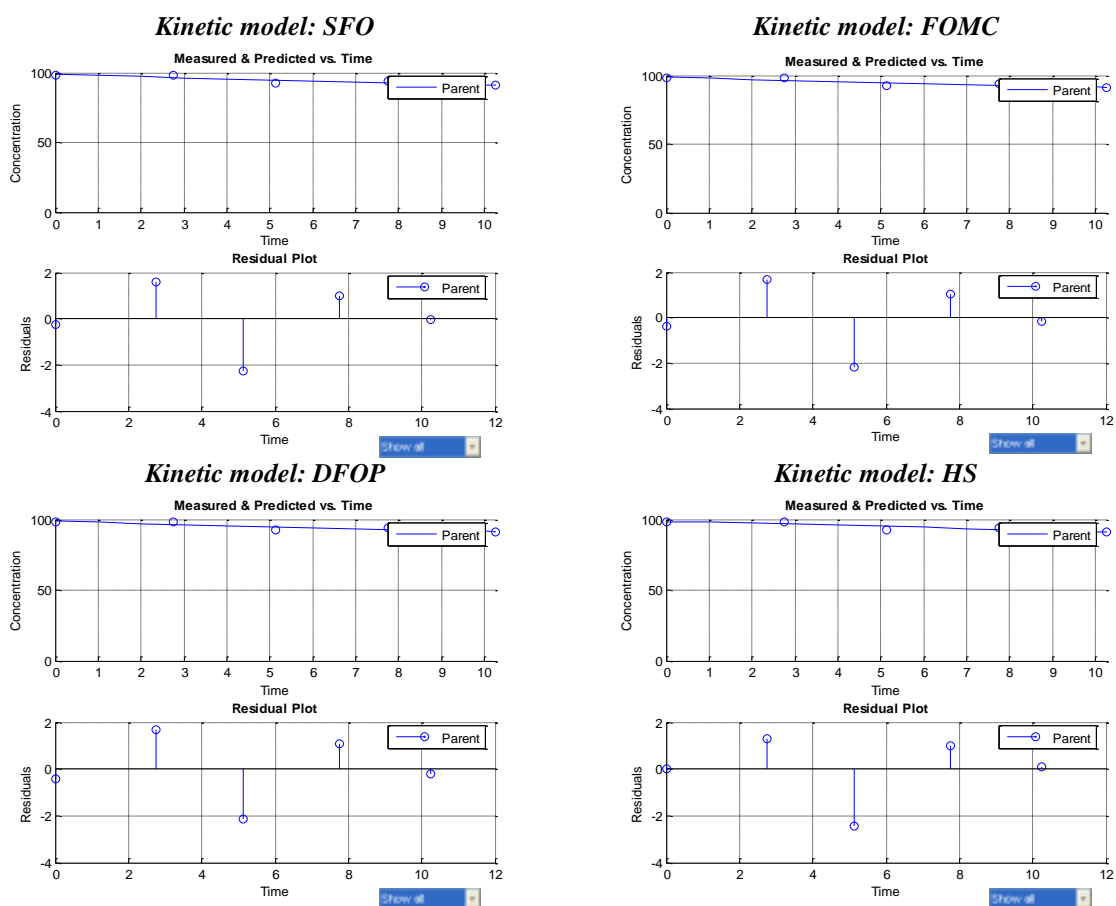


Figure B.8.1.1.2.1.3._CA-1: The graphical results of the kinetic analysis.

Table B.8.1.1.2.1.3._CA-2: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Statistical evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2
				Lower	Upper			
SFO	M_0	98.670	1.355	94.359	102.982	----	1.116	0.796
	k	0.0076	0.0022	5.3 E-4	0.0148	0.0209		
FOMC	M_0	98.795	2.014	90.129	107.462	----	1.270	0.798
	α	0.3032	2.7929	-11.7138	12.3201	0.4617		
	β	34.7810	362.7821	<-1000	>1000	0.4662		
DFOP	M_0	98.821	2.934	61.545	136.098	----	1.585	0.798
	k_1	0.0437	10.4171	-132.3184	132.4058	0.4987		
	k_2	9.5 E-4	1.9303	-24.5263	24.5282	0.4998		
	g	0.1866	81.5933	<-1000	>1000	0.4993		
HS	M_0	98.405	2.918	61.205	135.605	----	1.574	0.800
	k_1	0.0042	0.0235	-0.2945	0.3030	0.4436		
	k_2	0.0083	0.0055	-0.0623	0.0788	0.1885		
	t_b	0.1802	n. c. ¹⁾	n. c. ¹⁾	n. c. ¹⁾	n. c. ¹⁾		

Footnotes to the table:

1) n. c. = not calculated by the model;

Also the kinetic endpoints – DT₅₀ and DT₉₀ values for each of the kinetic models were calculated. These are presented below in the table B.8.1.1.2.1.3_CA-3.

Table B.8.1.1.2.1.3._CA-3: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested			
		SFO	FOMC	DFOP	HS
Flufenacet	DT ₅₀ [days]	90.72	307.43	512.70	84.88
	DT ₉₀ [days]	301.36	> 1000	> 1000	279.91

Evaluation:

The results of the kinetic analysis show that only SFO model returned reliable results. That may be due to the very low level of degradation of Flufenacet observed during the experiment combined with short incubation/irradiation period (~10% degradation within ~10 days).

b) results of the kinetic analysis of the data for irradiated sample and Natural Sunlight days as time points:

The obtained results are presented below in the numerical form in table B.8.1.1.2.1.3._CA-4 and in the graphical form on figure B.8.1.1.2.1.3_CA-2. For convenience the results for all kinetic models tested are presented together.

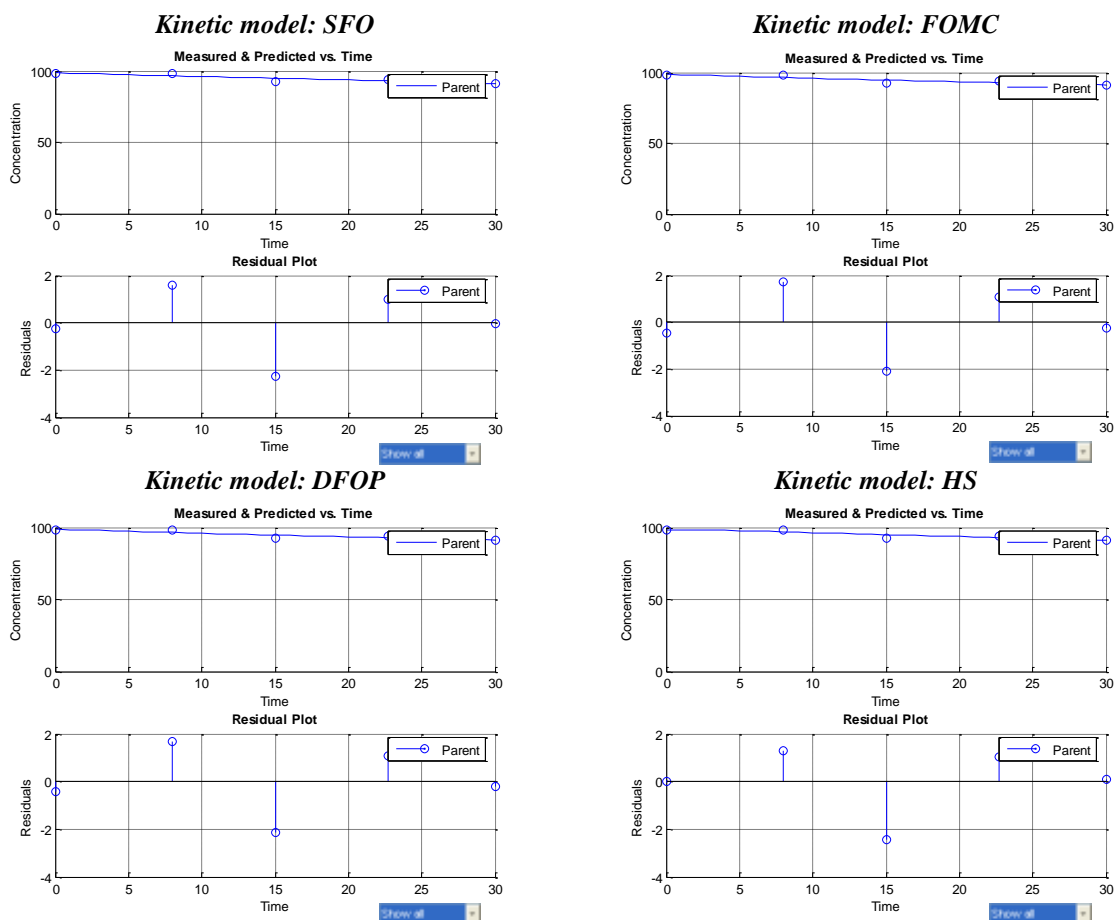


Figure B.8.1.1.2.1.3_CA-2: The graphical results of the kinetic analysis.

Table B.8.1.1.2.1.3_CA-4: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Statistical evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2
				Lower	Upper			
SFO	M_0	98.665	1.352	94.362	102.969	----	1.116	0.796
	k	0.0026	7.6 E-4	1.8 E-4	0.0050	0.0209		
FOMC	M_0	98.823	2.030	90.137	107.608	----	1.270	0.797
	α	0.1735	0.9236	-3.8003	4.1472	0.4342		
	β	52.7870	347.3942	<-1000	> 1000	0.4466		
DFOP	M_0	98.815	2.932	61.566	136.064	----	1.583	0.798
	k_1	0.0193	3.8466	-48.8558	48.8944	0.4984		
	k_2	9.2 E-4	0.3866	-4.9113	4.9131	0.4992		
	g	0.1161	42.3086	-537.4655	537.6978	0.4991		
HS	M_0	98.405	2.927	61.219	135.591	----	1.574	0.801
	k_1	0.0028	0.0019	-0.0212	0.0268	0.1886		
	k_2	8.5 E-4	94.0534	<-1000	> 1000	> 1000		
	t_b	3.6083	> 10000	<-1000	> 1000	0.5000		

Also the kinetic endpoints – DT_{50} and DT_{90} values for each of the kinetic models were calculated. These are presented below in the table B.8.1.1.2.1.3._CA-5.

Table B.8.1.1.2.1.3._CA-5: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested for Flufenacet			
		<i>SFO</i>	<i>FOMC</i>	<i>DFOP</i>	<i>HS</i>
<i>Flufenacet</i>	DT_{50} [days]	265.67	> 1000	618.16	249.26
	DT_{90} [days]	882.55	> 1000	> 1000	822.19

Evaluation:

The results of the kinetic analysis show that only SFO model returned reliable results. That may be due to the very low level of degradation of Flufenacet observed during the experiment combined with short actual incubation/irradiation period (~10% degradation within ~10 days).

c) results of the kinetic analysis of the data for the dark control sample (real time points):

The obtained results are presented below in the numerical form in table B.8.1.1.2.1.3._CA-6 and in the graphical form on figure B.8.1.1.2.1.3_CA-3. For convenience the results for all kinetic models tested are presented together.

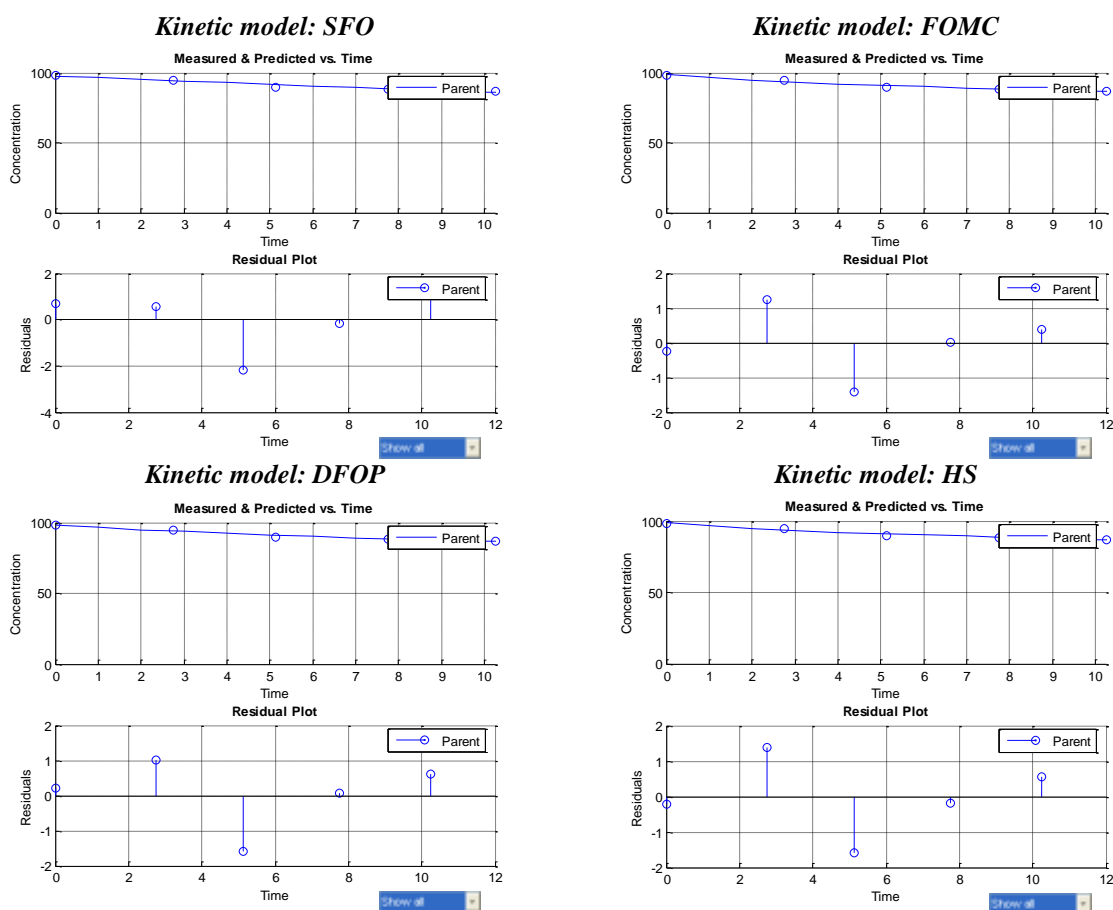


Figure B.8.1.1.2.1.3._CA-3: The graphical results of the kinetic analysis.

Table B.8.1.1.2.1.3._CA-6: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Statistical evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2
				Lower	Upper			
SFO	M_0	97.723	1.2143	93.859	101.587	----	1.027	0.923
	k	0.0124	0.0021	0.0059	0.0189	0.0046		
FOMC	M_0	98.642	1.368	92.758	104.526	----	0.868	0.958
	α	0.1106	0.1002	-0.3203	0.5416	0.1922		
	β	4.7131	7.0065	-25.4334	34.8595	0.2852		
DFOP	M_0	98.189	1.988	72.935	123.442	----	1.109	0.957
	k_1	0.0885	1.9700	-24.9431	25.1201	0.4857		
	k_2	2.3 E-4	0.3150	-4.0021	4.0021	0.5000		
	g	0.1980	7.0235	-89.0444	89.4405	0.4910		
HS	M_0	98.608	2.16	70.827	126.388	----	1.218	0.947
	k_1	0.0189	0.0102	-0.1109	0.1486	0.1580		
	k_2	0.0098	0.0048	-0.0514	0.0710	0.1454		
	t_b	3.214	n. c. ¹⁾	n. c. ¹⁾	n. c. ¹⁾	n. c. ¹⁾		

Footnotes to the table:

1) n. c. = not calculated by the model;

Also the kinetic endpoints – DT_{50} and DT_{90} values for each of the kinetic models were calculated. These are presented below in the table B.8.1.1.2.1.3._CA-7.

Table B.8.1.1.2.1.3._CA-7: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested for Flufenacet			
		SFO	FOMC	DFOP	HS
Flufenacet	DT_{50} [days]	55.90	> 1000	> 1000	67.80
	DT_{90} [days]	185.68	> 1000	> 1000	232.12

Evaluation:

The results of the kinetic analysis show that only SFO model returned reliable results. That may be due to the very low level of degradation of Flufenacet observed during the experiment, combined with short actual incubation/irradiation period (~10% degradation within ~10 days).

The data obtained for degradation products were not kinetically evaluated because of very low concentrations and/or the due to the fact that the decline phase was not reached at the end of incubation/irradiation period.

Results and their discussion:

The final set of the kinetic endpoints obtained for Flufenacet in the study examining its photolysis on the soil surface is presented below in the table B.8.1.1.2.1.3._CA-8.

Table B.8.1.1.2.1.3._CA-8: the definitive set of the kinetic endpoints obtained in the study.

Determined parameter	Results obtained for:		
	Dark control samples	Irradiated samples	
		Values not corrected (Suntest days)	Values corrected for summer sunlight intensity (Natural sunlight days) ¹⁾
Rate constant k [days ⁻¹]	0.0124	0.076	0.0026
DT_{50} [days]	55.90	90.72	265.67
DT_{90} [days]	185.68	301.36	882.55
Kinetic model	SFO	SFO	SFO

Footnotes to the table:

1) values calculated for conditions representative for summer sunny day in Phoenix, AZ, USA – longitude: 33° 27' N

On their basis it can be stated that Flufenacet is not expected to degrade in soil via its photolysis on the soil surface.

Conclusion:

The results clearly demonstrate that the degradation of Flufenacet was slower in irradiated samples than in the dark control. On that basis it can be stated that Flufenacet is not prone to the photolysis on the soil surface, hence soil photolysis will not be a relevant mechanism of degradation of Flufenacet in soil.

Second study – **Study 2**, was submitted to further examine the photolysis of Flufenacet on the soil surface, by determining the route and rate of photodegradation of FOE Thiadone – the primary degradation product of Flufenacet within the thiadiazole moiety.

The details of the kinetic analysis of its results are provided below.

Study 2:

Report: Lentz N. R., Bloomberg A. M., (2001): “Soil Photolysis of Thiadone on Loamy Sand (A Metabolite of FOE 5043).”; Ricerca LLC, Department of Environmental and Metabolic Fate, 7528 Auburn Road, Painesville, Ohio 44077, USA (performing laboratory) *for* Bayer Corporation, Agriculture Division, P. O. Box 4913, Kansas City, MO 64120, USA; Ricerca document No. 7410-0055-EF-001, study No. F3082103 (Bayer); Bayer Report No. 108721; 21 June 2001; study reference number: M-106297-01-1;

Guidelines: The study was performed to comply with the following Guidelines:

- US. EPA Guidelines for Pesticide Registration, Subdivision N, Section 161-3, Soil Photolysis Study.

GLP: Yes;

RMS comments: This is a newly submitted study, evaluated for the purpose of the current assessment and found acceptable for its part related to the determination of the route of degradation of FOE Thiadone on the soil surface when exposed to sunlight. It is summarised under the point B.8.1.1.1.3. of this Renewal Assessment Report. However, in its part dealing with rate of degradation it was stated not compliant with the provisions of the current Guidelines, namely FOCUS Kinetics Guidance document. For that reason RMS repeated the kinetic assessment of the data, the results of which are presented in the summary below.

Summary:

The aim of the study was to examine photodegradation of FOE Thiadone – the metabolite of Flufenacet, on the soil surface through:

- a) determining the half-life of that compound when exposed to artificial sunlight;
- b) identifying the transformation pattern, and in particular the degradation products formed in amounts greater than 10% AR.

The analysis of the kinetic assessment of the results presented in the study report showed that:

- it was performed using linear regression method, not recommended any more by the current guidelines;
- no statistical evaluation of the fit, as recommended by FOCUS Kinetics was provided, the only statistical parameter being coefficient of determination – R^2 ; RMS noted that it was due to the fact that the kinetic analysis of the data, as well as a whole study, pre-dated the introduction of FOCUS Kinetics.

All that taken into account RMS decided to repeat the kinetic analysis. It was performed following recommendations given by FOCUS Kinetics Workgroup (FOCUS; 2006), using the KinGUI 1.1 tool developed by Bayer CropScience. Only the data for FOE Thiadone were used. That was due to the fact that the concentrations of the only identified degradation product – propionic acid conjugate of FOE Thiadone, were too low to return a robust kinetic fit, in particular for irradiated samples.

The input data used in the evaluation are presented below in the table B.8.1.1.2.1.3._CA-9. In the analysis the average values were used.

Table B.8.1.1.2.1.3._CA-9: The data for FOE Thiadone used in the kinetic examination performed by RMS.

Time point	Concentration of FOE Thiadone in:					
	<i>Irradiated samples</i>			<i>Dark control samples</i>		
	Replicate 1	Replicate 2	Average	Replicate 1	Replicate 2	Average
Day 0	96.52	96.92	96.7	96.52	96.92	96.7
Day 0.5	74.22	84.03	79.2	85.08	82.10	83.6
Day 1	76.95	77.53	77.3	79.12	76.98	78.1
Day 2	52.80	51.65	52.3	67.66	63.64	65.7
Day 3	42.77	53.50	48.2	65.13	54.34	59.8
Day 5	35.51	34.67	35.2	47.31	34.82	41.1
Day 7	21.65	21.48	21.6	22.61	34.91	28.9
Day 10	11.13	13.85	12.5	21.80	14.71	18.3
Day 14	6.30	7.94	7.2	12.41	13.94	13.3

The results of the kinetic analysis are presented below, separately for irradiated samples and the dark control.

a) results of the kinetic analysis of the data for the irradiated samples:

The obtained results are presented below in the numerical form in table B.8.1.1.2.1.3._CA-10 and in the graphical form on figure B.8.1.1.2.1.3_CA-4. For convenience the results for all kinetic models tested are presented together.

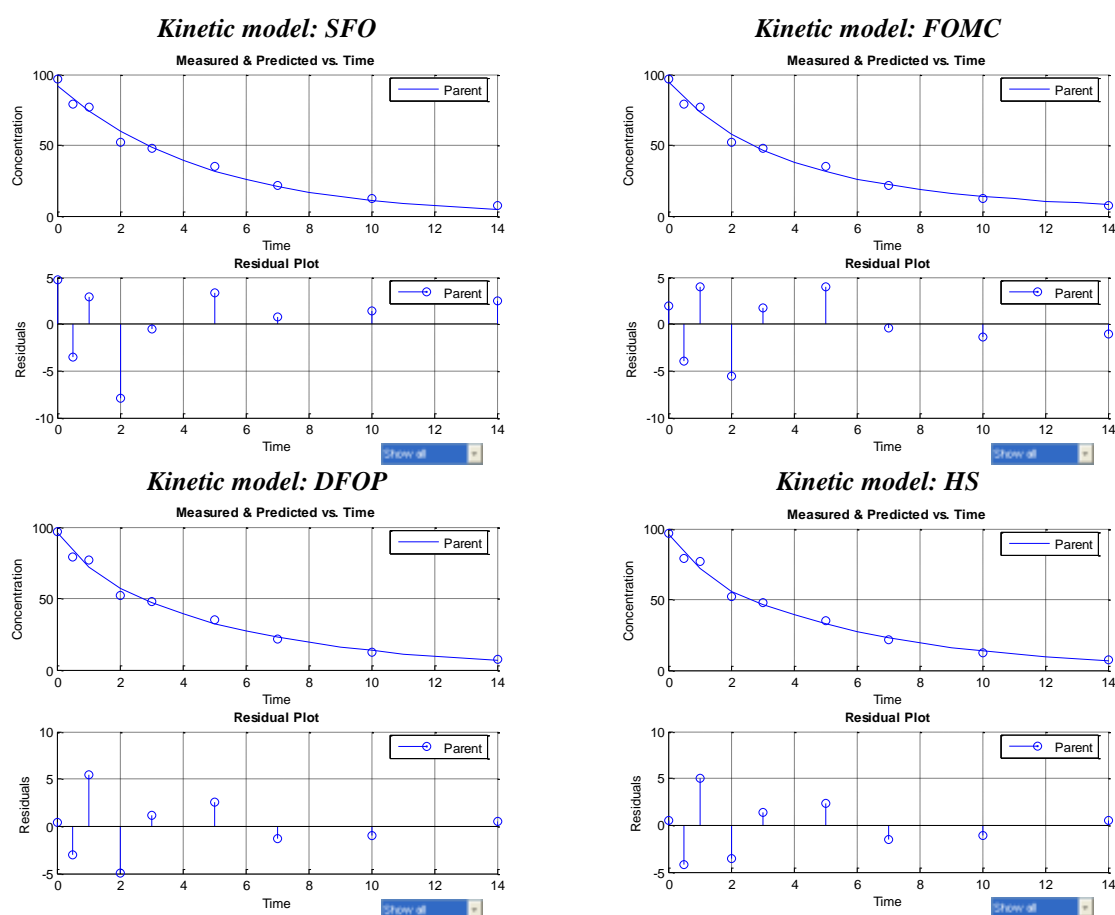


Figure B.8.1.1.2.1.3._CA-4: The graphical results of the kinetic analysis.

Table B.8.1.1.2.1.3._CA-10: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Statistical evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2
				Lower	Upper			
SFO	M_0	92.000	2.887	85.174	98.826	----	6.250	0.985
	k	0.2120	0.0162	0.1736	0.2503	1.8 E-6		
FOMC	M_0	94.786	3.179	87.008	102.563	----	5.525	0.989
	α	3.0248	1.8721	-1.5561	7.6058	0.0786		
	β	11.2741	8.5879	-9.7398	32.2881	0.1186		
DFOP	M_0	96.250	3.767	86.567	105.933	----	5.428	0.991
	k_1	1.0775	1.2470	-2.1279	4.2830	0.2135		
	k_2	0.1762	0.0352	0.0852	0.2668	0.0021		
	g	0.1840	0.1656	-0.2416	0.6095	0.1585		
HS	M_0	96.132	3.033	88.334	103.930	----	5.123	0.992
	k_1	0.2853	0.0332	0.2024	0.3681	1.5 E-4		
	k_2	0.1765	0.0203	0.1243	0.2288	1.7 E-4		
	t_b	1.7469	n. c. ¹⁾	n. c. ¹⁾	n. c. ¹⁾	n. c. ¹⁾		

Footnotes to the table:

1) n. c. = not calculated by the model;

Also the kinetic endpoints – DT_{50} and DT_{90} values for each of the kinetic models were calculated. These are presented below in the table B.8.1.1.2.1.3._CA-11.

Table B.8.1.1.2.1.3._CA-11: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested			
		SFO	FOMC	DFOP	HS
FOE Thiadone	DT_{50} [days]	3.27	2.90	2.87	2.85
	DT_{90} [days]	10.86	12.86	11.91	11.96

Evaluation:

The results of the kinetic analysis show that only SFO model returned reliable results. In case of FOMC and DFOP the lack of reliability was stated for the calculated kinetic parameters. For HS calculated kinetic parameters were reliable, but there was no statistical evaluation of t_b , and for that reason the kinetic fit cannot be considered acceptable.

b) results of the kinetic analysis of the data for the dark control samples:

The obtained results are presented below in the numerical form in table B.8.1.1.2.1.3._CA-12 and in the graphical form on figure B.8.1.1.2.1.3_CA-5. For convenience, as presented data are for a single compound – Flufenacet, the results for all kinetic models tested are presented together.

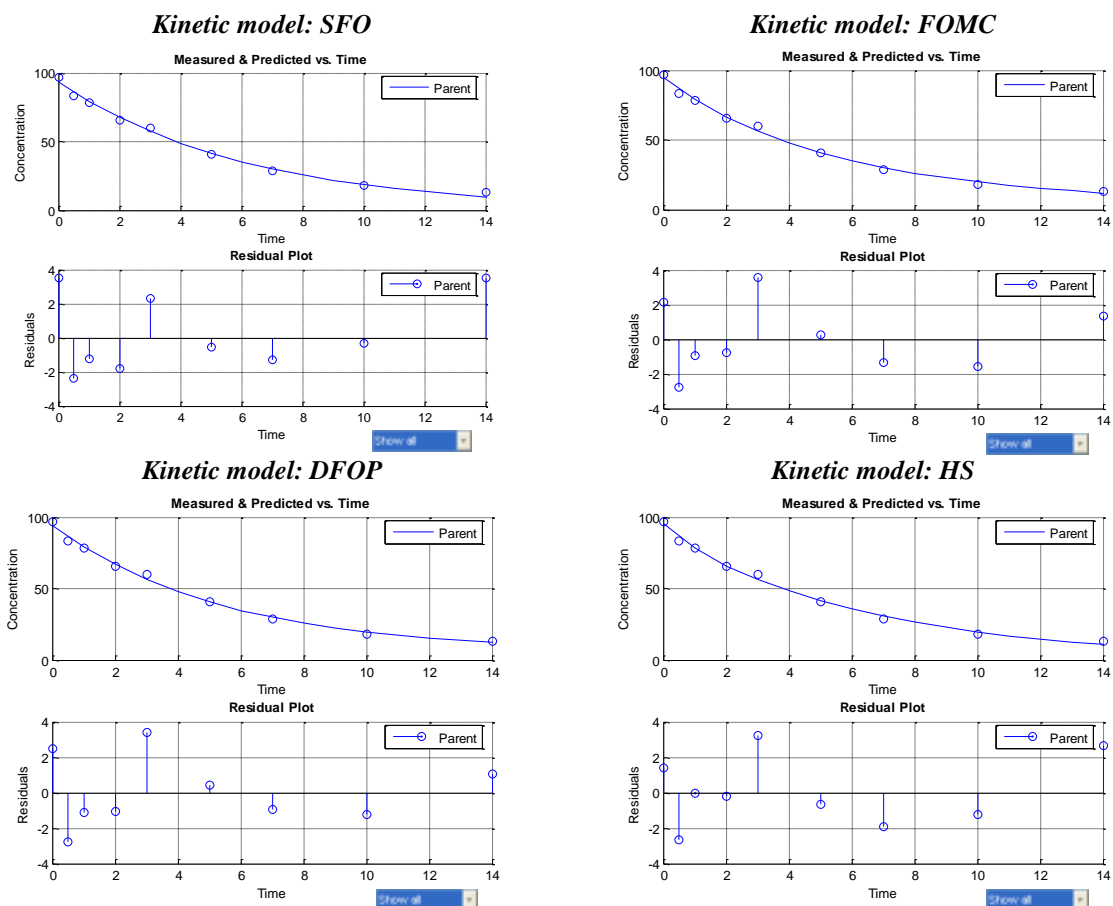


Figure B.8.1.1.2.1.3_CA-5: The graphical results of the kinetic analysis.

Table B.8.1.1.2.1.3_CA-12: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Statistical evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2
				Lower	Upper			
SFO	M_0	93.209	1.580	89.474	96.943	----	3.229	0.994
	k	0.1612	0.0070	0.1447	0.1776	3.6 E-8		
FOMC	M_0	94.538	1.801	90.130	98.946	----	2.996	0.995
	α	5.0823	3.5917	-3.7063	13.8709	0.1034		
	β	27.8478	22.1333	-26.3105	82.0062	0.1275		
DFOP	M_0	94.241	1.982	89.145	99.336	----	3.120	0.996
	k_1	0.1871	0.0914	-0.0480	0.4221	0.0481		
	k_2	0.0056	0.4264	-1.0904	1.1016	0.4950		
	g	0.9328	0.5191	-0.4017	2.2673	0.0661		
HS	M_0	95.274	2.923	89.379	101.169	----	3.162	0.996
	k_1	0.1985	0.0320	0.1163	0.2807	7.9 E-4		
	k_2	0.1519	0.0095	0.1275	0.1764	8.8 E-6		
	t_b	1.3690	n. c. ¹⁾	n. c. ¹⁾	n. c. ¹⁾	n. c. ¹⁾		

Footnotes to the table:

1) n. c. = not calculated by the model;

Also the kinetic endpoints – DT₅₀ and DT₉₀ values for each of the kinetic models were calculated. These are presented below in the table B.8.1.1.2.1.3_CA-13.

Table B.8.1.1.2.1.3_CA-13: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested			
		<i>SFO</i>	<i>FOMC</i>	<i>DFOP</i>	<i>HS</i>
<i>FOE Thiadone</i>	DT ₅₀ [days]	4.30	4.07	4.09	4.13
	DT ₉₀ [days]	14.29	15.96	16.98	14.73

Evaluation:

The results of the kinetic analysis show that only SFO model returned reliable results. In case of FOMC and DFOP the lack of reliability was stated for the calculated kinetic parameters. For HS calculated kinetic parameters were reliable, but there was no statistical evaluation of t_b, and for that reason the kinetic fit cannot be considered acceptable.

Results and their discussion:

The final set of the kinetic endpoints obtained for FOE Thiadone in the study examining its photolysis on the soil surface is presented below in the table B.8.1.1.2.1.3_CA-14.

Table B.8.1.1.2.1.3_CA-14: The definitive set of the kinetic endpoints obtained in the study.

Determined parameter	Results obtained for:	
	<i>Dark control samples</i>	<i>Irradiated samples</i>
Rate constant <i>k</i> [days ⁻¹]	0.1612	0.2120
DT ₅₀ [days]	4.30	3.27
DT ₉₀ [days]	14.29	10.86
Kinetic model	SFO	SFO

The results demonstrate that photolysis on the soil surface may contribute to degradation of FOE Thiadone in soil.

The net rate constant of the photolysis will be:

$$k_{\text{photolysis}} = k_{\text{irrad}} - k_{\text{dark control}} = 0.2120 - 0.1612 = 0.0508 [\text{days}^{-1}].$$

The resulting kinetic endpoints calculated using that value are: **DT₅₀ = 13.64 days** and **DT₉₀ = 45.33 days**.

Conclusion:

The results demonstrate that the photolysis on the soil surface might contribute to the degradation of FOE Thiadone in soil, if only that compound had been found on the soil surface in any substantial amounts. However, such possibility is minimal, because Flufenacet is photolytically stable, hence FOE Thiadone cannot be formed on the soil surface as a result of soil photolysis and, as aerobic metabolite is expected to be formed in deeper soil layers. On that basis it can be stated that soil photolysis will not be a relevant degradation mechanism of FOE Thiadone in soil, even though that compound is prone to it. As a result, the calculated kinetic endpoints will not be presented in the List of EndPoints nor further used in the exposure/risk assessment.

Summary – Rate of photodegradation of Flufenacet and its degradation products on the soil surface:

The photolysis of Flufenacet on the soil surface was examined in one experiment using one soil. Its results were kinetically examined, in line with the recommendations given by FOCUS [2006], by the RMS. The final set of the kinetic endpoints obtained for Flufenacet as a result of that examination is presented below in the table B.8.1.1.2.1.3._CA-15.

Table B.8.1.1.2.1.3._CA-15: The definitive set of the kinetic endpoints obtained for Flufenacet in the study examining soil photolysis of that compound.

Determined parameter	Results obtained for:		
	Dark control samples	Irradiated samples	
		Values not corrected (Suntest days)	Values corrected for summer sunlight intensity (Natural sunlight days) ¹⁾
Rate constant k [days ⁻¹]	0.0124	0.076	0.0026
DT_{50} [days]	55.90	90.72	265.67
DT_{90} [days]	185.68	301.36	882.55
Kinetic model	SFO	SFO	SFO

Footnotes to the table:

1) values calculated for conditions representative for summer sunny day in Phoenix, AZ, USA – longitude: 33° 27' N

On their basis it can be stated that Flufenacet is not expected to degrade in soil via its photolysis on the soil surface.

The conclusion drawn by the RMS from the study on the basis of the results presented above was following: “The results clearly demonstrate that the degradation of Flufenacet was slower in irradiated samples than in the dark control. On that basis it can be stated that Flufenacet is not prone to the photolysis on the soil surface, hence soil photolysis will not be a relevant mechanism of degradation of Flufenacet in soil.”

None of the degradation products of Flufenacet requiring further assessment were formed in that study, so the kinetic analysis for them was not performed. However, for one the major soil degradation product of Flufenacet – FOE Thiadone the photodegradation of that compound on the soil surface was examined in a separate study. The results were kinetically examined by the RMS and the definitive data set is presented below in the table B.8.1.1.2.1.3._CA-16.

Table B.8.1.1.2.1.3._CA-16: The definitive set of the kinetic endpoints obtained for FOE Thiadone in the study examining its photolysis on the soil surface.

Determined parameter	Results obtained for:	
	Dark control samples	Irradiated samples
Rate constant k [days ⁻¹]	0.1612	0.2120
DT_{50} [days]	4.30	3.27
DT_{90} [days]	14.29	10.86
Kinetic model	SFO	SFO

The results demonstrate that photolysis on the soil surface might contribute to degradation of FOE Thiadone in soil.

The net rate constant of the photolysis will be:

$$k_{\text{photolysis}} = k_{\text{irrad}} - k_{\text{dark control}} = 0.2120 - 0.1612 = 0.0508 \text{ [days}^{-1}\text{]}.$$

The resulting kinetic endpoints calculated using that value are: $DT_{50} = 13.64$ days and $DT_{90} = 45.33$ days.

At the same time it shall be pointed out however that the probability that that compound would be found on the soil surface in any substantial amounts is minimal. For that reason the process should be considered to have minimal relevance in the overall transformation of Flufenacet in soil.

The key results of the kinetic examination of the data obtained in the studies on the soil photolysis of Flufenacet are presented below in format of the new EU LoEP.

Rate of degradation on soil (photolysis) laboratory active substance (Regulation (EU) N° 283/2013, Annex Part A, point 7.1.1.3)

Parent	Soil photolysis					
Soil type	OC	pH ^{a)}	t. °C / % MWHC	DT ₅₀ / DT ₉₀ (d) calculated at 27°C	St. (x ²)	Method of calculation
US Sandy loam	0.67%	6.4	T = 25 ± 1°C; 75% of 1/3 bar (75% FC)	DT ₅₀ = 265.67 d; DT ₉₀ = 882.55 d.; Calculated at 33° 27' N (Phoenix, AZ; USA)	1.03	SFO, non-linear regression, OLS

^{a)} Measured in: medium for performing measurements not given

B.8.1.1.2.1.4. – Summary: rate of degradation, laboratory studies

Below are presented the key results of the kinetic examination of the data on the degradation of in soil obtained in the laboratory.

Aerobic degradation in biologically viable soil:

The degradation kinetics of Flufenacet in aerobic soil was extensively examined by the Applicant and its results presented in 26 study reports, of which 24 were found by the RMS acceptable and relevant for the current assessment. Additionally two literature studies were identified by the RMS which also provided the data on the degradation kinetics of Flufenacet in aerobic soils. These reports were found by the RMS relevant as supplementary source of data, however not suitable for deriving the regulatory endpoints.

The key results for each of the evaluated compounds are presented below, in tabularised form, individually for each of the test compounds.

a) Kinetic endpoints determined for Flufenacet:

The degradation kinetics of Flufenacet in aerobic soil was examined in ten trials using nine soils. One of the test soils – Howe, Indiana, Sandy loam soil, was used in two trials in which was used Flufenacet differently radiolabelled (either in phenyl ring or in C2 position of thiadiazole moiety), but the resulting kinetic endpoints cannot be averaged prior to calculating the overall geomean because they were derived in two separate studies, significantly differing in sample processing method.

The persistence (best-fit) kinetic endpoints obtained for Flufenacet are presented below in the table B.8.1.1.2.1.4._CA-1. The modelling endpoints are given in the table B.8.1.1.2.1.4._CA-2.

Table B.8.1.1.2.1.4._CA-1: The persistence kinetic endpoints determined for Flufenacet in aerobic soil.

Soil		Soil properties		Incubation conditions	Kinetic model	Evaluation of the fit		Kinetic parameters		Kinetic endpoints	
Soil name	Soil type (USDA)	OC	pH			χ^2 error	Visual fit ¹⁾ /R ²	Param.	Value	DT ₅₀ [days]	DT ₉₀ [days]
BBA 2,2; [Phenyl-U- ¹⁴ C] label	Loamy sand	2.58	6.2 ²⁾	20°C; 40% MWHC	SFO	8.53	A/ 0.974	<i>k</i>	0.0217	31.9	106.1
Laacherhof; [Phenyl-U- ¹⁴ C] label	Silt loam	0.9	6.2 ²⁾	20°C; 40% MWHC	SFO	11.0	G/0.978	<i>k</i>	0.0411	16.9	56
Höfchen im Tal; [Phenyl-U- ¹⁴ C] label	Silt loam	2.40	6.2 ²⁾	20°C; 40% MWHC	SFO	5.47	G/ 0.990	<i>k</i>	0.0339	20.4	67.9
Howe, Indiana; [Phenyl-U- ¹⁴ C] label	Sandy loam	0.35	6.2 ³⁾	21°C; 75% of ½ bar	SFO	2.36	G/ 0.981	<i>k</i>	0.0215	32.2	107.0
Laacherhof AXXa; [Phenyl-U- ¹⁴ C] label	Sandy loam	1.41	6.1 ⁴⁾	20°C; 50% MWHC	SFO	11.23	A/ 0.975	<i>k</i>	0.0943	7.35	24.4
Hoefchen Am Hohenseh 4a; [Thiadiazole-5- ¹⁴ C] label	Silt loam	2.5	6.7 ⁴⁾	19.1°C; 55% MWHC	SFO	4.88	G/ 0.995	<i>k</i>	0.0438	15.8	52.6
Laacherhof AXXa; [Thiadiazole-5- ¹⁴ C] label	Loamy sand	2.4	6.1 ⁴⁾	19.9°C; 55% MWHC	SFO	3.03	G/ 0.997	<i>k</i>	0.0349	19.85	65.9
Dollendorf II; [Thiadiazole-5- ¹⁴ C] label	Clay loam	5.3	7.2 ⁴⁾	19.9°C; 55% MWHC	SFO	4.67	G/ 0.994	<i>k</i>	0.0425	16.3	54.2
Laacherhof Wurmweise; [Thiadiazole-5- ¹⁴ C] label	Loam	2.2	5.4 ⁴⁾	19.9°C; 55% MWHC	SFO	4.27	G/ 0.994	<i>k</i>	0.0465	14.9	49.5
Howe, Indiana; [Thiadiazole-2- ¹⁴ C] label	Sandy loam	0.35	6.2 ³⁾	21°C; 75% of ½ bar	SFO	2.80	A/ 0.940	<i>k</i>	0.0120	57.6	191.42

Footnotes to the table:

- 1) The abbreviations used to describe the visual fit: G. – good, A. – acceptable, P. – poor;
- 2) Declared to be measured in CaCl₂/Water;
- 3) Measured in distilled water;
- 4) Measured in CaCl₂

The DT₅₀ = **57.6 days** value, determined in Howe, Indiana Sandy loam soil treated with [Thiadiazole-2-¹⁴C] Flufenacet was identified as appropriate input parameter for soil exposure assessment.

Table B.8.1.1.2.1.4._CA-2: The modelling kinetic endpoints determined for Flufenacet in aerobic soil.

Soil		Soil properties		Incubation conditions	Kinetic model	Evaluation of the fit		Kinetic parameters		Kinetic endpoints	
Soil name	Soil type (USDA)	OC	pH			χ^2 error	Visual fit ¹⁾ /R ²	Param.	Value	DT ₅₀ [days]	DT ₉₀ [days]
<i>BBA 2.2;</i> [Phenyl-U- ¹⁴ C] label	Loamy sand	2.58	6.2 ²⁾	20°C; 40% MWHC	SFO	8.53	A/ 0.974	<i>k</i>	0.0217	31.9	106.1
<i>Laacherhof;</i> [Phenyl-U- ¹⁴ C] label	Silt loam	0.9	6.2 ²⁾	20°C; 40% MWHC	SFO	11.0	G/0.978	<i>k</i>	0.0500	13.86	45.92
<i>Höfchen im Tal;</i> [Phenyl-U- ¹⁴ C] label	Silt loam	2.40	6.2 ²⁾	20°C; 40% MWHC	SFO	5.47	G/ 0.990	<i>k</i>	0.0339	20.44	67.9
<i>Howe, Indiana;</i> [Phenyl-U- ¹⁴ C] label	Sandy loam	0.35	6.2 ³⁾	21°C; 75% of ½ bar	SFO	2.36	G/ 0.981	<i>k</i>	0.0332	20.90	69.44
<i>Laacherhof AXXa;</i> [Phenyl-U- ¹⁴ C] label	Sandy loam	1.41	6.1 ⁴⁾	20°C; 50% MWHC	SFO	11.23	A/ 0.975	<i>k</i>	0.0985	7.04	23.37
<i>Hoefchen Am Hohenseh 4a;</i> [Thiadiazole-5- ¹⁴ C] label	Silt loam	2.5	6.7 ⁴⁾	19.1°C; 55% MWHC	SFO	4.88	G/ 0.995	<i>k</i>	0.0451	15.36	51.02
<i>Laacherhof AXXa;</i> [Thiadiazole-5- ¹⁴ C] label	Loamy sand	2.4	6.1 ⁴⁾	19.9°C; 55% MWHC	SFO	3.03	G/ 0.997	<i>k</i>	0.0356	19.45	64.58
<i>Dollendorf II;</i> [Thiadiazole-5- ¹⁴ C] label	Clay loam	5.3	7.2 ⁴⁾	19.9°C; 55% MWHC	SFO	4.67	G/ 0.994	<i>k</i>	0.0447	15.49	51.52
<i>Laacherhof Wurmweise;</i> [Thiadiazole-5- ¹⁴ C] label	Loam	2.2	5.4 ⁴⁾	19.9°C; 55% MWHC	SFO	4.27	G/ 0.994	<i>k</i>	0.0474	14.61	48.51
<i>Howe, Indiana;</i> [Thiadiazole-2- ¹⁴ C] label	Sandy loam	0.35	6.2 ³⁾	21°C; 75% of ½ bar	SFO	2.80	A/ 0.940	<i>k</i>	0.0185	37.40	124.23
Geometric mean (n = 10)									0.0387	17.89	59.42
Median (n = 10)									0.0402	17.47	58.05

Footnotes to the table:

- 1) The abbreviations used to describe the visual fit: G. – good, A. – acceptable, P. – poor;
- 2) Declared to be measured in CaCl₂/Water;
- 3) Measured in distilled water;
- 4) Measured in CaCl₂

For GW and SW model exposure assessment the **geomean DT₅₀ = 17.89 days** and **geomean *k* = 0.0387 [days⁻¹]** are the kinetic endpoints recommended as input parameters.

b) Kinetic endpoints determined for FOE Sulfonic acid:

The degradation kinetics of FOE Sulfonic acid in aerobic soil was examined in seventeen trials on the same number of the test soils. The experiments were performed in two variants – four trials with soils treated with Flufenacet (active substance) and the remaining thirteen trials with soils treated with FOE Sulfonic acid.

The performed kinetic analysis resulted in a data base consisting of twelve reliable kinetic endpoints, all determined in trials in which the test soils were treated with FOE Sulfonic acid. In case of the experiments on soils treated with Flufenacet it was not possible to obtain reliable kinetic endpoints characterising degradation of FOE Sulfonic acid in soil because decline of that compound was not observed. As a result, the default values – DT₅₀ = 1000 days and DT₉₀ > 1000 days, were proposed for these trials. These values, due to their nature and uncertainty related to them, were not used either as input parameters in soil exposure assessment or to calculate normalised mean values used subsequently in GW/SW exposure assessment. They are however provided in the table presenting the persistence endpoints, as with them are associated reliable kinetic formation fractions for

FOE Sulfonic acid, recommended to be used in GW exposure assessment. RMS however decided not to provide them in the table presenting the kinetic endpoints recommended for modelling.

In case of the kinetic analysis of the data obtained in Laacherhof IIIA Silt loam soil in the study by [Hellpointner; 1996], it was not possible to obtain a reliable kinetic fit and hence kinetic endpoints. For that reason the trial was removed from both summary table presenting persistence and modelling endpoints.

The persistence (best-fit) kinetic endpoints obtained for FOE Sulfonic acid are presented below in the table B.8.1.1.2.1.4._CA-3. The modelling endpoints are given in the table B.8.1.1.2.1.4._CA-4.

Table B.8.1.1.2.1.4._CA-3: The persistence kinetic endpoints determined for FOE Sulfonic acid in aerobic soil.

Soil		Soil properties		Incubation conditions	Kinetic model	Evaluation of the fit		Kinetic parameters		Kinetic endpoints		
Soil name	Soil type (USDA)	OC	pH ¹⁾			χ^2 error	Vis. fit ²⁾	Par.	Value	DT ₅₀ [days]	DT ₉₀ [days]	Kinetic formation fraction ff
BBA 2.2	Loamy sand	2.58	6.2 ^{a)}	20 ⁰ C; 40% MWHC	SFO	15.4	G	k	n. d. ³⁾	1000	>1000	0.257
Laacherhof	Silt loam	0.9	7.3 ^{a)}	20 ⁰ C; 40% MWHC	SFO	8.42	G	k	n. d. ³⁾	1000	>1000	0.272
Höfchen im Tal	Silt loam	2.40	5.8 ^{a)}	20 ⁰ C; 40% MWHC	SFO	6.56	G	k	n. d. ³⁾	1000	>1000	0.143
Howe, Indiana;	Sandy loam	0.35	6.2 ^{b)}	21 ⁰ C; 75% of 1/3 bar	SFO	6.28	G	k	n. d. ³⁾	1000	>1000	0.108
BBA 2.1	Sand	0.57	5.3 ^{c)}	20 ± 2 ⁰ C; 75% of 1/3 bar	SFO	1.78	G	k	2.18 E-3	318	1060	n. a. ⁴⁾
BBA 2.2	Loamy sand	2.48	6.3 ^{c)}	20 ± 2 ⁰ C; 75% of 1/3 bar	SFO	1.88	G	k	3.28 E-3	211	701	n. a. ⁴⁾
Laacherhof AXXa	Sandy loam	1.47	6.3 ^{c)}	20 ± 2 ⁰ C; 40% MWHC	SFO	3.05	G	k	0.0111	62.31	206.99	n. a. ⁴⁾
Laacherhof AIII	Silt loam	0.88	6.8 ^{c)}	20 ± 2 ⁰ C; 40% MWHC	SFO	3.03	G	k	0.0115	60.26	200.18	n. a. ⁴⁾
Laacherhof AXXa	Loamy sand	1.7	6.2 ^{c)}	19.6 ⁰ C; 55% MWHC	SFO	1.28	G	k	9.45 E-3	73.38	243.77	n. a. ⁴⁾
Dollendorf II	Loam	4.6	7.0 ^{c)}	19.6 ⁰ C; 55% MWHC	SFO	5.59	G	k	0.1033	6.71	22.30	n. a. ⁴⁾
Hoefchen Am Hohenseh 4a;	Silt loam	2.0	6.1 ^{c)}	19.6 ⁰ C; 55% MWHC	SFO	7.68	G	k	0.0242	28.58	94.95	n. a. ⁴⁾
Wurm-wiese	Sandy loam	1.8	5.0 ^{c)}	19.6 ⁰ C; 55% MWHC	SFO	3.66	G	k	0.0139	49.77	165.32	n. a. ⁴⁾
Hanscheider Hof	Loam	2.8	5.6 ^{c)}	19.9 ⁰ C; 55% MWHC	SFO	3.25	G	k	0.02539	27.30	90.70	n. a. ⁴⁾
Frankenforst	Silt loam	1.8	6.8 ^{c)}	19.9 ⁰ C; 55% MWHC	SFO	6.41	G	k	0.03181	21.79	72.39	n. a. ⁴⁾
LUFA 2.3	Sandy loam	1.1	6.8 ^{c)}	19.9 ⁰ C; 55% MWHC	SFO	1.45	G	k	0.0108	63.87	212.16	n. a. ⁴⁾
LUFA 6S	Clay	1.9	7.0 ^{c)}	19.9 ⁰ C; 55% MWHC	SFO	6.49	G	k	0.01838	37.71	125.28	n. a. ⁴⁾
Arithmetic mean for ff (n = 4)												0.195

Footnotes to the table:

- 1) Measured in:
 - CaCl₂/water for values marked a);
 - distilled water for results marked b);
 - 0.01M CaCl₂ for results marked c);
- 2) The abbreviations used to describe the visual fit: G. – good, A. – acceptable, P. – poor;
- 3) Value not determined – the decline phase not reached;
- 4) Value not available – the test compound applied as parent.

The DT₅₀ = **318 days** value, determined in BBA 2.1 Sand soil treated with FOE Sulfonic acid was identified as appropriate input parameter for soil exposure assessment.

Table B.8.1.1.2.1.4._CA-4: The modelling kinetic endpoints determined for FOE Sulfonic acid in aerobic soil.

Soil		Soil properties		Incubation conditions	Kinetic model	Evaluation of the fit		Kinetic parameters		Kinetic endpoints		
Soil name	Soil type (USDA)	OC	pH ¹⁾			χ^2 error	Vis. fit ²⁾	Par.	Value	DT ₅₀ [days]	DT ₉₀ [days]	Kinetic formation fraction <i>ff</i>
BBA 2.2	Loamy sand	2.58	6.2 ^{a)}	20 ⁰ C; 40% MWHC	SFO	15.4	G	<i>k</i>	n. d. ³⁾	n. d. ³⁾	n. d. ³⁾	0.257
Laacherhof	Silt loam	0.9	7.3 ^{a)}	20 ⁰ C; 40% MWHC	SFO	8.42	G	<i>k</i>	n. d. ³⁾	n. d. ³⁾	n. d. ³⁾	0.272
Höfchen im Tal	Silt loam	2.40	5.8 ^{a)}	20 ⁰ C; 40% MWHC	SFO	6.56	G	<i>k</i>	n. d. ³⁾	n. d. ³⁾	n. d. ³⁾	0.143
Howe, Indiana;	Sandy loam	0.35	6.2 ^{b)}	21 ⁰ C; 75% of 1/3 bar	SFO	6.28	G	<i>k</i>	n. d. ³⁾	n. d. ³⁾	n. d. ³⁾	0.108
BBA 2.1	Sand	0.57	5.3 ^{c)}	20 ± 2 ⁰ C; 75% of 1/3 bar	SFO	1.78	G	<i>k</i>	2.66 E-3	260.76	869.2	n. a. ⁴⁾
BBA 2.2	Loamy sand	2.48	6.3 ^{c)}	20 ± 2 ⁰ C; 75% of 1/3 bar	SFO	1.88	G	<i>k</i>	3.28 E-3	211.00	701	n. a. ⁴⁾
Laacherhof AXXa	Sandy loam	1.47	6.3 ^{c)}	20 ± 2 ⁰ C; 40% MWHC	SFO	3.05	G	<i>k</i>	0.0139	49.85	165.59	n. a. ⁴⁾
Laacherhof AIII	Silt loam	0.88	6.8 ^{c)}	20 ± 2 ⁰ C; 40% MWHC	SFO	3.03	G	<i>k</i>	0.0172	40.37	134.12	n. a. ⁴⁾
Laacherhof AXXa	Loamy sand	1.7	6.2 ^{c)}	19.6 ⁰ C; 55% MWHC	SFO	1.28	G	<i>k</i>	9.84 E-3	70.44	234.02	n. a. ⁴⁾
Dollendorf II	Loam	4.6	7.0 ^{c)}	19.6 ⁰ C; 55% MWHC	SFO	5.59	G	<i>k</i>	0.1109	6.25	20.77	n. a. ⁴⁾
Hoefchen Am Hohenseh 4a;	Silt loam	2.0	6.1 ^{c)}	19.6 ⁰ C; 55% MWHC	SFO	7.68	G	<i>k</i>	0.0269	25.79	85.68	n. a. ⁴⁾
Wurm-wiese	Sandy loam	1.8	5.0 ^{c)}	19.6 ⁰ C; 55% MWHC	SFO	3.66	G	<i>k</i>	0.0145	47.78	158.71	n. a. ⁴⁾
Hanscheider Hof	Loam	2.8	5.6 ^{c)}	19.9 ⁰ C; 55% MWHC	SFO	3.25	G	<i>k</i>	0.0256	27.03	89.79	n. a. ⁴⁾
Frankenforst	Silt loam	1.8	6.8 ^{c)}	19.9 ⁰ C; 55% MWHC	SFO	6.41	G	<i>k</i>	0.0321	21.57	70.68	n. a. ⁴⁾
LUFA 2.3	Sandy loam	1.1	6.8 ^{c)}	19.9 ⁰ C; 55% MWHC	SFO	1.45	G	<i>k</i>	0.0110	63.23	210.04	n. a. ⁴⁾
LUFA 6S	Clay	1.9	7.0 ^{c)}	19.9 ⁰ C; 55% MWHC	SFO	6.49	G	<i>k</i>	0.02158	32.11	106.60	n. a. ⁴⁾
Geometric mean (n = 12)									0.0154	45.11	149.74	----
Median (n = 12)									0.0159	44.08	146.42	----
Arithmetic mean for <i>ff</i> (n = 4)												0.195

Footnotes to the table:

- 1) Measured in:
 - CaCl₂/water for values marked a);
 - distilled water for results marked b);
 - (0.01M) CaCl₂ for results marked c);
- 2) The abbreviations used to describe the visual fit: G. – good, A. – acceptable, P. – poor;
- 3) Value not determined – the decline phase not reached;
- 4) Value not available – the test compound applied as parent.

For GW and SW model exposure assessment the **geomean DT₅₀ = 45.11 days** and **geomean *k* = 0.0154 [days⁻¹]** are the kinetic endpoints recommended as input parameters. The corresponding recommended *ff* value is ***ff* = 0.195** (arithmetic mean) for Flufenacet as a precursor.

c) Kinetic endpoints determined for FOE Oxalate:

The degradation kinetics of FOE Oxalate in aerobic soil was examined in four trials on the same number of the test soils. The experiments were performed with soils treated with Flufenacet (active substance).

The performed kinetic analysis resulted in a data base consisting of three reliable kinetic endpoints. In case of the experiment in Howe, Indiana, Sandy loam soil it was not possible to obtain reliable kinetic endpoints characterising degradation of FOE Oxalate because the decline of that compound was not observed. As a result, the default values – DT₅₀ = 1000 days and DT₉₀ > 1000 days, were proposed for that trial. These values, due to

their nature and uncertainty related to them, were not used either as input parameters in soil exposure assessment or to calculate normalised mean values used subsequently in GW/SW exposure assessment. They are however provided in the table presenting the persistence endpoints, as with them are associated reliable kinetic formation fraction for FOE Oxalate, recommended to be used in GW exposure assessment. RMS however decided not to provide them in the table presenting the kinetic endpoints recommended for modelling.

The persistence (best-fit) kinetic endpoints obtained for FOE Oxalate are presented below in the table B.8.1.1.2.1.4._CA-5. The modelling endpoints are given in the table B.8.1.1.2.1.4._CA-6.

Table B.8.1.1.2.1.4._CA-5: The persistence kinetic endpoints determined for FOE Oxalate in aerobic soil.

Soil		Soil properties		Incubation conditions	Kinetic model	Evaluation of the fit		Kinetic parameters		Kinetic endpoints		
Soil name	Soil type (USDA)	OC	pH ¹⁾			χ^2 error	Vis. fit ²⁾	Par.	Value	DT ₅₀ [days]	DT ₉₀ [days]	Kinetic formation fraction ff
BBA 2.2	Loamy sand	2.58	6.2 ^{a)}	20 ⁰ C; 40% MWHC	SFO	25.2	A	k	0.1011	6.9	22.8	0.448
Laacherhof	Silt loam	0.9	7.3 ^{a)}	20 ⁰ C; 40% MWHC	SFO	12.7	G	k	0.0366	18.9	62.9	0.422
Höfchen im Tal	Silt loam	2.40	5.8 ^{a)}	20 ⁰ C; 40% MWHC	SFO	10.5	G	k	0.0530	13.09	43.48	0.350
Howe, Indiana;	Sandy loam	0.35	6.2 ^{b)}	21 ⁰ C; 75% of 1/3 bar	SFO	3.99	G	k	n. d. ³⁾	1000	>1000	0.484
Arithmetic mean for ff (n = 4)												0.426

Footnotes to the table:

- 1) Measured in:
- CaCl₂/water for values marked a);
- distilled water for results marked b);
- 2) The abbreviations used to describe the visual fit: G. – good, A. – acceptable, P. – poor;
- 3) Value not determined – the decline phase not reached;

The DT₅₀ = **18.9 days** value, determined in Laacherhof Silt loam soil was identified as appropriate input parameter for soil exposure assessment.

Table B.8.1.1.2.1.4._CA-6: The modelling kinetic endpoints determined for FOE Oxalate in aerobic soil.

Soil		Soil properties		Incubation conditions	Kinetic model	Evaluation of the fit		Kinetic parameters		Kinetic endpoints		
Soil name	Soil type (USDA)	OC	pH ¹⁾			χ^2 error	Vis. fit ²⁾	Par.	Value	DT ₅₀ [days]	DT ₉₀ [days]	Kinetic formation fraction ff
BBA 2.2	Loamy sand	2.58	6.2 ^{a)}	20 ⁰ C; 40% MWHC	SFO	25.2	A	k	0.1011	6.7	22.8	0.448
Laacherhof	Silt loam	0.9	7.3 ^{a)}	20 ⁰ C; 40% MWHC	SFO	12.7	G	k	0.0447	15.5	51.58	0.422
Höfchen im Tal	Silt loam	2.40	5.8 ^{a)}	20 ⁰ C; 40% MWHC	SFO	10.5	G	k	0.0530	13.09	43.48	0.350
Howe, Indiana;	Sandy loam	0.35	6.2 ^{b)}	21 ⁰ C; 75% of 1/3 bar	SFO	3.99	G	k	n. d. ³⁾	n. d. ³⁾	n. d. ³⁾	0.484
Geometric mean (n = 3)									0.0639	11.08	37.12	----
Arithmetic mean for ff (n = 4)												0.426

Footnotes to the table:

- 1) Measured in:
- CaCl₂/water for values marked a);
- distilled water for results marked b);
- 2) The abbreviations used to describe the visual fit: G. – good, A. – acceptable, P. – poor;
- 3) Value not determined – the decline phase not reached;

For GW and SW model exposure assessment the **geomean DT₅₀ = 11.08 days** and **geomean k = 0.0639 [days⁻¹]** are the kinetic endpoints recommended as input parameters. The corresponding recommended ff value is **ff = 0.426** (arithmetic mean) for Flufenacet as a precursor.

d) Kinetic endpoints determined for FOE Methylsulfone:

The degradation kinetics of FOE Methylsulfone in aerobic soil was examined in eleven trials using the same number of the test soils. The experiments were performed in two variants – three trials with soils treated with Flufenacet (active substance) and the remaining eight trials with soils treated with FOE Methylsulfone.

The performed kinetic analysis resulted in a data base consisting of nine reliable kinetic endpoints, one with soil treated with Flufenacet as a precursor of FOE Methylsulfone and remaining eight with soils treated with FOE Methylsulfone. In case of two trials on soils treated with Flufenacet – BBA 2.2 Loamy sand soil and Hoefchen im Tal Silt loam soil, it was not possible to obtain reliable kinetic endpoints characterising degradation of FOE Methylsulfone in soil, because decline of that compound was not observed. As a result, the default values – $DT_{50} = 1000$ days and $DT_{90} > 1000$ days, were proposed for these trials. These values, due to their nature and uncertainty related to them, were not used either as input parameters in soil exposure assessment or to calculate normalised mean values used subsequently in GW/SW exposure assessment. They are however provided in the table presenting the persistence endpoints, as with them are associated reliable kinetic formation fractions for FOE Methylsulfone, recommended to be used in GW exposure assessment. RMS however decided not to provide them in the table presenting the kinetic endpoints recommended for modelling.

The persistence (best-fit) kinetic endpoints obtained for FOE Methylsulfone are presented below in the table B.8.1.1.2.1.4._CA-7. The modelling endpoints are given in the table B.8.1.1.2.1.4._CA-8.

Table B.8.1.1.2.1.4._CA-7: The persistence kinetic endpoints determined for FOE Methylsulfone in aerobic soil.

Soil		Soil properties		Incubation conditions	Kinetic model	Evaluation of the fit		Kinetic parameters		Kinetic endpoints		
Soil name	Soil type (USDA)	OC	pH ¹⁾			χ^2 error	Vis. fit ²⁾	Par.	Value	DT_{50} [days]	DT_{90} [days]	Kinetic formation fraction <i>ff</i>
BBA 2.2	Loamy sand	2.58	6.2 ^{a)}	20 ⁰ C; 40% MWHC	SFO	28.5	G	<i>k</i>	n. d. ³⁾	1000	>1000	0.061
Laacherhof	Silt loam	0.9	7.3 ^{a)}	20 ⁰ C; 40% MWHC	SFO	14.4	G	<i>k</i>	3.99 E-3	174	576	0.096
Höfchen im Tal	Silt loam	2.40	5.8 ^{a)}	20 ⁰ C; 40% MWHC	SFO	17.3	G	<i>k</i>	n. d. ³⁾	1000	>1000	0.052
Laacherhof AXXa	Loamy sand	1.7	6.2 ^{b)}	19.6 ⁰ C; 55% MWHC	SFO	3.37	G	<i>k</i>	1.61 E-2	43.14	143.32	n. a. ⁴⁾
Dollendorf II	Loam	4.6	7.0 ^{b)}	19.6 ⁰ C; 55% MWHC	SFO	3.04	G	<i>k</i>	2.98 E-2	23.30	77.41	n. a. ⁴⁾
Hoefchen Am Hohenseh 4a;	Silt loam	2.0	6.1 ^{b)}	19.6 ⁰ C; 55% MWHC	SFO	3.58	G	<i>k</i>	1.58 E-2	43.84	145.64	n. a. ⁴⁾
Wurm-wiese	Sandy loam	1.8	5.0 ^{b)}	19.6 ⁰ C; 55% MWHC	SFO	3.32	G	<i>k</i>	7.21 E-3	96.13	319.32	n. a. ⁴⁾
Hanscheider Hof	Loam	2.8	5.6 ^{b)}	19.9 ⁰ C; 55% MWHC	SFO	2.11	G	<i>k</i>	8.40 E-3	82.53	274.14	n. a. ⁴⁾
Frankenforst	Silt loam	1.8	6.8 ^{b)}	19.9 ⁰ C; 55% MWHC	SFO	2.88	G	<i>k</i>	0.01083	63.98	212.53	n. a. ⁴⁾
LUFA 2.3	Sandy loam	1.1	6.8 ^{b)}	19.9 ⁰ C; 55% MWHC	SFO	2.10	G	<i>k</i>	4.72 E-3	146.78	487.60	n. a. ⁴⁾
LUFA 6S	Clay	1.9	7.0 ^{b)}	19.9 ⁰ C; 55% MWHC	SFO	1.70	G	<i>k</i>	4.25 E-3	163.06	541.68	n. a. ⁴⁾
Arithmetic mean for <i>ff</i> (n = 3)												0.070

Footnotes to the table:

- 1) Measured in:
- CaCl₂/water for values marked a);
- (0.01M) CaCl₂ for results marked b);
- 2) The abbreviations used to describe the visual fit: G. – good, A. – acceptable, P. – poor;
- 3) Value not determined – the decline phase not reached;
- 4) Value not available – the test compound applied as parent.

The **DT₅₀ = 174 days** value, determined in Laacherhof Silt loam soil was identified as appropriate input parameter for soil exposure assessment.

Table B.8.1.1.2.1.4_CA-8: The modelling kinetic endpoints determined for FOE Methylsulfone in aerobic soil.

Soil		Soil properties		Incubation conditions	Kinetic model	Evaluation of the fit		Kinetic parameters		Kinetic endpoints		
Soil name	Soil type (USDA)	OC	pH ¹⁾			χ^2 error	Vis. fit ²⁾	Par.	Value	DT ₅₀ [days]	DT ₉₀ [days]	Kinetic formation fraction <i>ff</i>
BBA 2.2	Loamy sand	2.58	6.2 ^{a)}	20 ⁰ C; 40% MWHC	SFO	28.5	G	<i>k</i>	n. d. ³⁾	n. d. ³⁾	n. d. ³⁾	0.061
Laacherhof	Silt loam	0.9	7.3 ^{a)}	20 ⁰ C; 40% MWHC	SFO	14.4	G	<i>k</i>	4.86 E-3	142.68	472.32	0.096
Höfchen im Tal	Silt loam	2.40	5.8 ^{a)}	20 ⁰ C; 40% MWHC	SFO	17.3	G	<i>k</i>	n. d. ³⁾	n. d. ³⁾	n. d. ³⁾	0.052
Laacherhof AXXa	Loamy sand	1.7	6.2 ^{b)}	19.6 ⁰ C; 55% MWHC	SFO	3.37	G	<i>k</i>	1.66 E-2	41.85	139.00	n. a. ⁴⁾
Dollendorf II	Loam	4.6	7.0 ^{b)}	19.6 ⁰ C; 55% MWHC	SFO	3.04	G	<i>k</i>	3.07 E-2	22.60	75.09	n. a. ⁴⁾
Hoefchen Am Hohenseh 4a;	Silt loam	2.0	6.1 ^{b)}	19.6 ⁰ C; 55% MWHC	SFO	3.58	G	<i>k</i>	1.63 E-2	42.52	141.23	n. a. ⁴⁾
Wurm-wiese	Sandy loam	1.8	5.0 ^{b)}	19.6 ⁰ C; 55% MWHC	SFO	3.32	G	<i>k</i>	7.43 E-3	93.25	309.74	n. a. ⁴⁾
Hanscheider Hof	Loam	2.8	5.6 ^{b)}	19.9 ⁰ C; 55% MWHC	SFO	2.11	G	<i>k</i>	8.48 E-3	81.70	271.40	n. a. ⁴⁾
Frankenforst	Silt loam	1.8	6.8 ^{b)}	19.9 ⁰ C; 55% MWHC	SFO	2.88	G	<i>k</i>	1.09 E-2	63.34	210.40	n. a. ⁴⁾
LUFA 2.3	Sandy loam	1.1	6.8 ^{b)}	19.9 ⁰ C; 55% MWHC	SFO	2.10	G	<i>k</i>	4.77 E-3	145.31	482.72	n. a. ⁴⁾
LUFA 6S	Clay	1.9	7.0 ^{b)}	19.9 ⁰ C; 55% MWHC	SFO	1.70	G	<i>k</i>	4.99 E-3	138.83	461.19	n. a. ⁴⁾
Geometric mean (n = 9)									9.55 E-3	72.57	240.99	----
Median (n = 9)									8.48 E-3	81.70	271.40	----
Arithmetic mean for <i>ff</i> (n = 3)												0.070

Footnotes to the table:

- 1) Measured in:
 - CaCl₂/water for values marked a);
 - (0.01M) CaCl₂ for results marked b);
- 2) The abbreviations used to describe the visual fit: G. – good, A. – acceptable, P. – poor;
- 3) Value not determined – the decline phase not reached;
- 4) Value not available – the test compound applied as parent.

For GW and SW model exposure assessment the **median DT₅₀ = 81.70 days** and **median *k* = 0.00848 [days⁻¹]** are the kinetic endpoints recommended as input parameters. The corresponding recommended *ff* value is ***ff* = 0.070** (arithmetic mean) for Flufenacet as a precursor.

e) Kinetic endpoints determined for FOE Thiadone:

The degradation kinetics of FOE Thiadone in aerobic soil was examined in eight trials using the equal number of the test soils. The experiments were performed in two variants – five trials with soils treated with Flufenacet (active substance) and the remaining eight trials with soils treated with FOE Methylsulfone.

The performed kinetic analysis resulted in a data base consisting of eight reliable kinetic endpoints, four with soil treated with Flufenacet as a precursor of FOE Thiadone and three with soils treated with FOE Thiadone. In case of one trial on soil treated with Flufenacet – Howe, Indiana Sandy loam soil, it was not possible to obtain reliable fit for FOE Thiadone in combination with the parent compound. Such fit however was obtained when the data were kinetically analysed for FOE Thiadone alone using the top-down approach. That solution however implied that no reliable value for kinetic formation fraction in that trial could be obtained and reported. RMS decided not to report the default value *ff* = 1.00, proposed by the Applicant. The persistence (best-fit) kinetic

endpoints obtained for FOE Thiadone are presented below in the table B.8.1.1.2.1.4._CA-9. The modelling endpoints are given in the table B.8.1.1.2.1.4._CA-10.

Table B.8.1.1.2.1.4._CA-9: The persistence kinetic endpoints determined for FOE Thiadone in aerobic soil.

Soil		Soil properties		Incubation conditions	Kinetic model	Evaluation of the fit		Kinetic parameters		Kinetic endpoints		
Soil name	Soil type (USDA)	OC	pH			χ^2 error	Vis. fit ¹⁾	Par.	Value	DT ₅₀ [days]	DT ₉₀ [days]	Kinetic formation fraction ff
<i>Hoefchen Am Hohenseh 4a;</i>	Silt loam	2.5	6.7 ²⁾	19.1 ⁰ C; 55% MWHC	SFO	16.42	G	k	0.6110	1.13	3.77	0.913
<i>Laacherhof AXXa;</i>	Loamy sand	2.4	6.1 ²⁾	19.9 ⁰ C; 55% MWHC	SFO	15.65	G	k	0.5087	1.36	4.53	0.524
<i>Dollendorf II;</i>	Clay loam	5.3	7.2 ²⁾	19.9 ⁰ C; 55% MWHC	SFO	16.36	G	k	0.2438	2.84	9.45	0.438
<i>Laacherhof Wurm-wiese;</i>	Loam	2.2	5.4 ²⁾	19.9 ⁰ C; 55% MWHC	SFO	14.73	G	k	0.3490	1.99	6.60	0.404
<i>Howe, Indiana;</i>	Sandy loam	0.35	6.2 ³⁾	21 ⁰ C; 75% of 1/3 bar	SFO	4.95	G	k	0.0435	15.9	52.9	n. d. ⁵⁾
<i>Iowa</i>	Loamy sand	1.91	7.2 ⁴⁾	20 ⁰ C; 75% of 1/3 bar	SFO	6.72	A	k	0.3494	1.98	6.59	n. d. ⁶⁾
<i>Indiana</i>	Sandy loam	1.28	6.5 ⁴⁾	20 ⁰ C; 75% of 1/3 bar	SFO	5.67	A	k	0.4945	1.40	4.66	n. d. ⁶⁾
<i>Nebraska</i>	Silt loam	1.66	7.7 ⁴⁾	20 ⁰ C; 75% of 1/3 bar	SFO	3.71	A	k	0.2363	2.93	9.74	n. d. ⁶⁾
Arithmetic mean for ff (n = 3)												0.570

Footnotes to the table:

- 1) The abbreviations used to describe the visual fit: G. – good, A. – acceptable, P. – poor;
- 2) Measured in 0.01M CaCl₂;
- 3) Measured in distilled water;
- 4) Medium for measuring pH not given;
- 5) Value not available – kinetic endpoints determined using the top-down approach;
- 6) Value not available – the test compound applied as parent.

The DT₅₀ = **15.9 days** value, determined in Howe, Indiana Sandy loam soil was identified as appropriate input parameter for soil exposure assessment.

Table B.8.1.1.2.1.4._CA-10: The modelling kinetic endpoints determined for FOE Thiadone in aerobic soil.

Soil		Soil properties		Incubation conditions	Kinetic model	Evaluation of the fit		Kinetic parameters		Kinetic endpoints		
Soil name	Soil type (USDA)	OC	pH			χ^2 error	Vis. fit ¹⁾	Par.	Value	DT ₅₀ [days]	DT ₉₀ [days]	Kinetic formation fraction <i>ff</i>
<i>Hoefchen Am Hohenseh 4a;</i>	Silt loam	2.5	6.7 ²⁾	19.1 ⁰ C; 55% MWHC	SFO	16.42	G	<i>k</i>	0.6301	1.10	3.66	0.913
<i>Laacherhof AXx;</i>	Loamy sand	2.4	6.1 ²⁾	19.9 ⁰ C; 55% MWHC	SFO	15.65	G	<i>k</i>	0.5212	1.33	4.44	0.524
<i>Dollendorf II;</i>	Clay loam	5.3	7.2 ²⁾	19.9 ⁰ C; 55% MWHC	SFO	16.36	G	<i>k</i>	0.2567	2.70	8.98	0.438
<i>Laacherhof Wurm-wiese;</i>	Loam	2.2	5.4 ²⁾	19.9 ⁰ C; 55% MWHC	SFO	14.73	G	<i>k</i>	0.3555	1.95	6.47	0.404
<i>Howe, Indiana;</i>	Sandy loam	0.35	6.2 ³⁾	21 ⁰ C; 75% of 1/3 bar	SFO	4.95	G	<i>k</i>	0.0672	10.32	34.33	n. d. ⁵⁾
<i>Iowa</i>	Loamy sand	1.91	7.2 ⁴⁾	20 ⁰ C; 75% of 1/3 bar	SFO	6.72	A	<i>k</i>	0.5458	1.27	4.22	n. d. ⁶⁾
<i>Indiana</i>	Sandy loam	1.28	6.5 ⁴⁾	20 ⁰ C; 75% of 1/3 bar	SFO	5.67	A	<i>k</i>	0.7702	0.90	2.98	n. d. ⁶⁾
<i>Nebraska</i>	Silt loam	1.66	7.7 ⁴⁾	20 ⁰ C; 75% of 1/3 bar	SFO	3.71	A	<i>k</i>	0.3027	2.29	7.60	n. d. ⁶⁾
Geometric mean (n = 8)									0.3557	1.95	6.48	----
Median (n = 8)									0.4384	1.64	5.46	----
Arithmetic mean for <i>ff</i> (n = 3)												0.570

Footnotes to the table:

- 1) The abbreviations used to describe the visual fit: G. – good, A. – acceptable, P. – poor;
- 2) Measured in 0.01M CaCl₂;
- 3) Measured in distilled water;
- 4) Medium for measuring pH not given;
- 5) Value not available – kinetic endpoints determined using the top-down approach;
- 6) Value not available – the test compound applied as parent.

For GW and SW model exposure assessment the **geomean DT₅₀ = 1.95 days** and **geomean *k* = 0.3557 [days⁻¹]** are the kinetic endpoints recommended as input parameters. The corresponding recommended *ff* value is ***ff* = 0.570** (arithmetic mean) for Flufenacet as a precursor.

f) Kinetic endpoints determined for FOE 5043-Trifluoroethanesulfonic acid (TFESA):

The degradation kinetics of FOE 5043-Trifluoroethanesulfonic acid (TFESA) in aerobic soil was examined in four trials using the equal number of the test soils. The experiments were performed with soils treated with Flufenacet (active substance).

The performed kinetic analysis resulted in a data base consisting of four reliable kinetic endpoints. In case of two trials – on the Dollendorf II Clay loam soil and Laacherhof Wurm-wiese Loam soil it was not possible to obtain reliable kinetic fits for the whole transformation scheme, therefore the top-down approach was used. RMS however decided to keep the determined values of kinetic formation fraction *ff*. The persistence (best-fit) kinetic endpoints obtained for FOE 5043-Trifluoroethanesulfonic acid (TFESA) are presented below in the table B.8.1.1.2.1.4._CA-11. The modelling endpoints are given in the table B.8.1.1.2.1.4._CA-12.

Table B.8.1.1.2.1.4_CA-11: The persistence kinetic endpoints determined for FOE 5043-Trifluoroethanesulfonic acid in aerobic soil.

Soil		Soil properties		Incubation conditions	Kinetic model	Evaluation of the fit		Kinetic parameters		Kinetic endpoints		
Soil name	Soil type (USDA)	OC	pH ¹⁾			χ^2 error	Vis. fit ²⁾	Par.	Value	DT ₅₀ [days]	DT ₉₀ [days]	Kinetic formation fraction <i>ff</i>
<i>Hoefchen Am Hohenseh 4a;</i>	Silt loam	2.5	6.7	19.1 ⁰ C; 55% MWHC	SFO	5.85	G	<i>k</i>	0.0761	9.10	30.23	0.264
<i>Laacherhof AXXa;</i>	Loamy sand	2.4	6.1	19.9 ⁰ C; 55% MWHC	SFO	18.25	G	<i>k</i>	0.1548	4.48	14.87	0.534
<i>Dollendorf II;</i>	Clay loam	5.3	7.2	19.9 ⁰ C; 55% MWHC	SFO	4.31	G	<i>k</i>	0.0331	20.9	69.5	0.422
<i>Laacherhof Wurm-wiese;</i>	Loam	2.2	5.4	19.9 ⁰ C; 55% MWHC	SFO	12.3	G	<i>k</i>	0.3090	2.24	7.45	0.655
Arithmetic mean for <i>ff</i> (n = 3)												0.469

Footnotes to the table:

- 1) Measured in 0.01M CaCl₂;
 2) The abbreviations used to describe the visual fit: G. – good, A. – acceptable, P. – poor;

The DT₅₀ = **20.9 days** value, determined in Dollendorf II Clay loam soil was identified as appropriate input parameter for soil exposure assessment.

Table B.8.1.1.2.1.4_CA-12: The modelling kinetic endpoints determined for FOE-5043 Trifluoroethanesulfonic acid in aerobic soil.

Soil		Soil properties		Incubation conditions	Kinetic model	Evaluation of the fit		Kinetic parameters		Kinetic endpoints		
Soil name	Soil type (USDA)	OC	pH ¹⁾			χ^2 error	Vis. fit ²⁾	Par.	Value	DT ₅₀ [days]	DT ₉₀ [days]	Kinetic formation fraction <i>ff</i>
<i>Hoefchen Am Hohenseh 4a;</i>	Silt loam	2.5	6.7	19.1 ⁰ C; 55% MWHC	SFO	5.85	G	<i>k</i>	0.0785	8.83	29.32	0.264
<i>Laacherhof AXXa;</i>	Loamy sand	2.4	6.1	19.9 ⁰ C; 55% MWHC	SFO	18.25	G	<i>k</i>	0.1579	4.39	14.57	0.534
<i>Dollendorf II;</i>	Clay loam	5.3	7.2	19.9 ⁰ C; 55% MWHC	SFO	4.31	G	<i>k</i>	0.0349	19.87	66.01	0.422
<i>Laacherhof Wurm-wiese;</i>	Loam	2.2	5.4	19.9 ⁰ C; 55% MWHC	SFO	12.3	G	<i>k</i>	0.3165	2.19	7.30	0.655
Geometric mean (n = 4)									0.1082	6.41	21.30	----
Arithmetic mean for <i>ff</i> (n = 3)												0.469

Footnotes to the table:

- 1) Measured in 0.01M CaCl₂;
 2) The abbreviations used to describe the visual fit: G. – good, A. – acceptable, P. – poor;

For GW and SW model exposure assessment the **geomean DT₅₀ = 6.41 days** and **geomean *k* = 0.1082 [days⁻¹]** are the kinetic endpoints recommended as input parameters. The corresponding recommended *ff* value is ***ff* = 0.469** (arithmetic mean) for FOE Thiadone as a precursor.

g) Kinetic endpoints determined for Trifluoroacetic acid (TFA):

The degradation kinetics of Trifluoroacetic acid (TFA) in aerobic soil was examined in eight trials using the equal number of the test soils. The experiments were performed in two variants – four trials with soils treated with Flufenacet (active substance) and the remaining four trials with soils treated with TFA.

Due to the high persistence of the test compound – TFA, in none of the test soils it was possible to obtain the reliable kinetic endpoints. For that reason the default values were proposed.

Due to the difference between the modelling tools, for the persistence endpoints two sets of the default values were provided. For trials on test soils treated with Flufenacet as precursor of TFA, where the analysis performed by the Applicant was accepted, the default kinetic endpoints were: **DT₅₀ = 1000 days** and **DT₉₀ > 1000 days**. In case however of the trials with TFA applied as parent compound, for which RMS had to repeat the kinetic analysis, the kinetic endpoints were: **DT₅₀ = 10000 days** and **DT₉₀ > 10000 days** – the values returned by the applied tool. RMS considers these defaults to be representative for the persistence of TFA in soil, as that indicated the results of the examination of the fate of TFA in environment presented in the open-source literature.

However for modelling the recommended input value is **DT₅₀ = 1000 days**, because of the constraints of the current modelling tools. It shall be noted that due to the nature of the determined endpoint – a default value, its normalisation was not performed as not necessary.

For TFA a set for two kinetic formation fraction values were determined – one for formation of TFA from Flufenacet and the second for its formation from FOE Thiadone.

The persistence (best-fit) kinetic endpoints obtained for TFA are presented below in the table B.8.1.1.2.1.4._CA-13. The modelling endpoints are given in the table B.8.1.1.2.1.4._CA-14.

Table B.8.1.1.2.1.4._CA-13: The persistence kinetic endpoints determined for Trifluoroacetic acid (TFA) in aerobic soil.

Soil		Soil properties		Incubation conditions	Kinetic model	Evaluation of the fit		Kinetic parameters		Kinetic endpoints		
Soil name	Soil type (USDA)	OC	pH ¹⁾			χ^2 error	Vis. fit ¹⁾	Par.	Value	DT ₅₀ [days]	DT ₉₀ [days]	Kinetic formation fraction <i>ff</i> ⁴⁾
<i>Hoefchen Am Hohenseh 4a;</i>	Silt loam	2.5	6.7	19.1 ⁰ C; 55% MWHC	SFO	10.49	G	<i>k</i>	n. d. ³⁾	1000	>1000	<i>ff</i> ₁ = 0.087 <i>ff</i> ₂ = 0.736
<i>Laacherhof AXXa;</i>	Loamy sand	2.4	6.1	19.9 ⁰ C; 55% MWHC	SFO	10.34	G	<i>k</i>	n. d. ³⁾	1000	>1000	<i>ff</i> ₁ = 0.476 <i>ff</i> ₂ = 0.466
<i>Dollendorf II;</i>	Clay loam	5.3	7.2	19.9 ⁰ C; 55% MWHC	SFO	9.45	G	<i>k</i>	n. d. ³⁾	1000	>1000	<i>ff</i> ₁ = 0.562 <i>ff</i> ₂ = 0.578
<i>Laacherhof Wurm-wiese;</i>	Loam	2.2	5.4	19.9 ⁰ C; 55% MWHC	SFO	9.44	G	<i>k</i>	n. d. ³⁾	1000	>1000	<i>ff</i> ₁ = 0.596 <i>ff</i> ₂ = 0.345
<i>Hanscheider Hof</i>	Loam	2.8	5.6	19.9 ⁰ C; 55% MWHC	SFO	4.95	G	<i>k</i>	n. d. ³⁾	10000	>10000	n. d. ³⁾
<i>Frankenforst</i>	Silt loam	1.8	6.8	19.9 ⁰ C; 55% MWHC	SFO	6.72	A	<i>k</i>	n. d. ³⁾	10000	>10000	n. d. ³⁾
<i>LUFA 2.3</i>	Sandy loam	1.1	6.8	19.9 ⁰ C; 55% MWHC	SFO	5.67	A	<i>k</i>	n. d. ³⁾	10000	>10000	n. d. ³⁾
<i>LUFA 6S</i>	Clay	1.9	7.0	19.9 ⁰ C; 55% MWHC	SFO	3.71	A	<i>k</i>	n. d. ³⁾	10000	>10000	n. d. ³⁾
Arithmetic mean for <i>ff</i> (n = 4)												<i>ff</i> ₁ = 0.430 <i>ff</i> ₂ = 0.531

Footnotes to the table:

- 1) Measured in 0.01M CaCl₂;
- 2) The abbreviations used to describe the visual fit: G. – good, A. – acceptable, P. – poor;
- 3) n. d. – not determined
- 4) *ff*₁ – kinetic formation fraction for formation of TFA from Flufenacet; *ff*₂ – kinetic formation fraction for formation of TFA from FOE Thiadone.

The default **DT₅₀ = 10000 days** value was identified as appropriate input parameter for soil exposure assessment.

Table B.8.1.1.2.1.4._CA-14: The modelling kinetic endpoints determined for Trifluoroacetic acid (TFA) in aerobic soil.

Soil		Soil properties		Incubation conditions	Kinetic model	Evaluation of the fit		Kinetic parameters		Kinetic endpoints		
Soil name	Soil type (USDA)	OC	pH ¹⁾			χ^2 error	Vis. fit ¹⁾	Par.	Value	DT ₅₀ [days]	DT ₉₀ [days]	Kinetic formation fraction $ff^{4)}$
Hoefchen Am Hohenseh 4a;	Silt loam	2.5	6.7	19.1 ⁰ C; 55% MWHC	SFO	10.49	G	k	n. d. ³⁾	1000	>1000	$ff_1 = 0.087$ $ff_2 = 0.736$
Laacherhof AXXa;	Loamy sand	2.4	6.1	19.9 ⁰ C; 55% MWHC	SFO	10.34	G	k	n. d. ³⁾	1000	>1000	$ff_1 = 0.476$ $ff_2 = 0.466$
Dollendorf II;	Clay loam	5.3	7.2	19.9 ⁰ C; 55% MWHC	SFO	9.45	G	k	n. d. ³⁾	1000	>1000	$ff_1 = 0.562$ $ff_2 = 0.578$
Laacherhof Wurm-wiese;	Loam	2.2	5.4	19.9 ⁰ C; 55% MWHC	SFO	9.44	G	k	n. d. ³⁾	1000	>1000	$ff_1 = 0.596$ $ff_2 = 0.345$
Hanscheider Hof	Loam	2.8	5.6	19.9 ⁰ C; 55% MWHC	SFO	4.95	G	k	n. d. ³⁾	1000	>1000	n. d. ³⁾
Frankenforst	Silt loam	1.8	6.8	19.9 ⁰ C; 55% MWHC	SFO	6.72	A	k	n. d. ³⁾	1000	>1000	n. d. ³⁾
LUFA 2.3	Sandy loam	1.1	6.8	19.9 ⁰ C; 55% MWHC	SFO	5.67	A	k	n. d. ³⁾	1000	>1000	n. d. ³⁾
LUFA 6S	Clay	1.9	7.0	19.9 ⁰ C; 55% MWHC	SFO	3.71	A	k	n. d. ³⁾	1000	>1000	n. d. ³⁾
Geometric mean (n = 8)										1000	>1000	----
Arithmetic mean for ff (n = 4)												$ff_1 = 0.430$ $ff_2 = 0.531$

Footnotes to the table:

- 1) Measured in 0.01M CaCl₂;
- 2) The abbreviations used to describe the visual fit: G. – good, A. – acceptable, P. – poor;
- 3) n. d. – not determined
- 4) ff_1 – kinetic formation fraction for formation of TFA from Flufenacet; ff_2 – kinetic formation fraction for formation of TFA from FOE Thiadone.

For GW and SW model exposure assessment the default **DT₅₀ = 1000 days** is a kinetic endpoint recommended as input parameter. The corresponding recommended ff values are $ff_1 = 0.430$ (arithmetic mean) for Flufenacet as a precursor and $ff_2 = 0.531$ (arithmetic mean) for FOE Thiadone as a precursor.

The kinetic endpoints identified by RMS as appropriate to be used in model exposure assessment for soil, groundwater and surface water compartments are summarised below in the table B.8.1.1.2.1.4._CA-15. For completeness also the maximum concentrations observed in soils are provided. That table will be directly transferred to the List of EndPoints.

Table B.8.1.1.2.1.4._CA-15: The kinetic endpoints determined in laboratory studies on aerobic soils, recommended to be used in model exposure assessment for soil, groundwater and surface water compartments.

Compound	Compartment	Recommended endpoints					
		Maximum observed in soil		Kinetic formation fraction - <i>ff</i>		Persistence in soil – <i>DT</i> ₅₀ value	
		Observed soil maximum [%]	Remark	<i>ff</i>	Remark	<i>DT</i> ₅₀ [days]	Remark
Flufenacet	Soil	Not applicable	Not applicable – parent compound	----	Not applicable – parent compound	57.6	Longest not normalised lab value
	Groundwater			----		17.89	Normalised lab geomean value
	Surface Water			----		17.89	Normalised lab geomean value
FOE Sulfonic acid	Soil	26.5	Recommended for simple modelling ¹⁾	0.272	Precursor: flufenacet; highest <i>ff</i> , to be used in complex modelling ²⁾	318	Longest not normalised lab value
	Groundwater	----	Not applicable	0.195	Precursor: flufenacet;	45.11	Normalised lab geomean value
	Surface Water	26.5	To be used in calculations at Steps 1 and 2	0.195	Precursor: flufenacet; to be used in Step 3-4 assessment	45.11	Normalised lab geomean value
FOE Oxalate	Soil	26.3	Recommended for simple modelling ¹⁾	0.484	Precursor: flufenacet; highest <i>ff</i> , to be used in complex modelling ²⁾	18.9	Longest not normalised lab value
	Groundwater	----	Not applicable	0.426	Precursor: flufenacet;	11.08	Normalised lab geomean value
	Surface Water	26.3	To be used in calculations at Steps 1 and 2	0.426	Precursor: flufenacet; to be used in Step 3-4 assessment	11.08	Normalised lab geomean value
FOE Methylsulfone	Soil	6.6	Recommended for simple modelling ¹⁾	0.096	Precursor: flufenacet; highest <i>ff</i> , to be used in complex modelling ²⁾	174	Longest not normalised lab value
	Groundwater	----	Not applicable	0.070	Precursor: flufenacet;	81.70	Normalised lab median value
	Surface Water	6.6	To be used in calculations at Steps 1 and 2	0.070	Precursor: flufenacet; to be used in Step 3-4 assessment	81.70	Normalised lab median value
FOE Thiadone	Soil	5.8	Recommended for simple modelling ¹⁾	0.913	Precursor: flufenacet; highest <i>ff</i> , to be used in complex modelling ²⁾	15.9	Longest not normalised lab value
	Groundwater	----	Not applicable	0.570	Precursor: flufenacet;	1.95	Normalised lab geomean value
	Surface Water	5.8	To be used in calculations at Steps 1 and 2	0.570	Precursor: flufenacet; to be used in Step 3-4 assessment	1.95	Normalised lab geomean value
FOE 5043-Trifluoroethane-sulfonic acid	Soil	6.0	Recommended for simple modelling ¹⁾	0.655	Precursor: Thiadone; highest <i>ff</i> , to be used in complex modelling ²⁾	20.9	Longest not normalised lab value
	Groundwater	----	Not applicable	0.469	Precursor: Thiadone;	6.41	Normalised lab geomean value
	Surface Water	6.0	To be used in calculations at Steps 1 and 2	0.469	Precursor: Thiadone; to be used in Step 3-4 assessment	6.41	Normalised lab geomean value
Trifluoroacetic acid (TFA)	Soil	81.5	Recommended for simple modelling ¹⁾	0.430	Precursor: flufenacet; average <i>ff</i> , to be used in complex modelling ^{2, 3)}	10000	Longest lab value (default)
				0.531	Precursor: Thiadone; average <i>ff</i> , to be used in complex modelling ^{2, 3)}		
	Groundwater	----	Not applicable	0.430	Precursor: flufenacet;	1000	FOCUS default for non-degrading compounds
				0.531	Precursor: Thiadone;		
	Surface Water	81.5	To be used in calculations at Steps 1 and 2	0.430	Precursor: flufenacet; to be used in Step 3-4 assessment	1000	FOCUS default for non-degrading compounds
				0.531	Precursor: Thiadone; to be used in Step 3-4 assessment		

Footnotes to the table:

- 1) By the term “simple modelling” are understood calculations performed using simple models with metabolites applied as parent;
- 2) The term “complex models” concerns calculations performed using more sophisticated tools, e.g. ESCAPE, in which metabolites are calculated as formed from their precursor (parent compound or preceding degradation product);
- 3) For that compound, due to the complex formation scheme, average *ff* values are proposed to be used in complex soil exposure assessment with the average *ff* for Thiadone to be used in case it becomes necessary to recalculate the value to obtain the bet formation of TFA in that process (as if from parent).

Finally, the key results of the two literature studies examining the rate of degradation of Flufenacet in aerobic soil incubated under controlled – laboratory, conditions are presented below in the table B.8.1.1.2.1.4._CA-16. As already indicated, these results may be considered only as indicative and were not used to derive the regulatory endpoints.

Table B.8.1.1.2.1.4._CA-16: The key results of the relevant publications examining the rate of degradation of Flufenacet in aerobic soils.

Study	Test soil	Key soil properties			Incubation conditions		Fortification level [µg a. s./g soil]	Kinetic endpoints – DT ₅₀ [days]		Method of calculation
		Soil type (USDA)	pH	OC [%]	T [°C]	Soil moisture		T=25°C; FC	T=20°C; FC	
<i>Gupta, Gajbhiye, Agnihotri [2001]</i>	Sandy loam	Sandy loam	7.1	0.34	25	FC	1	9.3	13.4	1 st order, linear regression, r =0.99
							10	13.0	20.4	1 st order, linear regression, r =0.99
<i>Gupta, Gajbhiye, [2002]</i>	Dehli sandy loam	US Loamy sand	7.69	0.50	25	FC	1	10.1	15.8	1 st order, linear regression, r =0.99
							10	13.0	20.4	1 st order, linear regression, r =0.99
	Ranchi sandy loam	US Sandy clay loam	5.54	0.04	25	FC	1	10.5	16.5	1 st order, linear regression, r =0.99
							10	21.3	33.4	1 st order, linear regression, r =0.99
	Nagpur clayey soil	US Clay	8.25	0.40	25	FC	1	31.0	48.6	1 st order, linear regression, r =0.99
							10	29.2	45.8	1 st order, linear regression, r =0.94

Anaerobic degradation:

The determination of the kinetic parameters of the process of degradation of Flufenacet in anaerobic soil was performed for the results obtained in two studies, on three soils using the test compound radiolabelled in two different positions:

- uniformly in phenyl ring (one test soil);
- in C5 position of thiadiazole moiety (two test soils).

The conclusions and key results are presented below, individually for each test soil.

- The conclusions and key results obtained for Sandy loam (Howe) soil treated with Phenyl-U-¹⁴C] Flufenacet (study by [Pangilinan and Smith; 1995]):

The kinetic analysis of the data for Flufenacet and its major degradation products – FOE Oxalate and FOE Sulfonic acid, obtained for Sandy loam (Howe) soil incubated under anaerobic conditions demonstrated that:

- The degradation of Flufenacet in that soil was most adequately described by DFOP kinetic model. Therefore that model should be considered as providing the kinetic endpoints describing the persistence of Flufenacet in anaerobic sandy loam soil;
- DFOP kinetic model – its slow phase, should be also considered as providing the kinetic endpoints appropriate for modelling. That conclusion is drawn by the RMS and is different from the Applicant's proposal – to consider the SFO kinetic model as a source of the kinetic endpoints appropriate for modelling. That conclusion is based on the fact that DFOP fit was superior to SFO both when the fitting was performed for the parent compound alone and for the parent and degradation products.
- It was not possible to obtain the reliable kinetic fit for either of the degradation products – FOE Oxalate and FOE Sulfonic acid kinetically examined together with parent. Slightly better results were obtained when the data for these two compounds were fitted alone using the top-down approach. In both cases SFO was identified as returning visually and statistically reliable fits with reliable parameters. RMS however is of the opinion that the kinetic endpoints derived from those fits should be considered indicative with regard to the persistence of both compounds in anaerobic sandy loam soil and cannot be further used to derive any modelling endpoints. It shall be also noted that it was not possible to derive reliable kinetic formation fractions for either FOE Oxalate or FOE Sulfonic acid.

The proposed set of the kinetic endpoints derived from that study is following:

- Flufenacet, persistence endpoints: $DT_{50} = 229.63$ days, $DT_{90} = 895.64$ days, DFOP model ($k_1 = 0.9976$ days⁻¹, $k_2 = 2.416 \text{ E-}3$ days⁻¹, $g = 0.1291$);
- Flufenacet, modelling endpoints not normalised: $k = 2.416 \text{ E-}3$ [days⁻¹], $DT_{50} = 286.90$ days, $DT_{90} = 953.06$ days, SFO (slow phase DFOP);
- Flufenacet, modelling endpoints normalized for temperature: $k = 2.205 \text{ E-}3$ [days⁻¹], $DT_{50} = 314.35$ days, $DT_{90} = 1044.26$ days, SFO (slow phase DFOP);
- FOE Oxalate, persistence endpoints (indicative): $DT_{50} = 311$ days, $DT_{90} = 1030$ days, SFO model – top-down approach ($k = 0.002233$ days⁻¹);
- FOE Sulfonic acid, persistence endpoints (indicative): $DT_{50} = 352$ days, $DT_{90} = 1170$ days, SFO model – top-down approach ($k_1 = 0.001986$ days⁻¹).

- The conclusions and key results obtained for Silt loam (Hoefchen am Hohenseh 4a) soil treated with [Thiadiazole-5-¹⁴C]Flufenacet (study by [Heinemann; 2012]):

The kinetic analysis of the data for Flufenacet and its major degradation products – FOE Thiadone, FOE-5043 Trifluoroethanesulfonic acid and Trifluoroacetic acid, obtained for Silt loam (Hoefchen am Hohenseh 4 a) soil incubated under anaerobic conditions demonstrated that:

- The degradation of Flufenacet in that soil was most adequately described by DFOP kinetic model. Therefore that model should be considered as providing the kinetic endpoints describing the persistence of Flufenacet in anaerobic Silt loam soil;
- DFOP kinetic model – its slow phase, should be also considered as providing the kinetic endpoints appropriate for modelling.
- It was possible to obtain reliable kinetic fit and kinetic endpoints for FOE Thiadone;
- Although it was possible to obtain reliable kinetic fit for Trifluoroacetic acid, the reliable kinetic parameters describing degradation of that compound could not be derived due to the fact that the decline

phase was not reached. Therefore RMS proposed to use the default DT_{50} and DT_{90} values instead of those calculated by the model;

- It was not possible to obtain the reliable kinetic fit for FOE 5043-Trifluoroethanesulfonic acid, therefore for that compound no reliable kinetic endpoints are available. RMS attributed that to the low concentrations of the compound recorded in the test system and their significant scattering, what may indicate that the compound of concern is transient and rapidly degrades in anaerobic silt loam soil.

The proposed set of the kinetic endpoints derived from that study is following:

- Flufenacet, persistence endpoints: $DT_{50} = 22.66$ days, $DT_{90} = 156.90$ days, DFOP model ($k_1 = 0.1214$ days⁻¹, $k_2 = 0.01162$ days⁻¹, $g = 0.3810$);
- Flufenacet, modelling endpoints: $k = 0.01162$ [days⁻¹], $DT_{50} = 59.65$ days, $DT_{90} = 198.16$ days, SFO (slow phase DFOP), normalisation was not required as the experiment was carried out at $T = 20^{\circ}\text{C}$ and the correction for soil moisture was not necessary (soil was permanently flooded);
- FOE Thiadone, persistence and modelling endpoints: $DT_{50} = 97.04$ days, $DT_{90} = 322.30$ days, $ff = 0.425$ (from parent compound), SFO model ($k = 0.0071$ days⁻¹);
- Trifluoroacetic acid persistence endpoints (indicative): $DT_{50} = 1000$ days, $DT_{90} > 1000$ days, $ff = 0.575$ (from parent compound), SFO model;
- FOE 5043-Trifluoroethanesulfonic acid: it was not possible to derive reliable kinetic endpoints.

- The conclusions and key results obtained for Loam (Dollendorf II) soil treated with [Thiadiazole-5-¹⁴C] Flufenacet (study by [Heinemann; 2012]):

The kinetic analysis of the data for Flufenacet and its major degradation products – FOE Thiadone, FOE-5043 Trifluoroethanesulfonic acid and Trifluoroacetic acid, obtained for Loam (Dollendorf II) soil incubated under anaerobic conditions demonstrated that:

- The degradation of Flufenacet in that soil was most adequately described by DFOP kinetic model. Therefore that model should be considered as providing the kinetic endpoints describing the persistence of Flufenacet in anaerobic Silt loam soil;
- DFOP kinetic model – its slow phase, should be also considered as providing the kinetic endpoints appropriate for modelling.
- It was possible to obtain reliable kinetic fit and kinetic endpoints for FOE Thiadone;
- Although it was possible to obtain reliable kinetic fit for Trifluoroacetic acid, the reliable kinetic parameters describing degradation of that compound could not be derived due to the fact that the well pronounced decline phase was not reached. Therefore RMS proposed to use the default DT_{50} and DT_{90} values instead of those calculated by the model;
- It was not possible to obtain the reliable kinetic fit for FOE 5043-Trifluoroethanesulfonic acid, therefore for that compound no reliable kinetic endpoints are available. RMS attributed that to the low concentrations of the compound recorded in the test system and their significant scattering, what may indicate that the compound of concern is transient and rapidly degrades in anaerobic silt loam soil.

The proposed set of the kinetic endpoints derived from that study is following:

- Flufenacet, persistence endpoints: $DT_{50} = 13.51$ days, $DT_{90} = 110.02$ days, DFOP model ($k_1 = 0.4756$ days⁻¹, $k_2 = 0.0167$ days⁻¹, $g = 0.3745$);
- Flufenacet, modelling endpoints not normalised: $k = 0.0167$ [days⁻¹], $DT_{50} = 41.51$ days, $DT_{90} = 137.88$ days, SFO (slow phase DFOP), normalisation was not required as the experiment was carried out at $T = 20^{\circ}\text{C}$ and the correction for soil moisture was not necessary (soil was permanently flooded);
- FOE Thiadone, persistence and modelling endpoints: $DT_{50} = 97.04$ days, $DT_{90} = 322.30$ days, $ff = 0.425$ (from parent compound), SFO model ($k = 0.0071$ days⁻¹);
- Trifluoroacetic acid persistence endpoints (indicative): $DT_{50} = 1000$ days, $DT_{90} > 1000$ days, $ff = 0.575$ (from parent compound), SFO model;
- FOE 5043-Trifluoroethanesulfonic acid: it was not possible to derive reliable kinetic endpoints.

Additionally the results of the determination of the rate of degradation of Flufenacet in anaerobic soils incubated under controlled (laboratory) conditions were provided by two literature studies, summarised under the point B.8.1.1.2.1.1. as **Study 27** and **Study 28**. The key results obtained in these two studies with regard to the rate of degradation of Flufenacet in anaerobic soils are provided in the table B.8.1.1.2.1.4._CA-17. As already indicated, these results may be considered only as indicative and were not used to derive the regulatory endpoints.

Table B.8.1.1.2.1.4._CA-17: The key results of the relevant publications examining the rate of degradation of Flufenacet in anaerobic (submerged) soils.

Study	Test soil	Key soil properties			Incubation conditions		Fortification level [µg a. s./g soil]	Kinetic endpoints – DT ₅₀ [days]		Method of calculation
		Soil type (USDA)	pH	OC [%]	T [°C]	Soil moisture		T=25°C; FC	T=20°C; FC	
<i>Gupta, Gajbhiye, Agnihotri [2001]</i>	Sandy loam	Sandy loam	7.1	0.34	25	FC	10	22.5	35.3	1 st order, linear regression, r =0.99
<i>Gupta, Gajbhiye, [2002]</i>	Dehli sandy loam	US Loamy sand	7.69	0.50	25	FC	10	22.3	35.0	1 st order, linear regression, r =0.99
	Ranchi sandy loam	US Sandy clay loam	5.54	0.04	25	FC	10	24.1	37.8	1 st order, linear regression, r =0.99
	Nagpur clayey soil	US Clay	8.25	0.40	25	FC	10	30.1	47.2	1 st order, linear regression, r =0.93

Soil photolysis:

The photolysis of Flufenacet on the soil surface was examined in one experiment using one soil. Its results were kinetically examined, in line with the recommendations given by FOCUS [2006], by the RMS. The final set of the kinetic endpoints obtained for Flufenacet as a result of that examination is presented below in the table B.8.1.1.2.1.4._CA-18.

Table B.8.1.1.2.1.4._CA-18: The definitive set of the kinetic endpoints obtained for Flufenacet in the study examining soil photolysis of that compound.

Determined parameter	Results obtained for:		
	Dark control samples	Irradiated samples	
		Values not corrected (Suntest days)	Values corrected for summer sunlight intensity (Natural sunlight days) ¹⁾
<i>Rate constant k [days⁻¹]</i>	0.0124	0.076	0.0026
<i>DT₅₀ [days]</i>	55.90	90.72	265.67
<i>DT₉₀ [days]</i>	185.68	301.36	882.55
<i>Kinetic model</i>	SFO	SFO	SFO

Footnotes to the table:

1) values calculated for conditions representative for summer sunny day in Phoenix, AZ, USA – longitude: 33° 27' N

On their basis it can be stated that Flufenacet is not expected to degrade in soil via its photolysis on the soil surface.

The conclusion drawn by the RMS from the study on the basis of the results presented above was following: “The results clearly demonstrate that the degradation of Flufenacet was slower in irradiated samples than in the dark control. On that basis it can be stated that Flufenacet is not prone to the photolysis on the soil surface, hence soil photolysis will not be a relevant mechanism of degradation of Flufenacet in soil.”.

None of the degradation products of Flufenacet requiring further assessment were formed in that study, so the kinetic analysis for them was not performed. However, for one the major soil degradation product of Flufenacet – FOE Thiadone the photodegradation of that compound on the soil surface was examined in a separate study. The results were kinetically examined by the RMS and the definitive data set is presented below in the table B.8.1.1.2.1.4._CA-19.

Table B.8.1.1.2.1.4._CA-19: The definitive set of the kinetic endpoints obtained for FOE Thiadone in the study examining its photolysis on the soil surface.

Determined parameter	Results obtained for:	
	<i>Dark control samples</i>	<i>Irradiated samples</i>
Rate constant k [days ⁻¹]	0.1612	0.2120
DT ₅₀ [days]	4.30	3.27
DT ₉₀ [days]	14.29	10.86
Kinetic model	SFO	SFO

The results demonstrate that photolysis on the soil surface might contribute to degradation of FOE Thiadone in soil.

The net rate constant of the photolysis will be:

$$k_{\text{photolysis}} = k_{\text{irrad}} - k_{\text{dark control}} = 0.2120 - 0.1612 = 0.0508 \text{ [days}^{-1}\text{]}.$$

The resulting kinetic endpoints calculated using that value are: **DT₅₀ = 13.64 days** and **DT₉₀ = 45.33 days**.

At the same time it shall be pointed out however that the probability that that compound would be found on the soil surface in any substantial amounts is minimal. For that reason the process should be considered to have minimal relevance in the overall transformation of Flufenacet in soil.

B.8.1.1.2.2. – Field studies

To cover this data requirement the Applicant submitted seven study reports, of which five examined the soil dissipation of Flufenacet. Two additional studies were aimed on the examination of the storage stability of Flufenacet and its seven soil degradation products in freezed soil. All they are summarised below under the point B.8.1.1.2.2.1. No studies examining the issues of soil residues (data point B.8.1.1.2.2.2.) and soil accumulation (data point B.8.1.1.2.2.3.) were submitted. In case of soil accumulation studies the Applicant gave the justification for their non-submission. No such justification was provided in case of soil residue studies. Still applicable, however, is the justification for not performing them presented in the Assessment Report prepared by the then-RMS – France, for the previous authorisation of Flufenacet in the EU.

B.8.1.1.2.2.1. – Soil dissipation studies

The Applicant submitted four study reports presenting the results of the examination of dissipation of Flufenacet in soil under field conditions. These studies are the existing studies, already used in the previous evaluation of Flufenacet for its authorisation in the EU. They were then found acceptable by the RMS – France and used to derive regulatory endpoints characterising persistence of Flufenacet in soil under field conditions. For the purpose of the present assessment they were evaluated by the RMS – Poland and summarised below as **Studies 1-4**. They contain the kinetic analysis of the results, but it cannot be considered acceptable, being not in line with the recommendations of the current Guidelines, primarily FOCUS Kinetics GD [FOCUS; 2006]. For that reason the RMS performed own kinetic analysis of the data, aimed on the identification of the best-fit kinetic model for Flufenacet and detected degradation products, and the determination of the persistence kinetic endpoints.

The Applicant submitted two other studies, also evaluated for the previous authorisation of Flufenacet in the EU. They presented the results of the examination of storage stability of Flufenacet and its seven degradation products in frozen soil. These studies, being closely related to the four studies examining field dissipation of Flufenacet, are summarised as **Study 5** and **Study 6** immediately after the **Studies 1-4**. They precede the kinetic analysis of the results obtained in **Studies 1-4**.

Finally, the Applicant submitted a new study, summarised as **Study 7**, presenting the results of the kinetic examination of the results of the **Studies 1-4** to determine the modelling kinetic endpoints for Flufenacet and FOE Sulfonic acid.

Additionally the literature search resulted in the identification of three open-source publication identified as relevant for the purpose of the current assessment as source of the supplementary data. They will be summarised at the end of this section as **Studies 8-10**.

Study 1:

Report: Sommer H., (1995): “Dissipation of FOE 5043 in Soil under Field Conditions (Germany, France).” Bayer AG, Crop Protection Business Group, Crop Protection-Development, Institute for Metabolism Research & Residue Analysis, D-51368 Leverkusen-Baywerk, Germany (performing laboratory) *for* Bayer Corporation, Agriculture Division, P. O. Box 4913, Hawthorne Road, Kansas City, MO 64120-0013, USA; Study Report RA-2112/93; Bayer Report No. 107724; 1 September 1995; study reference number: M-002172-01-2;

Guidelines: The study was performed to comply with the following Guidelines:

- BBA Guideline IV-4.1, (1986);
- US. EPA Guidelines for Pesticide Registration, Subdivision N, Section 164-1, Terrestrial Field Dissipation (Supplemental).

GLP: Yes;

RMS comments: The study had been evaluated for the previous authorisation of Flufenacet in the EU, by inclusion of the compound into the Annex I of the Directive 91/414/EEC. Its brief summary can be found under the point B.7.1.2.2., in section B.7 of the Annex B to the Monograph prepared by the RMS – France, for Flufenacet. Assessing it, as well as other three similar studies, the RMS stated that it was acceptable, although at the same time indicated that the study was not triggered, and hence required according to the provisions of the Commission Directive 95/36/EC of the 14th July 1994, amending the Council Directive 91/414/EEC. It was however required according to the provisions of the German BBA guideline for assessing Plant Protection Products, part IV, 4.1.

For the purpose of the current assessment the study was evaluated for its compliance with the following guidelines:

- Lynch M. R., editor, (1995): “Procedures for assessing the environmental fate and ecotoxicology of pesticides.”, SETAC; chapter 3.1. – Soil dissipation study;
- NAFTA Guidance Document for Conducting Terrestrial Field Dissipation Studies, 31 March 2006;
- US EPA Fate, Transport and Transformation Test Guidelines, OPPTS Guideline 835.6100 – Terrestrial Field Dissipation;

Additionally, in the area of the kinetic assessment of the results, it was evaluated for the compliance with the following Guidelines:

- FOCUS (2006): “Guidance Document on Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration.” Report of the FOCUS Work Group on Degradation Kinetics, EC Document Reference SANCO/10058/2005 version 2.0, 434 pp.;
- FOCUS, 2011: “Generic Guidance for Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration.” Version 1.0, Nov. 23, 2011.

The following deviations from the Guidelines cited above were stated:

- The history of the test fields over 5 years preceding the trials was not provided, therefore it is not possible to state whether Flufenacet or other plant protection products belonging to the same group – oxyacetamides, acetamides or amides, were used there during that period;
- The analytical method used in the study was generally adequately characterised, with exception of the instrumental methods used for identification and quantitation of the test compounds. That was indicated solely to be HPLC-MS/MS. However, as the method was declared to be a validated method, it was probably very similar or the same as used in other studies aimed on the determination of the route and rate of degradation of Flufenacet in soil;
- The characteristic of the trial plots was very limited – only the area was provided without the plot’s dimension (width, length) and other physical features usually required, such as the plot’s slope;
- The soil cores were sampled to the depth of 50 cm, while the relevant Guidelines recommend 1-metre deep sampling;
- The kinetic analysis of the results was performed according to Timme and Frehse, the method not compliant with the currently recommended procedure for kinetic evaluation of the data;

- The study report contains the weather data, but reported, for the first 30 days in 7-days intervals, and afterwards in ~30 days intervals; additionally average monthly values and average monthly values of many years are given, what may substantially complicate the normalisation procedure;
- The analysis in the area of degradation products was performed only for the metabolites formed by the degradation within the phenyl moiety – FOE Oxalate, FOE Alcohol, and FOE Sulfonic acid; the would-be fate of Flufenacet within the thiadiazole moiety was not examined.

Despite these deficiencies RMS found the study acceptable and possible to be used for the regulatory purposes, at least as a source of the data characterising persistence of Flufenacet and its selected major soil degradation products in soil under field conditions. The study is summarised below.

Summary:

The aim of the study was to examine the dissipation of Flufenacet and formation and fate of its degradation products in soil under field conditions. The experiment was carried out on eight trial locations, in Germany (four locations) and in France (four locations – two in northern France and two other in southern France). It was performed on bare fields – German trials, and cropped fields - French trials. The characteristic of trial sites is presented below in two tables – table B.8.1.1.2.2.1._CA-1 for German trials and B.8.1.1.2.2.1._CA-2 for French trials.

Table B.8.1.2.2.1._CA-1: The characteristic of the German trial sites.

Information			Trial:			
			Breitenfelde	Kirchlauter ¹⁾	Monheim ²⁾	Burscheid ³⁾
Trial data	Trial code number		30159/0	30162/0	30163/9	30164/7
	Trial location		D-23881 Breitenfelde	D-96166 Kirchlauter	D-40789 Monheim, trial station Laacherhof	D-51399 Burscheid, trial station Hoefchen
	Size of the test plot [m ²]		200	200	255	225
	Duration of the field trial		240 days	237 days	231 days	239 days
	Soil cultivation and maintenance activities	Crop cover	Bare soil	Bare soil	Bare soil	Bare soil
		Date of sowing	Not applicable	Not applicable	Not applicable	Not applicable
		Date of harvest	Not applicable	Not applicable	Not applicable	Not applicable
		Sowing density	Not applicable	Not applicable	Not applicable	Not applicable
		Maintenance practices	Local agricultural practices, mechanical weed control, no irrigation, no PPP used			
	Data on application of the test compound	Test compound	Flufenacet	Flufenacet	Flufenacet	Flufenacet
		Formulation – Test Substance	FOE 5043 60 WG	FOE 5043 60 WG	FOE 5043 60 WG	FOE 5043 60 WG
		Application rate [g a. s./ ha]	480	480	480	480
		Number of applications	1	1	1	1
		Type of application	Spraying	Spraying	Spraying	Spraying
		Application equipment	Agrotop Spraying-boom	Agrotop Spraying-boom	Agrotop Spraying-boom	Agrotop Spraying-boom
		Water rate [L/ha]	300	300	300	300
		Date of application	15/04/1993	13/04/1993	30/04/1993	22/04/1993
		Air temperature at application	14°C	13°C	21°C	20°C
Soil properties for the trial field	Soil textural class	DIN 19682	Silty sand	Heavy sandy loam	Loamy sand	Heavy loamy silt
		USDA	Sandy loam	Not determined	Sandy loam	Silt loam
	Particle size distribution (USDA)	Sand	66.8	No data	69.2	12.8
		Silt	27.6	No data	22.3	69.9
		Clay	5.6	No data	8.5	17.3
	pH (in 0.01M CaCl ₂ aq)		6.2	7.1	6.7	6.5
	OC [%]		1.69	0.61	1.45	0.97
	OM [%]		2.91	1.05	2.49	1.67
	Soil moisture [g/100 g soil d.w.]		38.7	Not reported	41.3	44.6
	N content [mg/100 g soil d.w.]		160	70	100	120

Footnotes to the table:

1) For that trial soil textural class was determined only using DIN 19682;

2) In the study report the trial bore the name "Laacherhof", but to maintain the consistency with the former DAR and other reports RMS renamed it "Monheim";

3) In the study report the trial bore the name "Höfchen", but to maintain the consistency with the former DAR and other reports RMS renamed it "Burscheid".

Table B.8.1.2.2.1._CA-2: The characteristic of the French trial sites.

Information			Trial:			
			<i>Fresne-L'Archeveque</i>	<i>Fresne-L'Archeveque 1</i>	<i>Laudun</i>	<i>St. Etienne du Gres</i>
Trial data	Trial code number		30248/1	30250/3	30251/1	30253/8
	Trial location		F-27700 Fresne-L'Archeveque; Northern France	F-27700 Fresne-L'Archeveque; Northern France	F-30290 Laudun; Southern France	F-13150 St. Etienne du Gres; Southern France
	Size of the test plot [m ²]		312	312	300	300
	Duration of the field trial		303 days	287 days	255 days	260 days
	Soil cultivation and maintenance activities	Crop cover	Maize, variety DK 250	Maize, variety DK 250	Sunflower, variety Erika	Sunflower, variety Erika
		Date of sowing	04/05/1993	24/05/1993	22/04/1993	16/05/1993
		Date of harvest	09/11/1993	19/11/1993	Not given	Not given
		Sowing density [plants/ha]	100000	100000	80800	80800
		Maintenance practices	Local agricultural practices, mechanical weed control, no irrigation, two PPP used ¹⁾	Local agricultural practices, mechanical weed control, no irrigation, two PPP used ¹⁾	Local agricultural practices, mechanical weed control, no irrigation, no PPP used	Local agricultural practices, mechanical weed control, no irrigation, no PPP used
	Data on application of the test compound	Test compound	Flufenacet	Flufenacet	Flufenacet	Flufenacet
		Formulation – Test Substance	FOE 5043 60 WG	FOE 5043 60 WG	FOE 5043 60 WG	FOE 5043 60 WG
		Application rate [g a. s./ha]	600	600	600	600
		Number of applications	1	1	1	1
		Type of application	Spraying	Spraying	Spraying	Spraying
		Application equipment	Knapsack sprayer	Knapsack sprayer	Knapsack sprayer	Knapsack sprayer
		Water rate [L/ha]	280	280	280	280
		Date of application	11/05/1993	27/05/1993	18/05/1993	17/05/1993
		Air temperature at application	18°C	17°C	20°C	24°C
Soil properties for the trial field	Soil textural class	DIN 19682	Loamy silt	Loamy silt	Sandy loamy silt	Sandy loamy silt
		USDA	Silt loam	Silt loam	Loam	Loam
	Particle size distribution (USDA)	Sand	7.7	12.2	37.6	41.6
		Silt	76.6	72.7	46.7	48.2
		Clay	15.7	15.1	15.7	10.2
	pH (in 0.01M CaCl ₂ aq)		6.0	5.2	7.16	7.7
	OC [%]		1.11	1.86	0.62	0.80
	OM [%]		1.91	3.20	1.07	1.38
	Soil moisture [g/100 g soil d.w.]		42.1	50.6	37.3	39.2
	N content [mg/100 g soil d.w.]		140	210	120	130

Footnotes to the table:

1) The information on the use of the Plant Protection Products during the trial is provided in a separate table.

The information provided in the study report on the use of the Plant Protection Products, other than the test compound, in trials Fresne-L'Archeveque and Fresne-L'Archeveque 1 is given below in the table B.8.1.1.2.2.1._CA-3.

Table B.8.1.1.2.2.1._CA-3: The information on the use of other Plant Protection Products in French trials.

Parameter		Trial site			
		<i>Fresne-L'Archeveque – trial 30248/1</i>		<i>Fresne-L'Archeveque 1 – trial 30250/3</i>	
		Pesticide 1	Pesticide 2	Pesticide 1	Pesticide 2
Date of the treatment		04/05/1993	18/06/1993	24/05/1993	24/05/1994
PPP data	Name of the formulation	Dacamox	Cadock	Curater	Gesaprime
	Type of formulation	5 GR	200 + 200 SC	MGR	500 SI
	Active substances	Not specified	Bentazone and atrazine	Not specified	Atrazine
	Content of a. s.	5%	200 g/L each	5%	500 g/L
	Application dose of formulated product	10 kg/ha	2 L/ha	12 kg/ha	4 L/ha

The Test Substance – Flufenacet formulated as FOE 5043 60 WG, was applied at spring to either still bare soil or, in case of one French trial – Laudun 30251/1, soil already having 10%-plant cover (sunflower). Prior to the application from each trial site 50-cm soil cores were sampled for the characterisation of the soil on the test plot.

After application 50-cm soil cores were taken from each test field at pre-designated time point. The sampling points were statistically distributed over the plot to get the representative samples. The cores were taken using a pushing sampling system – Wacker Hammer. The first samples – DAT 0 samples (DAT stands for “Days After Treatment”), were taken directly after application, immediately after drying of the spray film. For that time point, as well as for the last time point, two types of soil cores were sampled for the further analysis – treated samples and control samples (from the non-treated plots). For the remaining time points only the cores from the treated plots were samples. At each sampling interval 20 cores were taken from the treated plot and 10 (for German trial sites) or 20 (for French trial sites) from the control, untreated, plot. The sampled cores were deep-frozen ($T < -18^{\circ}\text{C}$) on the sampling site and on the day of sampling. In that state they were shipped to the laboratory for further analysis. The sampling protocol for each trial site is presented below, in tables B.8.1.1.2.2.1_CA-4 and B.8.1.1.2.2.1_CA-5 for German trials and in tables B.8.1.1.2.2.1_CA-6 and B.8.1.1.2.2.1_CA-7 for French trials. The deep-frozen samples were stored for 2-181 days, depending on the trial and sample, before being processed.

In the laboratory the cores were cut into 10 cm segments and segments from the same layer were milled and homogenised. A part of such sample, further called laboratory samples, was used in the analysis, performed using the internal analytical method developed by Bachlechner and Allemendinger. It consisted of a cold-solvent extraction followed by the qualitative and quantitative analysis using HPLC-MS/MS technique.

The cold-solvent extraction looked as follows: soil samples were extracted by shaking for 60 minutes on mechanic shaker with 100 mL of 0.1N HCl/CH₃CN (1:1) solution. The liquid phase was decanted and purified by filtration. 40 mL of filtrate was concentrated to 5 mL on TurboVap and brought to the volume of 10 mL with 0.4 mL of 37% HCl_{aq}, followed by the appropriate amount of distilled water. After centrifugation the solution was analysed by HPLC-MS/MS. RMS noticed that the used extraction method was almost identical to that described in the open-source publication by [Lam, McKinney and Clay; 2002], summarised as **Study 8** under the point B.8.1.1.1.1. of this Renewal Assessment Report. This may indicate that it may be considered fully appropriate for the purpose it was used for.

The identification and quantitation was performed using HPLC-MS/MS method in comparison to internal standards – deuterised derivatives of the analytes, added after extraction. The qualitative and quantitative analysis was performed for the following compounds: Flufenacet, FOE Alcohol, FOE Oxalate and FOE Sulfonic acid.

The method was validated and controlled by determining the procedural recoveries for each of the test compounds in range 10 – 600 µg/kg. They were following:

- for Flufenacet the mean recovery was 89.6% with RSD = 6.2%;
- for FOE Alcohol the mean recovery was 94.3% with RSD = 4.3%;
- for FOE Oxalate the mean recovery was 96.6% with RSD = 7.9%;
- for FOE Sulfonic acid the mean recovery was 102% with RSD = 3.8%.

The performance of the method was also determined in terms of LOD = 3 µg/kg and LOQ = 10 µg/kg. These values were relevant for each compound of interest.

Additionally were determined the procedural recovery rates for each analysed compound and each trial site. The results are presented in the table B.8.1.1.2.2.1_CA-8. They were used to verify the integrity of the analysis of residues.

The verification of the application rate was performed for each trial site using 0-10 cm layers of sampled soil cores. The resulting values were the averages of four replicates. They were compared to the theoretical concentrations of Flufenacet in soil, calculated using the following assumptions: the compound was evenly distributed in 0-10cm layer and the soil density was 1.5 g/cm³. The theoretical concentrations of the test compound were therefore following:

- for the application rate of 480 g/ha it was **320 µg/kg**;
- for the application rate of 600 g/ha it was **400 µg/kg**.

The detailed results of the verification of application rate for each trial are provided in the table B.8.1.1.2.2.1_CA-9.

The main results of the study are presented in tabularised form further down this summary (tables B.8.1.1.2.2.1_CA-10 – B.8.1.1.2.2.1_CA-19). Finally, on figures B.8.1.1.2.2.1_CA-1 – B.8.1.1.2.2.1_CA-8 are presented the weather data as they were provided in the study report.

Table B.8.1.1.2.2.1_CA-4: The sampling data for the German trials Breitenfelde and Kirchlauter.

Trial: Breitenfelde (30159/0)					Trial: Kirchlauter (30162/0)				
Sampling point - DAT	Type of sample	Soil layer [cm]	Mass of the sample [kg]		Sampling point - DAT	Type of sample	Soil layer [cm]	Mass of the sample [kg]	
			Field sample	Laboratory sample				Field sample	Laboratory sample
0	Control	0-10	16.8	3.02	0	Control	0-10	17.44	2.86
		10-20	16.8	3.20			10-20	17.44	3.48
		20-30	16.8	3.27			20-30	17.44	3.56
		30-40	16.8	3.36			30-40	17.44	3.53
		40-50	16.8	3.19			40-50	17.44	3.48
	Treated	0-10	35.0	6.04		Treated	0-10	36.76	6.04
		10-20	35.0	6.32			10-20	36.76	7.01
		20-30	35.0	6.74			20-30	36.76	7.07
		30-40	35.0	7.00			30-40	36.76	6.90
		40-50	35.0	6.95			40-50	36.76	6.82
7	Treated	0-10	36.30	6.20	7	Treated	0-10	33.87	6.44
		10-20	36.30	6.38			10-20	33.87	6.95
		20-30	36.30	6.87			20-30	33.87	6.95
		30-40	36.30	7.14			30-40	33.87	6.82
		40-50	36.30	6.65			40-50	33.87	6.56
14	Treated	0-10	35.20	5.89	14	Treated	0-10	35.46	6.12
		10-20	35.20	6.28			10-20	35.46	7.12
		20-30	35.20	6.74			20-30	35.46	7.33
		30-40	35.20	7.06			30-40	35.46	7.28
		40-50	35.20	6.56			40-50	35.46	6.70
28	Treated	0-10	34.10	6.08	28	Treated	0-10	35.05	5.77
		10-20	34.10	6.18			10-20	35.05	6.87
		20-30	34.10	6.70			20-30	35.05	6.95
		30-40	34.10	6.91			30-40	35.05	7.07
		40-50	34.10	6.32			40-50	35.05	7.52
56	Treated	0-10	34.00	5.88	56	Treated	0-10	36.08	6.67
		10-20	34.00	6.20			10-20	36.08	7.28
		20-30	34.00	6.73			20-30	36.08	7.58
		30-40	34.00	6.99			30-40	36.08	7.35
		40-50	34.00	6.14			40-50	36.08	5.86
90	Treated	0-10	34.20	6.10	90	Treated	0-10	35.28	6.38
		10-20	34.20	6.46			10-20	35.28	7.16
		20-30	34.20	6.86			20-30	35.28	7.35
		30-40	34.20	6.99			30-40	35.28	7.29
		40-50	34.20	6.58			40-50	35.28	5.37
120	Treated	0-10	36.10	6.61	120	Treated	0-10	34.49	6.54
		10-20	36.10	6.74			10-20	34.49	7.32
		20-30	36.10	7.17			20-30	34.49	7.47
		30-40	36.10	7.43			30-40	34.49	7.49
		40-50	36.10	6.01			40-50	34.49	5.70
180	Treated	0-10	36.40	6.87	181	Treated	0-10	36.83	7.27
		10-20	36.40	6.88			10-20	36.83	7.58
		20-30	36.40	7.11			20-30	36.83	7.65
		30-40	36.40	7.56			30-40	36.83	7.57
		40-50	36.40	5.84			40-50	36.83	5.43
240	Control	0-10	18.10	3.55	237	Control	0-10	18.67	3.67
		10-20	18.10	3.42			10-20	18.67	3.84
		20-30	18.10	3.61			20-30	18.67	3.80
		30-40	18.10	3.61			30-40	18.67	3.69
		40-50	18.10	2.77			40-50	18.67	2.99
	Treated	0-10	36.30	6.83		Treated	0-10	35.81	7.23
		10-20	36.30	6.81			10-20	35.81	7.60
		20-30	36.30	7.18			20-30	35.81	7.40
		30-40	36.30	7.44			30-40	35.81	7.03
		40-50	36.30	6.87			40-50	35.81	5.24

Table B.8.1.1.2.2.1._CA-5 The sampling data for the German trials Monheim and Burscheid.

Trial: Monheim (30163/9)					Trial: Burscheid (30164/7)				
Sampling point - DAT	Type of sample	Soil layer [cm]	Mass of the sample [kg]		Sampling point - DAT	Type of sample	Soil layer [cm]	Mass of the sample [kg]	
			Field sample	Laboratory sample				Field sample	Laboratory sample
0	Control	0-10	17.7	3.03	0	Control	0-10	18.5	3.21
		10-20	17.7	3.26			10-20	18.5	3.38
		20-30	17.7	3.30			20-30	18.5	3.53
		30-40	17.7	3.53			30-40	18.5	3.74
		40-50	17.7	3.57			40-50	18.5	3.57
	Treated	0-10	38.5	6.72		Treated	0-10	36.1	5.40
		10-20	38.5	7.10			10-20	36.1	6.80
		20-30	38.5	7.38			20-30	36.1	7.65
		30-40	38.5	7.69			30-40	36.1	8.10
		40-50	38.5	7.31			40-50	36.1	8.30
7	Treated	0-10	38.2	6.39	7	Treated	0-10	40.6	7.02
		10-20	38.2	7.37			10-20	40.6	7.22
		20-30	38.2	7.56			20-30	40.6	7.59
		30-40	38.2	7.70			30-40	40.6	8.21
		40-50	38.2	6.29			40-50	40.6	8.33
14	Treated	0-10	37.5	6.29	14	Treated	0-10	40.0	7.25
		10-20	37.5	7.05			10-20	40.0	7.36
		20-30	37.5	7.21			20-30	40.0	7.59
		30-40	37.5	7.47			30-40	40.0	8.10
		40-50	37.5	7.35			40-50	40.0	7.24
28	Treated	0-10	35.60	6.68	27	Treated	0-10	40.3	7.42
		10-20	35.60	6.79			10-20	40.3	7.44
		20-30	35.60	7.10			20-30	40.3	7.70
		30-40	35.60	7.16			30-40	40.3	8.02
		40-50	35.60	5.98			40-50	40.3	7.34
56	Treated	0-10	38.50	7.11	60	Treated	0-10	36.70	6.75
		10-20	38.50	7.04			10-20	36.70	6.69
		20-30	38.50	8.09			20-30	36.70	7.05
		30-40	38.50	7.91			30-40	36.70	7.44
		40-50	38.50	5.71			40-50	36.70	6.72
90	Treated	0-10	36.8	6.73	90	Treated	0-10	37.34	6.56
		10-20	36.8	7.20			10-20	37.34	6.87
		20-30	36.0	7.55			20-30	37.34	7.27
		30-40	36.8	7.77			30-40	37.34	7.67
		40-50	36.8	5.33			40-50	37.34	6.47
122	Treated	0-10	36.2	6.54	120	Treated	0-10	37.5	6.76
		10-20	36.2	7.10			10-20	37.5	7.16
		20-30	36.2	7.54			20-30	37.5	7.21
		30-40	36.2	7.72			30-40	37.5	8.47
		40-50	36.2	5.43			40-50	37.5	5.99
180	Treated	0-10	37.6	7.13	180	Treated	0-10	38.2	6.70
		10-20	37.6	7.26			10-20	38.2	7.16
		20-30	37.6	7.67			20-30	38.2	7.66
		30-40	37.6	7.77			30-40	38.2	8.00
		40-50	37.6	5.81			40-50	38.2	6.53
231	Control	0-10	17.30	3.47	239	Control	0-10	18.7	3.43
		10-20	17.30	3.35			10-20	18.7	3.54
		20-30	17.30	3.26			20-30	18.7	3.47
		30-40	17.30	3.39			30-40	18.7	3.81
		40-50	17.30	2.71			40-50	18.7	3.53
	Treated	0-10	38.75	7.58		Treated	0-10	38.1	7.30
		10-20	38.75	7.42			10-20	38.1	7.60
		20-30	38.75	7.61			20-30	38.1	7.12
		30-40	38.75	7.82			30-40	38.1	7.77
		40-50	38.75	6.15			40-50	38.1	6.25

Table B.8.1.1.2.2.1_CA-6: The sampling data for the North-French trials Fresne-L'Archeveque and Fresne-L'Archeveque 1

Trial: Fresne-L'Archeveque (30248/1)					Trial: Fresne-L'Archeveque 1 (30250/3)				
Sampling point - DAT	Type of sample	Soil layer [cm]	Mass of the sample [kg]		Sampling point - DAT	Type of sample	Soil layer [cm]	Mass of the sample [kg]	
			Field sample	Laboratory sample				Field sample	Laboratory sample
0	Control	0-10	37.4	6.65	0	Control	0-10	34.30	6.34
		10-20	37.4	7.38			10-20	34.30	6.49
		20-30	37.4	7.57			20-30	34.30	6.93
		30-40	37.4	7.60			30-40	34.30	7.03
		40-50	37.4	6.20			40-50	34.30	5.66
	Treated	0-10	36.0	5.98		Treated	0-10	34.70	5.88
		10-20	36.0	7.17			10-20	34.70	6.64
		20-30	36.0	7.39			20-30	34.70	7.04
		30-40	36.0	7.53			30-40	34.70	7.18
		40-50	36.0	5.86			40-50	34.70	6.14
14	Treated	0-10	35.8	6.17	8	Treated	0-10	34.00	5.86
		10-20	35.8	7.02			10-20	34.00	6.39
		20-30	35.8	7.27			20-30	34.00	6.83
		30-40	35.8	7.42			30-40	34.00	6.98
		40-50	35.8	6.02			40-50	34.00	6.19
28	Treated	0-10	35.1	5.69	28	Treated	0-10	33.20	5.66
		10-20	35.1	6.76			10-20	33.20	6.21
		20-30	35.1	7.08			20-30	33.20	6.69
		30-40	35.1	7.08			30-40	33.20	6.92
		40-50	35.1	6.43			40-50	33.20	6.09
56	Treated	0-10	36.0	6.50	56	Treated	0-10	33.00	5.97
		10-20	36.0	7.07			10-20	33.00	5.99
		20-30	36.0	7.32			20-30	33.00	6.63
		30-40	36.0	7.18			30-40	33.00	6.82
		40-50	36.0	5.96			40-50	33.00	6.00
90	Treated	0-10	34.5	6.10	91	Treated	0-10	30.80	5.21
		10-20	34.5	6.76			10-20	30.80	5.76
		20-30	34.5	6.92			20-30	30.80	6.35
		30-40	34.5	7.07			30-40	30.80	6.41
		40-50	34.5	6.04			40-50	30.80	5.60
120	Treated	0-10	33.0	5.77	120	Treated	0-10	32.40	5.74
		10-20	33.0	6.47			10-20	32.40	6.27
		20-30	33.0	6.61			20-30	32.40	6.71
		30-40	33.0	6.54			30-40	32.40	6.61
		40-50	33.0	5.74			40-50	32.40	4.96
181	Treated	0-10	36.85	6.85	193	Treated	0-10	33.90	6.03
		10-20	36.85	7.03			10-20	33.90	6.30
		20-30	36.85	7.18			20-30	33.90	6.90
		30-40	36.85	7.38			30-40	33.90	7.02
		40-50	36.85	6.53			40-50	33.90	6.00
303	Control	0-10	36.35	6.87	287	Control	0-10	33.90	6.07
		10-20	36.35	6.79			10-20	33.90	6.19
		20-30	36.35	7.03			20-30	33.90	6.57
		30-40	36.35	7.19			30-40	33.90	6.80
		40-50	36.35	6.82			40-50	33.90	6.54
	Treated	0-10	36.48	6.97		Treated	0-10	33.55	5.95
		10-20	36.48	6.76			10-20	33.55	6.20
		20-30	36.48	6.90			20-30	33.55	6.64
		30-40	36.48	7.30			30-40	33.55	6.77
		40-50	36.48	6.90			40-50	33.55	6.27

Table B.8.1.1.2.2.1._CA-7: The sampling data for the South-French trials Laudun and St. Etienne du Gres.

Trial: Laudun (30251/1)					Trial: St. Etienne du Gres (30253/8)				
Sampling point - DAT	Type of sample	Soil layer [cm]	Mass of the sample [kg]		Sampling point - DAT	Type of sample	Soil layer [cm]	Mass of the sample [kg]	
			Field sample	Laboratory sample				Field sample	Laboratory sample
0	Control	0-10	36.70	6.00	0	Control	0-10	35.70	5.706
		10-20	36.70	7.07			10-20	35.70	6.69
		20-30	36.70	7.50			20-30	35.70	7.09
		30-40	36.70	7.57			30-40	35.70	7.30
		40-50	36.70	6.19			40-50	35.70	6.35
	Treated	0-10	36.05	5.73		Treated	0-10	35.40	5.66
		10-20	36.05	7.03			10-20	35.40	6.83
		20-30	36.05	7.29			20-30	35.40	7.07
		30-40	36.05	7.63			30-40	35.40	7.38
		40-50	36.05	6.33			40-50	35.40	6.26
7	Treated	0-10	36.00	6.06	7	Treated	0-10	37.60	5.88
		10-20	36.00	7.11			10-20	37.60	6.96
		20-30	36.00	7.34			20-30	37.60	7.18
		30-40	36.00	7.54			30-40	37.60	7.68
		40-50	36.00	5.84			40-50	37.60	6.47
15	Treated	0-10	34.00	6.08	15	Treated	0-10	34.80	5.33
		10-20	34.00	6.33			10-20	34.80	6.58
		20-30	34.00	6.61			20-30	34.80	6.84
		30-40	34.00	7.35			30-40	34.80	7.15
		40-50	34.00	5.93			40-50	34.80	6.35
28	Treated	0-10	34.00	6.91	28	Treated	0-10	33.80	5.96
		10-20	34.00	6.29			10-20	33.80	6.45
		20-30	34.00	6.31			20-30	33.80	6.65
		30-40	34.00	6.65			30-40	33.80	7.20
		40-50	34.00	6.27			40-50	33.80	5.84
55	Treated	0-10	33.00	6.74	56	Treated	0-10	32.80	6.37
		10-20	33.00	6.52			10-20	32.80	6.46
		20-30	33.00	6.58			20-30	32.80	6.42
		30-40	33.00	6.99			30-40	32.80	6.94
		40-50	33.00	4.62			40-50	32.80	4.72
87	Treated	0-10	31.00	5.71	87	Treated	0-10	30.50	5.57
		10-20	31.00	5.86			10-20	30.50	5.71
		20-30	31.00	6.01			20-30	30.50	5.84
		30-40	31.00	6.57			30-40	30.50	6.55
		40-50	31.00	5.34			40-50	30.50	4.90
119	Treated	0-10	31.10	5.99	119	Treated	0-10	32.10	6.28
		10-20	31.10	5.96			10-20	32.10	6.19
		20-30	31.10	5.57			20-30	32.10	6.16
		30-40	31.10	6.52			30-40	32.10	6.63
		40-50	31.10	5.48			40-50	32.10	5.18
182	Treated	0-10	38.00	6.23	182	Treated	0-10	38.00	6.99
		10-20	38.00	7.10			10-20	38.00	7.26
		20-30	38.00	7.46			20-30	38.00	7.71
		30-40	38.00	7.78			30-40	38.00	7.81
		40-50	38.00	5.19			40-50	38.00	5.42
255	Control	0-10	36.80	7.02	260	Control	0-10	37.00	7.09
		10-20	36.80	6.81			10-20	37.00	7.05
		20-30	36.80	7.49			20-30	37.00	7.71
		30-40	36.80	7.78			30-40	37.00	7.23
		40-50	36.80	5.67			40-50	37.00	5.77
	Treated	0-10	36.20	6.37		Treated	0-10	36.00	6.77
		10-20	36.20	6.94			10-20	36.00	6.90
		20-30	36.20	7.26			20-30	36.00	7.30
		30-40	36.20	7.66			30-40	36.00	7.55
		40-50	36.20	6.09			40-50	36.00	5.63

Next table – B.8.1.1.2.2.1._CA-8, provides the results of the determination of recovery rates for each analyte during analyses. It is followed by the table B.8.1.1.2.2.1._CA-9 presenting the results of the verification of the application rate for each trial site.

Table B.8.1.1.2.2.1_CA-8: The results of the verification of the recovery rates for each analyte during the analysis of the collected samples.

Compound	Parameter	Results for the trial:							
		<i>Breitenfelde</i> (30159/0) Germany	<i>Kirchlauter</i> (30162/0) Germany	<i>Monheim</i> (30163/9) Germany	<i>Burscheid</i> (30164/7) Germany	<i>Fresne- L'Archeveque</i> (30248/1) North France	<i>Fresne- L'Archeveque</i> 1 (30250/3) North France	<i>Laudun</i> (30251/1) South France	<i>St. Etienne du Gres</i> (30253/8) South France
<i>Flufenacet</i>	Recovery rate [%]	91.0	90.6	90.5	89.4	91.3	88.6	91.8	88.1
	RSD [%]	4.1	2.6	3.0	3.7	5.4	4.8	3.7	4.4
	Number of experiments	12	8	10	7	8	7	8	10
<i>FOE Alcohol</i>	Recovery rate [%]	92.2	90.8	91.2	89.3	90.9	89.2	90.5	88.6
	RSD [%]	3.4	2.9	2.8	2.0	2.8	4.5	2.4	2.6
	Number of experiments	12	8	10	8	8	7	8	10
<i>FOE Oxalate</i>	Recovery rate [%]	79.0	75.0	78.4	79.3	80.8	79.6	81.3	81.3
	RSD [%]	2.9	7.1	2.4	2.7	2.7	1.3	3.7	2.8
	Number of experiments	12	8	10	8	8	7	8	10
<i>FOE Sulfonic acid</i>	Recovery rate [%]	97.9	98.2	97.4	96.6	98.6	98.6	98.6	98.0
	RSD [%]	3.1	2.2	2.2	3.0	1.7	1.8	2.2	3.0
	Number of experiments	12	8	10	8	8	7	8	10

Table B.8.1.1.2.2.1_CA-9: The results of the verification of the application rate for each trial site.

Trial	Application rate [g Flufenacet/ha]	Theoretical DAT-0 concentration of Flufenacet in top 10-cm soil layer [µg/kg soil]	Measured DAT-0 concentration of Flufenacet in top 10-cm soil layer [µg/kg soil]	Measured DAT-0 concentration of Flufenacet in top soil as % of Theoretical concentration
<i>Breitenfelde (30159/0); Germany</i>	480	320	236	73.8
<i>Kirchlauter (30162/0); Germany</i>	480	320	239	74.7
<i>Monheim (30163/9); Germany</i>	480	320	152	47.5
<i>Burscheid (30164/7); Germany</i>	480	320	331	103
<i>Fresne-L'Archeveque (30248/1); North France</i>	600	400	362	90.5
<i>Fresne-L'Archeveque 1 (30250/3); North France</i>	600	400	273	68.3
<i>Laudun (30251/1); South France</i>	600	400	376	94.0
<i>St. Etienne du Gres (30253/8); South France</i>	600	400	280	70.0

Below are presented the results of the study: the concentrations in [$\mu\text{g/kg}$] of Flufenacet and its degradation products – FOE Alcohol, FOE Oxalate and FOE Sulfonic acid, in soil for each trial. The results for German trial sites are presented in five tables. Table B.8.1.1.2.2.1._CA-10 provides the values obtained in samples from the control plots. Next, in tables B.8.1.1.2.2.1._CA-11 – B.8.1.1.2.2.1._CA-14, are provided the values for the treated plots, individually for each trial site. The values are given only for the the layers down to 30-cm depth. That was due to the fact that in case of Flufenacet the measurable residues – above the LOQ = 10 $\mu\text{g/kg}$, were found predominantly in the top layer 0-10 cm, and sporadically in the lower 10-20-cm layer. In the layer 20-30 cm Flufenacet was not detected, so in the study report it was stated that deeper its concentrations were also below the LOD = 3 $\mu\text{g/kg}$.

In case of the degradation products – FOE Alcohol, FOE Oxalate and FOE Sulfonic acid, their residues, if detected, were found in the top 0-10 cm layer. In the lower layers – 10-20 cm and 20-30 cm these compounds, if detected, were in amounts < LOQ (10 $\mu\text{g/kg}$). Additionally it was stated that in almost all cases they were < LOD (3 $\mu\text{g/kg}$), so in fact were not detected in deeper soil layers.

As a result the layers 30-40 cm and 40-50 cm were not analysed and consequently not taken into account in tables reporting the results.

Table B.8.1.1.2.2.1._CA-10: The results of the determination of the concentrations of the test compounds in samples from control (untreated) plots obtained in German trials.

Results obtained for the trial: Breitenfelde (30159/0)					
Sampling point - DAT	Soil layer [cm]	Concentration [$\mu\text{g/kg}$] of:			
		Flufenacet	FOE Alcohol	FOE Oxalate	FOE Sulfonic acid
0	0-10	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
	10-20	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
	20-30	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
240	0-10	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
	10-20	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
	20-30	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
Results obtained for the trial: Kirchlauter (30162/0)					
Sampling point - DAT	Soil layer [cm]	Concentration [$\mu\text{g/kg}$] of:			
		Flufenacet	FOE Alcohol	FOE Oxalate	FOE Sulfonic acid
0	0-10	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
	10-20	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
	20-30	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
237	0-10	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
	10-20	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
	20-30	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
Results obtained for the trial: Monheim (30163/9)					
Sampling point - DAT	Soil layer [cm]	Concentration [$\mu\text{g/kg}$] of:			
		Flufenacet	FOE Alcohol	FOE Oxalate	FOE Sulfonic acid
0	0-10	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
	10-20	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
	20-30	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
231	0-10	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
	10-20	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
	20-30	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
Results obtained for the trial: Burscheid (30164/7)					
Sampling point - DAT	Soil layer [cm]	Concentration [$\mu\text{g/kg}$] of:			
		Flufenacet	FOE Alcohol	FOE Oxalate	FOE Sulfonic acid
0	0-10	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
	10-20	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
	20-30	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
239	0-10	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
	10-20	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
	20-30	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾

Footnotes to the table:

1) n. d. = not detectable – the values below the LOD = 3 $\mu\text{g/kg}$ soil.

Table B.8.1.1.2.2.1_CA-11: The results of the determination of the concentrations of the test compounds in samples from treated plot obtained in the German trial Breitenfelde (30159/0).

Sampling point - DAT	Soil layer [cm]	Concentration of Flufenacet [µg/kg]					Concentration of FOE Alcohol [µg/kg]				
		Rep1	Rep 2	Rep 3	Rep 4	Mean	Rep1	Rep 2	Rep 3	Rep 4	Mean
0	0-10	237.8	240.0	231.0	236.9	236	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	< 10 ³⁾	< 10 ³⁾	---- ⁵⁾	---- ⁵⁾	< 10 ³⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
7	0-10	247.2	265.1	262.8	250.1	256	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
14	0-10	155.7	154.8	157.7	156.9	156	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	< 10 ³⁾	< 10 ³⁾	---- ⁵⁾	---- ⁵⁾	< 10 ³⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
28	0-10	145.4	131.5	138.8	133.9	137	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	< 10 ³⁾	< 10 ³⁾	---- ⁵⁾	---- ⁵⁾	< 10 ³⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
56	0-10	89.46	89.82	88.04	84.95	88.1	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
90	0-10	33.29	32.80	31.65	31.57	32.3	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
120	0-10	11.08	11.77	11.48	11.63	11.5	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
180	0-10	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
240	0-10	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
Sampling point - DAT	Soil layer [cm]	Concentration of FOE Oxalate [µg/kg]					Concentration of FOE Sulfonic acid [µg/kg]				
		Rep1	Rep 2	Rep 3	Rep 4	Mean	Rep1	Rep 2	Rep 3	Rep 4	Mean
0	0-10	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
7	0-10	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
14	0-10	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	< 10 ³⁾	< 10 ³⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
28	0-10	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
56	0-10	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	13.62	15.81	14.72	13.63	14.5
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
90	0-10	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	12.05	12.19	13.70	13.18	12.8
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
120	0-10	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
180	0-10	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
240	0-10	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾

Footnotes to the table:

- 1) for that layer usually the values for two replicates were reported;
- 2) for that layer the values for two or, more commonly, one replicate were reported;
- 3) <10 = values below the LOQ = 10 µg/kg soil;
- 4) n. d. = not detectable – the values below the LOD = 3 µg/kg soil.
- 5) No value.

Table B.8.1.1.2.2.1_CA-12: The results of the determination of the concentrations of the test compounds in samples from treated plot obtained in the German trial Kirchlauter (30162/0).

Sampling point - DAT	Soil layer [cm]	Concentration of Flufenacet [µg/kg]					Concentration of FOE Alcohol [µg/kg]				
		Rep1	Rep 2	Rep 3	Rep 4	Mean	Rep1	Rep 2	Rep 3	Rep 4	Mean
0	0-10	242.4	232.4	249.5	232.5	239	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	20.98	21.59	---- ⁵⁾	---- ⁵⁾	21.3	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
7	0-10	202.5	214.3	200.9	211.6	207	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
14	0-10	215.4	215.1	207.8	212.9	213	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	< 10 ³⁾	< 10 ³⁾	---- ⁵⁾	---- ⁵⁾	< 10 ³⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
28	0-10	295.9	257.3	279.5	276.2	277	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	< 10 ³⁾	< 10 ³⁾	---- ⁵⁾	---- ⁵⁾	< 10 ³⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
56	0-10	102.0	111.5	111.3	113.0	110	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
90	0-10	82.41	80.21	84.91	78.32	81.5	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
120	0-10	46.58	43.15	45.90	45.36	45.2	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
181	0-10	25.80	25.49	24.52	25.63	25.4	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
237	0-10	12.74	11.95	11.93	12.11	12.2	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
Sampling point - DAT	Soil layer [cm]	Concentration of FOE Oxalate [µg/kg]					Concentration of FOE Sulfonic acid [µg/kg]				
		Rep1	Rep 2	Rep 3	Rep 4	Mean	Rep1	Rep 2	Rep 3	Rep 4	Mean
0	0-10	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
7	0-10	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
14	0-10	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
28	0-10	< 10 ³⁾	n. d. ⁴⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	n. d. ⁴⁾	< 10 ³⁾	n. d. ⁴⁾	n. d. ⁴⁾	< 10 ³⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
56	0-10	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
90	0-10	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	10.20	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
120	0-10	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
181	0-10	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	< 10 ³⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	< 10 ³⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
237	0-10	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾

Footnotes to the table:

- 1) for that layer usually the values for two replicates were reported;
- 2) for that layer the values for two or, more commonly, one replicate were reported;
- 3) <10 = values below the LOQ = 10 µg/kg soil;
- 4) n. d. = not detectable – the values below the LOD = 3 µg/kg soil.
- 5) No value.

Table B.8.1.1.2.2.1_CA-13: The results of the determination of the concentrations of the test compounds in samples from treated plot obtained in the German trial Monheim (30163/9).

Sampling point - DAT	Soil layer [cm]	Concentration of Flufenacet [µg/kg]					Concentration of FOE Alcohol [µg/kg]				
		Rep1	Rep 2	Rep 3	Rep 4	Mean	Rep1	Rep 2	Rep 3	Rep 4	Mean
0	0-10	144.5	152.9	149.6	162.1	152	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
7	0-10	168.6	177.6	165.9	174.3	172	n. d. ⁴⁾	< 10 ³⁾	n. d. ⁴⁾	n. d. ⁴⁾	< 10 ³⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
14	0-10	173.8	187.0	164.3	165.7	173	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
28	0-10	145.9	149.4	149.7	151.9	149	n. d. ⁴⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
56	0-10	69.29	67.80	64.83	64.04	66.7	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
90	0-10	28.77	29.25	29.94	29.12	29.3	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
122	0-10 ⁶⁾	21.77	21.43	23.01	23.33	22.1	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
		22.03	21.43	21.97	21.84						
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
180	0-10	15.74	17.27	15.87	15.68	16.1	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
231	0-10	11.68	11.92	10.98	12.11	11.7	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
Sampling point - DAT	Soil layer [cm]	Concentration of FOE Oxalate [µg/kg]					Concentration of FOE Sulfonic acid [µg/kg]				
		Rep1	Rep 2	Rep 3	Rep 4	Mean	Rep1	Rep 2	Rep 3	Rep 4	Mean
0	0-10	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
7	0-10	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
14	0-10	n. d. ⁴⁾	n. d. ⁴⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
28	0-10	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
56	0-10	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
90	0-10	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	< 10 ³⁾	n. d. ⁴⁾	< 10 ³⁾	< 10 ³⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
122	0-10 ⁶⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	< 10 ³⁾	< 10 ³⁾	n. d. ⁴⁾	< 10 ³⁾	< 10 ³⁾
		n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾		< 10 ³⁾	< 10 ³⁾	n. d. ⁴⁾	n. d. ⁴⁾	
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
180	0-10	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
231	0-10	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾

Footnotes to the table:

1) For that layer usually the values for two replicates were reported;

2) for that layer the values for two or, more commonly, one replicate were reported;

3) <10 = values below the LOQ = 10 µg/kg soil;

4) n. d. = not detectable – the values below the LOD = 3 µg/kg soil.

5) No value.

6) For this time point, for the parent compound and FOE Sulfonic acid eight replicates were analysed. Each value is reported in the individual cell; RMS decided not to alter the general outline of the reporting table.

Table B.8.1.1.2.2.1_CA-14: The results of the determination of the concentrations of the test compounds in samples from treated plot obtained in the German trial Burscheid (30164/7).

Sampling point - DAT	Soil layer [cm]	Concentration of Flufenacet [µg/kg]					Concentration of FOE Alcohol [µg/kg]				
		Rep1	Rep 2	Rep 3	Rep 4	Mean	Rep1	Rep 2	Rep 3	Rep 4	Mean
0	0-10	323.3	313.0	363.7	322.5	331	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
7	0-10	211.6	209.8	219.7	205.5	212	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	< 10 ³⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	< 10 ³⁾
14	0-10	169.7	160.8	181.1	183.6	174	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	< 10 ³⁾	< 10 ³⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
27	0-10	108.1	110.1	102.2	109.8	108	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
60	0-10	26.56	26.54	25.38	25.57	26.0	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
90	0-10	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
120	0-10	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
180	0-10	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
239	0-10	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾

Sampling point - DAT	Soil layer [cm]	Concentration of FOE Oxalate [µg/kg]					Concentration of FOE Sulfonic acid [µg/kg]				
		Rep1	Rep 2	Rep 3	Rep 4	Mean	Rep1	Rep 2	Rep 3	Rep 4	Mean
0	0-10	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
7	0-10	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
14	0-10	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
27	0-10	n. d. ⁴⁾	< 10 ³⁾	n. d. ⁴⁾	< 10 ³⁾	< 10 ³⁾	n. d. ⁴⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
60	0-10	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	< 10 ³⁾	< 10 ³⁾	---- ⁵⁾	---- ⁵⁾	< 10 ³⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
90	0-10	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
120	0-10	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
180	0-10	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
239	0-10	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾

Footnotes to the table:

- 1) for that layer usually the values for two replicates were reported;
- 2) for that layer the values for two or, more commonly, one replicate were reported;
- 3) <10 = values below the LOQ = 10 µg/kg soil;
- 4) n. d. = not detectable – the values below the LOD = 3 µg/kg soil.
- 5) No value.

The results for French trial sites are presented in five table. Table B.8.1.1.2.2.1._CA-15 is summarising the values obtained in samples from the control plots. The tables - B.8.1.1.2.2.1._CA-16 – B.8.1.1.2.2.1._CA-19 provide the results for the treated plots, individually for each trial site. The values are given only for the the layers down to 30-cm depth. That was due to the fact that in case of Flufenacet the measurable residues – above the LOQ = 10 µg/kg, were found predominantly in the top layer 0-10 cm, and sporadically in the lower 10-20-cm layer. In the layer 20-30 cm Flufenacet was not detected, so in the study report it was stated that its concentrations there were below the LOD = 3 µg/kg.

In case of the degradation products – FOE Alcohol, FOE Oxalate and FOE Sulfonic acid, their residues, if detected, were found in the top 0-10 cm layer. In the lower layers – 10-20 cm and 20-30 cm these compounds, if detected, were in amounts < LOQ (10 µg/kg). Additionally it was stated that in almost all cases they were < LOD (3 µg/kg), so in fact were not detected in deeper soil layers.

As a result the layers 30-40 cm and 40-50 cm were not analysed and consequently not taken into account in tables reporting the results.

Table B.8.1.1.2.2.1._CA-15: The results of the determination of the concentrations of the test compounds in samples from control (untreated) plots obtained in French trials.

Results obtained for the trial: Fresne-L'Archeveque, North France (30248/1)					
Sampling point - DAT	Soil layer [cm]	Concentration [µg/kg] of:			
		Flufenacet	FOE Alcohol	FOE Oxalate	FOE Sulfonic acid
0	0-10	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
	10-20	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
	20-30	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
303	0-10	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
	10-20	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
	20-30	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
Results obtained for the trial: Fresne-L'Archeveque 1, North France ((30250/3)					
Sampling point - DAT	Soil layer [cm]	Concentration [µg/kg] of:			
		Flufenacet	FOE Alcohol	FOE Oxalate	FOE Sulfonic acid
0	0-10	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
	10-20	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
	20-30	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
287	0-10	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
	10-20	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
	20-30	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
Results obtained for the trial: Laudun, South France (30251/1)					
Sampling point - DAT	Soil layer [cm]	Concentration [µg/kg] of:			
		Flufenacet	FOE Alcohol	FOE Oxalate	FOE Sulfonic acid
0	0-10	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
	10-20	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
	20-30	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
255	0-10	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
	10-20	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
	20-30	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
Results obtained for the trial: St. Etienne du Gres, South France (30253/8)					
Sampling point - DAT	Soil layer [cm]	Concentration [µg/kg] of:			
		Flufenacet	FOE Alcohol	FOE Oxalate	FOE Sulfonic acid
0	0-10	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
	10-20	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
	20-30	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
260	0-10	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
	10-20	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
	20-30	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾

Footnotes to the table:

1) n. d. = not detectable – the values below the LOD = 3 µg/kg soil.

Table B.8.1.1.2.2.1_CA-16: The results of the determination of the concentrations of the test compounds in samples from treated plot obtained in the North French trial Fresne-L'Archeveque (30248/1).

Sampling point - DAT	Soil layer [cm]	Concentration of Flufenacet [µg/kg]					Concentration of FOE Alcohol [µg/kg]				
		Rep1	Rep 2	Rep 3	Rep 4	Mean	Rep1	Rep 2	Rep 3	Rep 4	Mean
0	0-10	370.9	367.8	335.4	374.5	362	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
14	0-10	200.2	200.8	221.4	212.3	209	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
28	0-10	232.7	229/4	232.9	233.5	232	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
56	0-10	124.5	132.9	119.0	121.3	124	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
90	0-10	92.41	90.94	95.29	92.68	92.8	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
120	0-10	54.47	57.12	56.83	57.47	56.5	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
181	0-10	29.91	28.91	31.41	30.46	30.2	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
303	0-10	22.67	24.92	24.01	23.24	23.7	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
Sampling point - DAT	Soil layer [cm]	Concentration of FOE Oxalate [µg/kg]					Concentration of FOE Sulfonic acid [µg/kg]				
		Rep1	Rep 2	Rep 3	Rep 4	Mean	Rep1	Rep 2	Rep 3	Rep 4	Mean
0	0-10	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
14	0-10	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
28	0-10	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	14.44	13.33	14.50	13.30	13.9
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
56	0-10	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	10.8	< 10 ³⁾	< 10 ³⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
90	0-10	n. d. ⁴⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	10.51	11.31	11.88	11.30	11.3
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
120	0-10	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	11.45	11.02	10.39	< 10 ³⁾	< 10 ³⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
181	0-10	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	< 10 ³⁾	n. d. ⁴⁾	< 10 ³⁾	n. d. ⁴⁾	< 10 ³⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
303	0-10	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾

Footnotes to the table:

- 1) for that layer usually the values for two replicates were reported;
- 2) for that layer the values for two or, more commonly, one replicate were reported;
- 3) <10 = values below the LOQ = 10 µg/kg soil;
- 4) n. d. = not detectable – the values below the LOD = 3 µg/kg soil.
- 5) No value.

Table B.8.1.1.2.2.1_CA-17: The results of the determination of the concentrations of the test compounds in samples from treated plot obtained in the North French trial Fresne-L'Archeveque 1 (30250/3).

Sampling point - DAT	Soil layer [cm]	Concentration of Flufenacet [µg/kg]					Concentration of FOE Alcohol [µg/kg]				
		Rep1	Rep 2	Rep 3	Rep 4	Mean	Rep1	Rep 2	Rep 3	Rep 4	Mean
0	0-10	258.2	273.4	283.3	278.7	273	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	< 10 ³⁾	< 10 ³⁾	---- ⁵⁾	---- ⁵⁾	< 10 ³⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
8	0-10	300.9	293.7	303.7	287.9	297	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
28	0-10	183.9	186.6	183.8	172.7	182	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	< 10 ³⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	< 10 ³⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
56	0-10	116.4	114.1	109.6	108.2	112	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
91	0-10	80.72	78.14	81.93	83.23	81.0	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
120	0-10	67.78	64.23	65.05	61.77	64.7	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
193	0-10	39.86	37.95	38.05	39.54	38.9	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
287	0-10	16.58	17.30	18.04	17.18	17.3	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
Sampling point - DAT	Soil layer [cm]	Concentration of FOE Oxalate [µg/kg]					Concentration of FOE Sulfonic acid [µg/kg]				
		Rep1	Rep 2	Rep 3	Rep 4	Mean	Rep1	Rep 2	Rep 3	Rep 4	Mean
0	0-10	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
8	0-10	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
28	0-10	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
56	0-10	11.35	10.70	< 10 ³⁾	10.65	< 10 ³⁾	10.54	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
91	0-10	12.22	12.77	12.19	12.15	12.3	11.61	13.23	10.09	12.91	12.0
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
120	0-10	10.48	11.18	11.05	10.53	10.8	11.72	10.42	11.37	12.34	11.5
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
193	0-10	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
287	0-10	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾

Footnotes to the table:

- 1) for that layer usually the values for two replicates were reported;
- 2) for that layer the values for two or, more commonly, one replicate were reported;
- 3) <10 = values below the LOQ = 10 µg/kg soil;
- 4) n. d. = not detectable – the values below the LOD = 3 µg/kg soil.
- 5) No value.

Table B.8.1.1.2.2.1_CA-18: The results of the determination of the concentrations of the test compounds in samples from treated plot obtained in the South French trial Laudun (30251/1).

Sampling point - DAT	Soil layer [cm]	Concentration of Flufenacet [µg/kg]					Concentration of FOE Alcohol [µg/kg]				
		Rep1	Rep 2	Rep 3	Rep 4	Mean	Rep1	Rep 2	Rep 3	Rep 4	Mean
0	0-10	360.5	366.1	388.7	390.4	376	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	< 10 ³⁾	< 10 ³⁾	---- ⁵⁾	---- ⁵⁾	< 10 ³⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
7	0-10	282.6	288.2	294.4	288.9	289	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	< 10 ³⁾	< 10 ³⁾	---- ⁵⁾	---- ⁵⁾	< 10 ³⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
15	0-10	320.8	295.7	303.8	321.0	310	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
28	0-10	214.7	183.8	211.1	197.0	202	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
55	0-10	76.92	69.82	89.27	83.17	79.8	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
87	0-10	40.41	44.61	45.50	39.23	42.4	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	< 10 ³⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	< 10 ³⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
119	0-10	28.26	28.65	29.45	25.43	27.9	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
182	0-10	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
255	0-10	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
Sampling point - DAT	Soil layer [cm]	Concentration of FOE Oxalate [µg/kg]					Concentration of FOE Sulfonic acid [µg/kg]				
		Rep1	Rep 2	Rep 3	Rep 4	Mean	Rep1	Rep 2	Rep 3	Rep 4	Mean
0	0-10	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
7	0-10	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
15	0-10	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
28	0-10	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
55	0-10	< 10 ³⁾	10.03	10.79	< 10 ³⁾	< 10 ³⁾	12.91	13.39	13.11	13.76	13.3
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
87	0-10	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	15.18	14.72	14.31	15.09	14.8
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
119	0-10	10.94	11.17	11.58	11.08	11.2	15.67	16.38	15.93	16.30	16.1
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
182	0-10	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	< 10 ³⁾	n. d. ⁴⁾	< 10 ³⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
255	0-10	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾

Footnotes to the table:

- 1) for that layer usually the values for two replicates were reported;
- 2) for that layer the values for two or, more commonly, one replicate were reported;
- 3) <10 = values below the LOQ = 10 µg/kg soil;
- 4) n. d. = not detectable – the values below the LOD = 3 µg/kg soil.
- 5) No value.

Table B.8.1.1.2.2.1_CA-19: The results of the determination of the concentrations of the test compounds in samples from treated plot obtained in the South French trial St. Etienne du Gres (30253/8).

Sampling point - DAT	Soil layer [cm]	Concentration of Flufenacet [µg/kg]					Concentration of FOE Alcohol [µg/kg]				
		Rep1	Rep 2	Rep 3	Rep 4	Mean	Rep1	Rep 2	Rep 3	Rep 4	Mean
0	0-10	286.6	277.2	273.3	283.0	280	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	< 10 ³⁾	< 10 ³⁾	---- ⁵⁾	---- ⁵⁾	< 10 ³⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
7	0-10 ⁶⁾	< 10 ³⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	< 10 ³⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
15	0-10	209.1	205.5	204.2	201.0	205	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	< 10 ³⁾	< 10 ³⁾	---- ⁵⁾	---- ⁵⁾	< 10 ³⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
28	0-10	203.9	188.8	181.7	182.7	189	n. d. ⁴⁾	< 10 ³⁾	< 10 ³⁾	n. d. ⁴⁾	< 10 ³⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
56	0-10	102.3	94.59	89.26	95.79	95.5	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
87	0-10	56.30	55.49	59.44	57.50	57.2	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
119	0-10	52.66	47.14	52.63	51.18	50.9	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
182	0-10	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
260	0-10	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	n. d. ⁴⁾	< 10 ³⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
Sampling point - DAT	Soil layer [cm]	Concentration of FOE Oxalate [µg/kg]					Concentration of FOE Sulfonic acid [µg/kg]				
		Rep1	Rep 2	Rep 3	Rep 4	Average	Rep1	Rep 2	Rep 3	Rep 4	Average
0	0-10	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
7	0-10	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
15	0-10	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
28	0-10	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	10.16	< 10 ³⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
56	0-10	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	10.15	< 10 ³⁾	10.39	10.73	< 10 ³⁾	10.15	< 10 ³⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
87	0-10	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
119	0-10	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
182	0-10	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
260	0-10	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾

Footnotes to the table:

- 1) for that layer usually the values for two replicates were reported;
- 2) for that layer the values for two or, more commonly, one replicate were reported;
- 3) <10 = values below the LOQ = 10 µg/kg soil;
- 4) n. d. = not detectable – the values below the LOD = 3 µg/kg soil;
- 5) No value;
- 6) The values for Flufenacet for that soil layer and that time point were lower than the LOQ = 10 µg/kg soil, so they were not taken into account in the further analysis.

The weather data for each trial site provided by the study report are presented below on figures B.8.1.1.2.2.1._CA-1 – B.8.1.1.2.2.1._CA-8.

Study No.: 30159/0
Origin of Data: German Weather Service, Lübeck
Test Location: D-23881 Breitenfelde

Date/Period of Time	Remark	Mean Temp. [°C]	Rainfall [mm]	Sunshine [hours]
04/15/93	T,S	6	0	12
04/16/93		8	0	10
04/17/93		9	2	0
04/18/93		7	4	0
04/19/93		6	0	13
04/20/93		7	0	3
04/21/93		14	2	10
04/22/93	S	12	5	8
04/23/93		14	0	12
04/24/93		18	0	11
04/25/93		17	0	7
04/26/93		18	0	8
04/27/93		19	0	12
04/28/93		18	0	13
04/29/93		11	0	13
04/30/93 - 05/12/93		12	0	120
05/13/93	S	17	1	12
05/14/93 - 06/09/93		15	50	192
06/10/93	S	22	0	12
06/11/93 - 07/13/93		14	75	182
07/14/93	S	15	0	7
07/15/93 - 08/12/93		16	130	134
08/13/93	S	13	0	11
08/14/93 - 10/11/93		12	186	243
10/12/93	S	14	5	0
10/13/93 - 12/10/93		3	122	73
12/11/93	S	3	10	0

T: Treatment
S: Sampling

Figure B.8.1.1.2.2.1._CA-1: The weather data presented in the study report for the German trial site Breitenfelde (30159/0); copied from the study report.

Study No.: 30162/0
Origin of Data: Weather station, 4 km from the trial
Test Location: D-96166 Kirchlauter

Date/Period of Time	Remark	Mean Temp. [°C]	Rainfall [mm]	Sunshine, Irradiation energy [watts/m ²]
04/13/93	ST: 7 T,S	7	0	149
04/20/93	ST: 9 S	12	0	229
04/27/93	ST:13 S	18	0	215
05/11/93	ST:14 S	18	0	262
06/08/93	ST:19 S	19	0	277
07/12/93	ST:16 S	12	3	196
08/11/93	ST:16 S	14	0	191
10/11/93	ST:11 S	12	7	0
12/06/93	ST: 0 S	0	0	12
04/13/93 - 04/20/93	ST: 8	9	9	143
04/21/93 - 04/27/93	ST:12	15	1	210
04/28/93 - 05/11/93	ST:13	14	5	200
05/12/93 - 06/08/93	ST:16	15	30	213
06/09/93 - 07/12/93	ST:17	15	45	190
07/13/93 - 08/11/93	ST:17	16	70	167
08/12/93 - 08/31/93	ST:18	16	4	176
09/01/93 - 09/30/93	ST:13	12	69	112
10/01/93 - 10/11/93	ST:11	10	27	78
10/12/93 - 10/31/93	ST: 7	4	25	53
11/01/93 - 11/30/93	ST: 2	-1	34	25
12/01/93 - 12/06/93	ST: 0	0	0	15

T: Treatment
 S: Sampling
 ST: Soil temperature in 0.2 m depth [°C]

Figure B.8.1.1.2.2.1._CA-2: The weather data presented in the study report for the German trial site Kirchlauter (30162/0); copied from the study report.

Study No.: 30163/9
 Origin of Data: Trial Station Laacherhof, D-40789 Monheim
 Test Location: Trial Station Laacherhof, D-40789 Monheim

Date/Period of Time	Remark	Mean Temp. [°C]	Rainfall [mm]	Sunshine [hours]
04/30/93	ST:14 T,S	19	0	13
05/07/93	ST:12 S	13	0	9
05/14/93	ST:16 S	11	0	0
05/28/93	ST:17 S	12	2	11
06/25/93	ST:15 S	14	0	4
07/29/93	ST:17 S	20	0	7
08/30/93	ST:14 S	13	1	0
10/27/93	ST: 9 S	8	0	0
12/17/93	ST: 4 S	6	7	0
*April	ST: 9	12	49	155
*May	ST:15	15	51	236
*June	ST:17	17	44	218
*July	ST:18	17	110	188
*August	ST:16	16	25	199
*September	ST:14	14	127	123
*October	ST: 9	9	113	83
*November	ST: 3	3	35	70
*December	ST: 4	6	148	14
**April	ST: 7	9	47	147
**May	ST:12	13	65	181
**June	ST:16	16	79	154
**July	ST:18	18	73	178
**August	ST:17	18	67	176
**September	ST:14	14	57	126
**October	ST:10	11	54	94
**November	ST: 6	6	62	51
**December	ST: 3	3	71	32

T: Treatment
 S: Sampling
 *: Average
 **: Average of many years
 ST: Soil temperature in 10 cm depth [°C]
 04/30/93: High maximum temperature 26°C, Humidity 38%

Figure B.8.1.1.2.2.1_CA-3: The weather data presented in the study report for the German trial site Monheim (30163/9); copied from the study report.

Study No.: 30164/7
Origin of Data: Trial Station Höfchen, D-51399 Burscheid
Test Location: Trial Station Höfchen, D-51399 Burscheid

Date/Period of Time	Remark	Mean Temp. [°C]	Rainfall [mm]	Sunshine [hours]
04/22/93	ST:10 T,S	15	0	1
04/29/93	ST:13 S	21	0	12
05/06/93	ST:10 S	10	0	2
05/19/93	ST:15 S	16	3	9
06/21/93	ST:15 S	17	0	13
07/21/93	ST:14 S	13	5	4
08/20/93	ST:15 S	18	0	5
10/19/93	ST: 4 S	5	0	4
12/17/93	ST: 3 S	4	11	0
*April	ST: 8	11	101	132
*May	ST:13	14	101	236
*June	ST:16	16	44	213
*July	ST:16	16	149	191
*August	ST:14	15	27	183
*September	ST:13	12	163	110
*October	ST: 8	8	125	86
*November	ST: 2	1	36	73
*December	ST: 3	3	194	5
**April	ST: 6	8	58	155
**May	ST:11	13	74	186
**June	ST:14	15	94	178
**July	ST:16	17	99	185
**August	ST:16	17	92	173
**September	ST:13	14	79	133
**October	ST:10	10	73	104
**November	ST: 5	5	86	47
**December	ST: 3	2	88	37

T: Treatment
 S: Sampling
 *: Average
 **: Average of many years
 ST: Soiltemperature in 10 cm depth [°C]

During the sample period, the amount of rainfall was 197 mm higher than the average of many years.

Figure B.8.1.1.2.2.1._CA-4: The weather data presented in the study report for the German trial site Burscheid (30159/0); copied from the study report..

Study No.: 30248/1
 Origin of Data: Météo France Station de Boos
 Test Location: F-27700 Fresno-L'Archevêque

Date/Period of Time	Remark	Mean Temp. [°C]	Rainfall [mm]	Sunshine [hours]
05/11/93 - 05/20/93		12	81	46
05/11/93	T S	17	22	5
05/21/93 - 05/31/93		15	11	57
05/18/93	S	13	3	2
05/25/93	S	20	0	2
06/01/93 - 06/10/93		17	63	59
06/08/93	S	20	0	12
06/11/93 - 06/20/93		13	48	36
06/21/93 - 06/30/93		16	3	96
07/01/93 - 07/10/93		16	6	86
07/06/93	S	14	0	12
07/11/93 - 07/20/93		14	44	30
07/21/93 - 07/31/93		16	42	44
08/01/93 - 08/10/93		16	4	65
08/09/93	S	15	0	0
08/11/93 - 08/20/93		16	6	81
08/21/93 - 08/31/93		14	3	73
09/01/93 - 09/10/93		14	23	46
09/08/93	S	16	5	2
09/11/93 - 09/20/93		12	67	32
09/21/93 - 09/30/93		11	37	26
10/01/93 - 10/10/93		11	33	23
10/11/93 - 10/20/93		8	39	31
10/21/93 - 10/31/93		6	1	25
11/01/93 - 11/10/93		7	13	15
11/08/93	S	8	0	0
11/11/93 - 11/20/93		3	21	48
11/21/93 - 11/30/93		-1	3	19
12/01/93 - 12/10/93		7	32	5
12/11/93 - 12/20/93		7	75	6
12/21/93 - 12/31/93		4	50	4
01/01/94 - 01/10/94		5	44	12
01/11/94 - 01/20/94		4	21	17
01/21/94 - 01/31/94		6	35	10
02/01/94 - 02/10/94		5	15	27
02/11/94 - 02/20/94		1	10	21
02/21/94 - 02/28/94		6	28	10
03/01/94 - 03/10/94		7	12	36
03/10/94	S	7	0	7

T: Treatment
 S: Sampling

Figure B.8.1.1.2.2.1. CA-5: The weather data presented in the study report for the North French trial site Fresno-L'Archevêque (30248/1); copied from the study report.

Study No.: 30250/3
 Origin of Data: Météo France Station de Boos
 Test Location: F-27700 Fresne-L'Archevêque

Date/Period of Time	Remark	Mean Temp. [°C]	Rainfall [mm]	Sunshine [hours]
05/21/93 - 05/31/93		15	11	57
05/27/93	T S	15	0	7
06/01/93 - 06/10/93		17	63	59
06/04/93	S	15	0	0
06/11/93 - 06/20/93		13	48	36
06/11/93	S	13	16	0
06/21/93 - 06/30/93		16	3	94
06/24/93	S	14	0	7
07/01/93 - 07/10/93		16	6	82
07/11/93 - 07/20/93		14	44	30
07/21/93 - 07/31/93		16	42	44
07/22/93	S	15	0	6
08/01/93 - 08/10/93		16	4	65
08/11/93 - 08/20/93		16	6	81
08/21/93 - 08/31/93		14	3	73
08/26/93	S	12	0	2
09/01/93 - 09/10/93		14	23	46
09/11/93 - 09/20/93		12	67	32
09/21/93 - 09/30/93		11	37	26
09/24/93	S	13	0	3
10/01/93 - 10/10/93		11	33	23
10/11/93 - 10/20/93		8	39	31
10/21/93 - 10/31/93		6	1	25
11/01/93 - 11/10/93		7	13	15
11/11/93 - 11/20/93		3	21	48
11/21/93 - 11/30/93		-1	3	19
12/01/93 - 12/10/93		7	32	5
12/06/93	S	5	0	1
12/11/93 - 12/20/93		7	75	6
12/21/93 - 12/31/93		4	50	4
01/01/94 - 01/10/94		5	44	12
01/11/94 - 01/20/94		4	21	17
01/21/94 - 01/31/94		6	35	10
02/01/94 - 02/10/94		5	15	27
02/11/94 - 02/20/94		1	10	21
02/21/94 - 02/28/94		6	28	10
03/01/94 - 03/10/94		7	12	36
03/20/94	S	7	0	7

T: Treatment
 S: Sampling

Figure B.8.1.1.2.2.1_CA-6: The weather data presented in the study report for the North French trial site Fresne-L'Archevêque 1 (30250/3); copied from the study report.

Study No.: 30251/1
 Origin of Data: Météo France Station Chusclan
 Test Location: F-30290 Laudun

Date/Period of Time	Remark	Mean Temp. [°C]	Rainfall [mm]	Sunshine [hours]
05/01/93 - 05/10/93		17	17	75
05/18/93	T S	17	0	7
05/11/93 - 05/20/93		18	39	71
05/25/93	S	21	0	12
05/21/93 - 05/31/93		18	1	106
06/02/93	S	20	0	11
06/01/93 - 06/30/93		21	28	294
06/15/93	S	20	0	8
07/01/93 - 07/31/93		22	31	314
07/12/93	S	16	0	10
08/01/93 - 08/31/93		24	27	314
08/13/93	S	27	0	12
09/01/93 - 09/30/93		18	247	187
09/14/93	S	17	0	6
10/01/93 - 10/31/93		14	96	125
11/01/93 - 11/30/93		8	74	125
11/16/93	S	12	15	1
12/01/93 - 12/31/93		7	15	124
01/01/94 - 01/31/94		6	125	178
01/28/94	S	7	0	7

T: Treatment
 S: Sampling

11/16/93 Rainfall has been after sampling

Figure B.8.1.1.2.2.1._CA-7: The weather data presented in the study report for the South French trial site Laudun (30251/1); copied from the study report.

Study No.: 30253/8
Origin of Data: Météo France Station Chateaurenard
Test Location: F-13150 St. Etienne du Gres

Date/Period of Time	Remark	Mean Temp. [°C]	Rainfall [mm]	Sunshine [hours]
05/01/93 - 05/10/93		16	6	70
05/17/93	T S	17	0	10
05/11/93 - 05/20/93		17	16	98
05/21/93 - 05/31/93		19	0	114
05/24/93	S	18	0	8
06/01/93	S	19	0	13
06/01/93 - 06/30/93		21	15	319
06/14/93	S	19	0	10
07/01/93 - 07/31/93		22	20	349
07/12/93	S	20	0	13
08/01/93 - 08/31/93		23	50	328
08/12/93	S	23	0	12
09/01/93 - 09/30/93		18	204	221
09/13/93	S	22	0	4
10/01/93 - 10/31/93		14	86	118
11/01/93 - 11/30/93		7	74	125
11/15/93	S	8	0	8
12/01/93 - 12/31/93		7	15	124
01/01/94 - 01/31/94		6	77	168
02/01/94	S	6	0	8
02/01/94 - 02/10/94		8	113	53

T: Treatment
 S: Sampling

Figure B.8.1.1.2.2.1_CA-8: The weather data presented in the study report for the South French trial site St. Etienne du Gres (30253/8); copied from the study report.

The results of the study were kinetically examined. It was stated that due to the fact that for the degradation products – FOE Oxalate and FOE Sulfonic acid, only in few samples from the layer 0-10 cm the concentrations were above the LOQ = 10 µg/kg soil (d. w.), while for FOE Alcohol the values were generally < LOQ, it was not possible to perform the kinetic examination of the data. Therefore only for the data obtained for Flufenacet kinetic analysis was performed.

The kinetic examination of the data was carried out using Timme and Frehse method. As that method of the kinetic analysis is not any longer considered valid for the regulatory purposes in the EU, RMS decided not to present its results in the summary. Instead the results will be kinetically evaluated, in line with the recommendations of the FOCUS Kineitcs Guidance Document [FOCUS; 2006], further down this Renewal Assessment Report.

Study 2:

Report: Sommer H., (1995): “Dissipation of FOE 5043 in Soil under Field Conditions (Germany).”; Bayer AG, Crop Protection Business Group, Crop Protection-Development, Institute for Metabolism Research & Residue Analysis, D-51368 Leverkusen-Baywerk, Germany (performing laboratory) for Bayer Corporation, Agriculture Division, P. O. Box 4913, Hawthorne Road, Kansas City, MO 64120-0013, USA; Study Report No. RA-2116/93; Bayer Report No. 107722; 5 October 1995; study reference number: M-002171-01-2;

Guidelines: The study was performed to comply with the following Guidelines:

- BBA Guideline IV-4.1, (1986);
- US. EPA Guidelines for Pesticide Registration, Subdivision N, Section 164-1, Terrestrial Field Dissipation (Supplemental).

GLP: Yes;

RMS comments: The study had been evaluated for the previous authorisation of Flufenacet in the EU, by inclusion of the compound into the Annex I of the Directive 91/414/EEC. Its brief summary can be found under the point B.7.1.2.2., in section B.7 of the Annex B to the Monograph prepared by the RMS – France, for Flufenacet. Assessing it, as well as other three similar studies, the RMS stated that it was acceptable, although at the same time indicated that the study was not triggered, and hence required, according to the provisions of the Commission Directive 95/36/EC of the 14th July 1994, amending the Council Directive 91/414/EEC. It was however required according to the provisions of the German BBA guideline for assessing Plant Protection Products, part IV, 4.1.

For the purpose of the current assessment the study was evaluated for its compliance with the following guidelines:

- Lynch M. R., editor, (1995): “Procedures for assessing the environmental fate and ecotoxicology of pesticides.”, SETAC; chapter 3.1. – Soil dissipation study;
- NAFTA Guidance Document for Conducting Terrestrial Field Dissipation Studies, 31 March 2006;
- US EPA Fate, Transport and Transformation Test Guidelines, OPPTS Guideline 835.6100 – Terrestrial Field Dissipation;

Additionally, in the area of the kinetic assessment of the results, it was evaluated for the compliance with the following Guidelines:

- FOCUS (2006): “Guidance Document on Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration.” Report of the FOCUS Work Group on Degradation Kinetics, EC Document Reference SANCO/10058/2005 version 2.0, 434 pp.;
- FOCUS, 2011: “Generic Guidance for Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration.” Version 1.0, Nov. 23, 2011.

The following deviations from the Guidelines cited above were stated:

- The history of the test fields over 5 years preceding the trials was not provided, therefore it is not possible to state whether Flufenacet or other plant protection products belonging to the same group – oxyacetamides, acetamides or amides, were used there during that period;
- The analytical method used in the study was generally adequately characterised, with exception of the instrumental methods used for identification and quantitation of the test compounds. That was indicated solely to be HPLC-MS/MS. However, as the method was declared to be a validated method, it was probably very similar or the same as used in other studies aimed on the determination of the route and rate of degradation of Flufenacet in soil;
- The characteristic of the trial plots was very limited – only the area was provided without the plot’s dimension (width, length) and other physical features usually required, such as the plot’s slope;
- The soil cores were sampled to the depth of 50 cm, while the relevant Guidelines recommend 1-metre deep sampling;
- The kinetic analysis of the results was performed according to Timme and Frehse, the method not compliant with the currently recommended procedure for kinetic evaluation of the data;

- The study report contains the weather data, but reported, for the first 30 days in 7-days intervals, and afterwards in ~30 days intervals; additionally average monthly values and average monthly values of many years are given, what may substantially complicate the normalisation procedure;
- The analysis in the area of degradation products was performed only for the metabolites formed by the degradation within the phenyl moiety – FOE Oxalate, FOE Alcohol, and FOE Sulfonic acid; the would-be fate of Flufenacet within the thiadiazole moiety was not examined.

Despite these deficiencies RMS found the study acceptable and possible to be used for the regulatory purposes, at least as a source of the data characterising persistence of Flufenacet and its selected major soil degradation products in soil under field conditions. The study is summarised below.

Summary:

The aim of the study was to examine the dissipation of Flufenacet and formation and fate of its degradation products in soil under field conditions. The experiment was carried out on two trial locations in Germany. It was performed on bare fields. The characteristic of trial sites is presented below in the table B.8.1.1.2.2.1._CA-20.

Table B.8.1.2.2.1._CA-20: The characteristic of the trial sites.

Information		Trial:	
		<i>Burscheid</i>	<i>Monheim</i>
Trial data	<i>Trial code number</i>	30499/9	30500/6
	<i>Trial location</i>	D-51399 Burscheid, Versuchsgut Höfchen, plot 4011	D-51399 Burscheid, Versuchsgut Laacherhof, plot 711/717
	<i>Size of the test plot [m²]</i>	225	255
	<i>Duration of the field trial</i>	240 days	240 days
	<i>Soil cultivation and maintenance activities</i>	Crop cover	Bare soil
		Date of sowing	Not applicable
		Date of harvest	Not applicable
		Sowing density	Not applicable
		Maintenance practices	Local agricultural practices, mechanical weed control, no irrigation, no PPP used
	<i>Data on application of the test compound</i>	Test compound	Flufenacet
		Formulation	FOE 5043 60 WG
		Application rate [g s.a./ ha]	240
		Number of Applications	1
		Type of application	Spraying
		Application equipment	Agrotop spraying boom
		Water rate [L/ha]	300
		Date of application	20/10/1993
		Air temperature at application	6°C
Soil properties for the trial field	<i>Soil textural class</i>	DIN 19682	Heavy loamy silt
		USDA	Silt loam
	<i>Particle size distribution (USDA)</i>	Sand	12.8
		Silt	69.9
		Clay	17.3
	<i>pH (in 0.01M CaCl₂aq)</i>	6.5	6.7
	<i>OC [%]</i>	0.97	1.45
	<i>OM [%]</i>	1.67	2.49
	<i>Soil moisture [g/100 g soil d.w.]</i>	44.6	41.3
	<i>N content [mg/100 g soil d.w.]</i>	120	100

The Test Substance – Flufenacet formulated as FOE 5043 60 WG, was applied in autumn to the bare soil. Prior to the application from each trial site 50-cm soil cores were sampled for the characterisation of the soil on the test plot.

After application 50-cm soil cores were taken from each test field at pre-designated time point. The sampling points were statistically distributed over the plot to get the representative samples. The cores were taken using a pushing sampling system – Wacker Hammer. The first samples – DAT 0 samples (DAT stands for “Days After Treatment”), were taken directly after application, immediately after drying of the spray film. For that time point, as well as for the last time point, two types of soil cores were sampled for the further analysis – treated samples and control samples (from the non-treated plots). For the remaining time points only the cores from the treated plots were samples. At each sampling interval 20 cores were sampled from the treated plot and 10 or 20 from the control. The sampled cores were deep-frozen ($T < -18^{\circ}\text{C}$) on the sampling site on the day of sampling and in that state shipped to the laboratory for further analysis. The sampling protocol for each trial site is presented below, in the table B.8.1.1.2.2.1._CA-21. The deep-frozen samples were stored for up to 365 days before being processed.

In the laboratory the cores were cut into 10 cm segments and segments of one layer, further called laboratory samples, were milled and homogenised. A part of such sample was used in the analysis, performed using the internal analytical method developed by Bachlechner and Allemendinger. It consisted of cold-solvent extraction followed by the quantitative analysis using HPLC-MS/MS technique.

The cold-solvent extraction looked as follows: soil samples were extracted by shaking for 60 minutes on mechanic shaker with 100 mL of 0.1N HCl/CH₃CN (1:1) solution. The liquid phase was decanted and purified by filtration. 40 mL of filtrate was concentrated to 5 mL on TurboVap and brought to the volume of 10 mL with first 0.4 mL of 37% HCl_{aq} followed by the appropriate amount of distilled water. After centrifugation it was analysed by HPLC-MS/MS. RMS noticed that the used extraction method was almost identical to that described in the open-source publication by [Lam, McKinney and Clay; 2002], summarised as **Study 8** under the point B.8.1.1.1.1. of this Renewal Assessment Report. This may indicate that it may be considered fully appropriate for the purpose it was used for.

The identification and quantitation was performed using HPLC-MS/MS method in comparison to internal standards – deuterised derivatives of the analytes, added after extraction. The qualitative and quantitative analysis was performed for the following compounds: Flufenacet, FOE Alcohol, FOE Oxalate and FOE Sulfonic acid.

The method was validated and controlled by determining the procedural recoveries for each of the test compounds in range 10 – 600 µg/kg. They were following:

- for Flufenacet the mean recovery was 89.6% with RSD = 6.2%;
- for FOE Alcohol the mean recovery was 94.3% with RSD = 4.3%;
- for FOE Oxalate the mean recovery was 96.6% with RSD = 7.9%;
- for FOE Sulfonic acid the mean recovery was 102% with RSD = 3.8%.

The performance of the method was also determined in terms of LOD = 3 µg/kg and LOQ = 10 µg/kg. These values were relevant for all analytes.

Additionally were determined the recovery rates during analyses for each analysed compound and each trial site. The results are presented in the table B.8.1.1.2.2.1._CA-22. They were used to verify the integrity of the analysis of residues.

The verification of the application rate was performed for each trial site using 0-10 cm layers of sampled soil cores. The resulting values were the averages of four replicates. They were compared to the theoretical concentrations of Flufenacet in soil calculated using the following assumptions: the compound was evenly distributed in 0-10cm layer and the soil density was 1.5 g/cm³. The theoretical concentration of the test compound for the application rate of 240 g Flufenacet/ha was **160 µg/kg soil**.

The detailed results of the verification of application rate for each trial are provided in the table B.8.1.1.2.2.1._CA-23.

The results of the analysis are presented in tabularised form further down this summary (tables B.8.1.1.2.2.1._CA-24 – B.8.1.1.2.2.1._CA-26). Finally, on figures B.8.1.1.2.2.1._CA-9 and B.8.1.1.2.2.1._CA-10 are presented the weather data as they were provided in the study report.

Table B.8.1.1.2.2.1._CA-21: The sampling data for the German trials Burscheid and Monheim.

Trial: Burscheid (30499/9)					Trial: Monheim (30500/6)				
Sampling point - DAT	Type of sample	Soil layer [cm]	Mass of the sample [kg]		Sampling point - DAT	Type of sample	Soil layer [cm]	Mass of the sample [kg]	
			Field sample	Laboratory sample				Field sample	Laboratory sample
0	Control	0-10	34.8	5.10	0	Control	0-10	18.1	3.53
		10-20	34.8	6.62			10-20	18.1	3.50
		20-30	34.8	7.46			20-30	18.1	3.60
		30-40	34.8	7.74			30-40	18.1	3.67
		40-50	34.8	5.96			40-50	18.1	2.82
	Treated	0-10	37.0	6.31		Treated	0-10	36.1	7.16
		10-20	37.0	7.23			10-20	36.1	6.79
		20-30	37.0	7.62			20-30	36.1	7.04
		30-40	37.0	7.83			30-40	36.1	7.42
		40-50	37.0	5.89			40-50	36.1	5.74
8	Treated	0-10	37.4	6.80	8	Treated	0-10	36.2	6.91
		10-20	37.4	7.23			10-20	36.2	6.99
		20-30	37.4	7.61			20-30	36.2	7.13
		30-40	37.4	7.56			30-40	36.2	7.43
		40-50	37.4	6.20			40-50	36.2	5.71
14	Treated	0-10	39.1	6.66	14	Treated	0-10	36.4	6.67
		10-20	39.1	7.53			10-20	36.4	6.84
		20-30	39.1	8.04			20-30	36.4	7.20
		30-40	39.1	8.20			30-40	36.4	7.55
		40-50	39.1	6.29			40-50	36.4	6.21
29	Treated	0-10	38.5	5.40	28	Treated	0-10	34.9	5.65
		10-20	38.5	7.59			10-20	34.9	6.74
		20-30	38.5	7.96			20-30	34.9	6.95
		30-40	38.5	8.26			30-40	34.9	7.58
		40-50	38.5	7.08			40-50	34.9	6.13
56	Treated	0-10	37.9	7.22	52	Treated	0-10	37.4	7.32
		10-20	37.9	7.23			10-20	37.4	7.10
		20-30	37.9	7.36			20-30	37.4	7.21
		30-40	37.9	7.62			30-40	37.4	7.53
		40-50	37.9	6.20			40-50	37.4	6.17
90	Treated	0-10	39.2	6.73	98	Treated	0-10	37.0	7.05
		10-20	39.2	7.87			10-20	37.0	7.13
		20-30	39.2	8.15			20-30	37.0	7.33
		30-40	39.2	8.36			30-40	37.0	7.60
		40-50	39.2	6.00			40-50	37.0	5.86
120	Treated	0-10	38.6	6.16	120	Treated	0-10	35.8	6.84
		10-20	38.6	7.63			10-20	35.8	6.51
		20-30	38.6	8.08			20-30	35.8	6.72
		30-40	38.6	8.38			30-40	35.8	7.34
		40-50	38.6	6.26			40-50	35.8	5.38
180	Treated	0-10	37.60	6.84	181	Treated	0-10	35.30	6.21
		10-20	37.60	7.39			10-20	35.30	6.63
		20-30	37.60	7.65			20-30	35.30	6.81
		30-40	37.60	7.91			30-40	35.30	7.13
		40-50	37.60	6.03			40-50	35.30	6.08
240	Control	0-10	18.0	3.14	240	Control	0-10	17.7	3.19
		10-20	18.0	3.59			10-20	17.7	3.40
		20-30	18.0	3.68			20-30	17.7	3.49
		30-40	18.0	3.91			30-40	17.7	3.73
		40-50	18.0	2.83			40-50	17.7	2.50
	Treated	0-10	39.7	7.42		Treated	0-10	34.7	6.39
		10-20	39.7	7.89			10-20	34.7	6.75
		20-30	39.7	8.12			20-30	34.7	6.90
		30-40	39.7	8.36			30-40	34.7	7.29
		40-50	39.7	6.04			40-50	34.7	5.10

Next table – B.8.1.1.2.2.1._CA-22 provides the results of the determination of recovery rates for each analyte during analyses. It is followed by the table B.8.1.1.2.2.1._CA-23 presenting the results of the verification of the application rate for each trial site.

Table B.8.1.1.2.2.1._CA-22: The results of the verification of the recovery rates for each analyte during the analysis of the collected samples.

Compound	Parameter	Results for the trial:	
		Burscheid (30499/9)	Monheim (30500/6)
<i>Flufenacet</i>	Recovery rate [%]	83.0	87.4
	RSD [%]	8.8	3.1
	Number of experiments	8	8
<i>FOE Alcohol</i>	Recovery rate [%]	84.7	86.5
	RSD [%]	4.3	3.6
	Number of experiments	8	8
<i>FOE Oxalate</i>	Recovery rate [%]	77.6	80.0
	RSD [%]	3.7	3.1
	Number of experiments	8	8
<i>FOE Sulfonic acid</i>	Recovery rate [%]	94.0	96.0
	RSD [%]	3.0	3.5
	Number of experiments	8	8

Table B.8.1.1.2.2.1._CA-23: The results of the verification of the application rate for each trial site.

Trial	Application rate [g Flufenacet/ha]	Theoretical DAT-0 concentration of Flufenacet in top 10-cm soil layer [µg/kg soil]	Measured DAT-0 concentration of Flufenacet in top 10-cm soil layer [µg/kg soil]	Measured DAT-0 concentration of Flufenacet in top soil as % of Theoretical concentration
Burscheid (30499/9)	240	160	141	88.1
Monheim (30500/6)	240	160	101	63.1

Below are presented the results of the study – the concentrations in [µg/kg] of Flufenacet and its degradation products – FOE Alcohol, FOE Oxalate and FOE Sulfonic acid, in soil for each trial. The results are presented in three tables – table B.8.1.1.2.2.1._CA-24, summarising the values obtained in samples from the control plots, and then for the treated plots individually for each trial in tables B.8.1.1.2.2.1._CA-25 and B.8.1.1.2.2.1._CA-26. The values are given only for the the layers down to 30-cm depth. That was due to the fact that in case of Flufenacet the measurable residues – above the LOQ = 10 µg/kg, were found predominantly in the top layer 0-10 cm, and sporadically in the lower 10-20-cm layer. In the layer 20-30 cm Flufenacet was not detected, so in the study report it was stated that its concentrations there were below the LOD = 3 µg/kg.

In case of the degradation products – FOE Alcohol, FOE Oxalate and FOE Sulfonic acid, their residues, if detected, were found in the top 0-10 cm layer. In the lower layers – 10-20 cm and 20-30 cm these compounds, if detected, were in amounts < LOQ (10 µg/kg). Additionally it was stated that in almost all cases they were < LOD (3 µg/kg), so in fact were not detected in deeper soil layers.

As a result the layers 30-40 cm and 40-50 cm were not analysed and consequently not taken into account in tables reporting the results.

Table B.8.1.1.2.2.1_CA-24: The results of the determination of the concentrations of the test compounds in samples from control (untreated) plots obtained in the trials.

Results obtained for the trial: Burscheid (30499/9)					
Sampling point - DAT	Soil layer [cm]	Concentration [$\mu\text{g/kg}$] of:			
		Flufenacet	FOE Alcohol	FOE Oxalate	FOE Sulfonic acid
0	0-10	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
	10-20	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
	20-30	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
240	0-10	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
	10-20	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
	20-30	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
Results obtained for the trial: Monheim (30500/6)					
Sampling point - DAT	Soil layer [cm]	Concentration [$\mu\text{g/kg}$] of:			
		Flufenacet	FOE Alcohol	FOE Oxalate	FOE Sulfonic acid
0	0-10	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
	10-20	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
	20-30	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
240	0-10	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
	10-20	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
	20-30	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾

Footnotes to the table:1) n. d. = not detectable – the values below the LOD = 3 $\mu\text{g/kg}$ soil.

Table B.8.1.1.2.2.1_CA-25: The results of the determination of the concentrations of the test compounds in samples from treated plot obtained in the German trial Burscheid (30499/9).

Sampling point - DAT	Soil layer [cm]	Concentration of Flufenacet [µg/kg]					Concentration of FOE Alcohol [µg/kg]				
		Rep1	Rep 2	Rep 3	Rep 4	Mean	Rep1	Rep 2	Rep 3	Rep 4	Mean
0	0-10	142.6	134.0	150.5	137.6	141	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
8	0-10	94.44	93.42	94.62	94.11	94.1	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
14	0-10	82.98	90.99	99.88	84.75	89.6	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
29	0-10	79.68	83.69	75.00	81.23	79.9	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
56	0-10	52.89	48.67	54.94	53.99	52.6	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
90	0-10	21.08	21.72	19.16	19.34	20.3	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
120	0-10	12.39	11.76	12.74	12.08	12.2	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
180	0-10	< 10 ³⁾	n. d. ⁴⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
240	0-10	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
Sampling point - DAT	Soil layer [cm]	Concentration of FOE Oxalate [µg/kg]					Concentration of FOE Sulfonic acid [µg/kg]				
		Rep1	Rep 2	Rep 3	Rep 4	Mean	Rep1	Rep 2	Rep 3	Rep 4	Mean
0	0-10	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
8	0-10	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
14	0-10	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
29	0-10	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
56	0-10	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	< 10 ³⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	< 10 ³⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
90	0-10	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
120	0-10	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
180	0-10	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
240	0-10	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾

Footnotes to the table:

- 1) for that layer usually the values for two replicates were reported;
- 2) for that layer the values for two or, more commonly, one replicate were reported;
- 3) <10 = values below the LOQ = 10 µg/kg soil;
- 4) n. d. = not detectable – the values below the LOD = 3 µg/kg soil.
- 5) No value.

Table B.8.1.1.2.2.1_CA-26: The results of the determination of the concentrations of the test compounds in samples from treated plot obtained in the German trial Monheim (30500/6).

Sampling point - DAT	Soil layer [cm]	Concentration of Flufenacet [µg/kg]					Concentration of FOE Alcohol [µg/kg]				
		Rep1	Rep 2	Rep 3	Rep 4	Mean	Rep1	Rep 2	Rep 3	Rep 4	Mean
0	0-10	105.0	102.3	98.99	97.76	101	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d.⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
8	0-10	97.87	100.5	101.8	104.8	101	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d.⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
14	0-10	90.34	90.34	89.65	85.19	88.9	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d.⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
28	0-10	111.7	110.2	106.7	107.0	109	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d.⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
52	0-10	66.64	66.32	68.23	67.11	67.1	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d.⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
98	0-10	36.29	35.76	36.15	34.88	35.8	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d.⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
120	0-10	26.74	28.56	29.24	30.69	27.6	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d.⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
181	0-10	12.74	12.95	12.63	12.90	12.8	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d.⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
240	0-10	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d.⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d.⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
Sampling point - DAT	Soil layer [cm]	Concentration of FOE Oxalate [µg/kg]					Concentration of FOE Sulfonic acid [µg/kg]				
		Rep1	Rep 2	Rep 3	Rep 4	Mean	Rep1	Rep 2	Rep 3	Rep 4	Mean
0	0-10	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d.⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d.⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
8	0-10	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d.⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d.⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
14	0-10	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d.⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d.⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
28	0-10	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d.⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d.⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
52	0-10	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d.⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d.⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
98	0-10	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d.⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d.⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
120	0-10	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d.⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d.⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
181	0-10	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d.⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d.⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
240	0-10	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d.⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d.⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾

Footnotes to the table:

- 1) for that layer usually the values for two replicates were reported;
- 2) for that layer the values for two or, more commonly, one replicate were reported;
- 3) <10 = values below the LOQ = 10 µg/kg soil;
- 4) n. d. = not detectable – the values below the LOD = 3 µg/kg soil.
- 5) No value.

The weather data for each trial site provided by the study report are presented below on figures B.8.1.1.2.2.1._CA-9 and B.8.1.1.2.2.1._CA-10.

Study No. : 30499/9
Origin of Data : Versuchsgut Höfchen, 41399 Burscheid
Test Location : 51399 Burscheid, Versuchsgut Höfchen

Date / Period of Time	Remark	Mean Air Temperature [°C]	Rainfall [mm]	Sunshine [hours]
10/26/93	ST: 7 T,S	7	0	0
10/28/93	ST: 4 S	5	0	8
11/03/93	ST: 5 S	9	0	4
11/18/93	ST: 1 S	-2	0	2
12/15/93	ST: 1 S	2	2	0
01/18/94	ST: 1 S	-1	0	1
02/17/94	ST: -2 S	-3	0	5
04/18/94	ST: 5 S	6	0	11
06/17/94	ST: 13 S	11	0	2
*October93	ST: 8	8	125	86
*November 93	ST: 2	1	36	73
*December 93	ST: 3	3	194	5
*January 94	ST: 3	3	119	22
*February 94	ST: 0	1	30	86
*March 94	ST: 5	6	126	95
*April 94	ST: 6	8	51	160
*May 94	ST: 11	12	55	171
*June 94	ST: 14	16	84	203
** October	ST: 9	9	74	104
** November	ST: 5	5	86	47
** December	ST: 3	2	89	38
** January	ST: 2	1	81	44
** February	ST: 1	2	60	71
** March	ST: 3	5	66	106
** April	ST: 6	8	59	154
** May	ST: 11	13	75	188
** June	ST: 14	15	94	180

T : Treatment

S : Sampling

Remarks:

* = Average

** = Average of many years

ST: = Soil temperature in 10 cm depth [°C]

Figure B.8.1.1.2.2.1._CA-9: The weather data presented in the study report for the German trial site Burscheid (30499/9); copied from the study report.

Study No. : 30500/6
 Origin of Data : Versuchsgut Laacherhof, 40789 Monheim
 Test Location : 40789 Monheim, Versuchsgut Laacherhof

Date/Period of Time	Remark	Mean Air Temperature [°C]	Rainfall [mm]	Sunshine [hours]
10/26/93	ST: 7 T,S	7	0	0
11/03/93	ST: 5 S	9	0	4
11/09/93	ST: 6 S	5	0	0
11/23/93	ST: -1 S	-5	1	0
12/17/93	ST: 3 S	4	11	0
02/01/94	ST: 3 S	3	1	0
02/23/94	ST: 0 S	0	5	1
04/25/94	ST: 11 S	9	3	0
06/23/94	ST: 14 S	17	0	13
*October 93	ST: 8	8	125	86
*November 93	ST: 2	1	36	73
*December93	ST: 3	3	194	5
*January94	ST: 3	3	119	22
*February94	ST: 0	1	30	86
*March94	ST: 5	6	126	95
*April94	ST: 6	8	51	160
*May94	ST: 11	12	55	171
*June94	ST: 14	16	84	203
** October	ST: 9	9	74	104
** November	ST: 5	5	86	47
** December	ST: 3	2	89	38
** January	ST: 2	1	81	44
** February	ST: 1	2	60	71
** March	ST: 3	5	66	106
** April	ST: 6	8	59	154
** May	ST: 11	13	75	188
** June	ST: 14	15	94	180

T : Treatment

S : Sampling

Remarks:

* = Average

** = Average of many years

ST: = Soil temperature in 10 cm depth [°C]

Figure B.8.1.1.2.2.1._CA-10: The weather data presented in the study report for the German trial site Monheim (30500/6); copied from the study report.

The results of the study were kinetically examined. It was stated that due to the fact that for the degradation products – FOE Oxalate and FOE Sulfonic acid, only in few samples from the layer 0-10 cm the concentrations were above the LOQ = 10 µg/kg soil (d. w.), while for FOE Alcohol the values were generally < LOQ, it was not possible to perform the kinetic examination of the data. Therefore only for the data obtained for Flufenacet kinetic analysis was performed.

The kinetic examination of the data was carried out using Timme and Frehse method. As that method of the kinetic analysis is not any longer considered valid for the regulatory purposes in the EU, RMS decided not to present its results in the summary. Instead the results will be kinetically evaluated, in line with the recommendations of the FOCUS Kineitics Guidance Document [FOCUS; 2006], further down this Renewal Assessment Report.

Study 3:

Report: Sommer H., (1995): “Dissipation of FOE 5043 in Soil under Field Conditions (France).” Bayer AG, Crop Protection Business Group, Crop Protection-Development, Institute for Metabolism Research & Residue Analysis, D-51368 Leverkusen-Baywerk, Germany (performing laboratory) for Bayer Corporation, Agriculture Division, P. O. Box 4913, Hawthorne Road, Kansas City, MO 64120-0013, USA; Study Report No. RA-2051/93; Bayer Report No. 107723; 6 October 1995; study reference number: M-002169-01-2;

Guidelines: The study was performed to comply with the following Guidelines:

- BBA Guideline IV-4.1, (1986);
- US. EPA Guidelines for Pesticide Registration, Subdivision N, Section 164-1, Terrestrial Field Dissipation (Supplemental).

GLP: Yes;

RMS comments: The study had been evaluated for the previous authorisation of Flufenacet in the EU, by inclusion of the compound into the Annex I of the Directive 91/414/EEC. Its brief summary can be found under the point B.7.1.2.2., in section B.7 of the Annex B to the Monograph prepared by the RMS – France, for Flufenacet. Assessing it, as well as other three similar studies, the RMS stated that it was acceptable, although at the same time indicated that the study was not triggered, and hence required, according to the provisions of the Commission Directive 95/36/EC of the 14th July 1994, amending the Council Directive 91/414/EEC. It was however required according to the provisions of the German BBA guideline for assessing Plant Protection Products, part IV, 4.1.

For the purpose of the current assessment the study was evaluated for its compliance with the following guidelines:

- Lynch M. R., editor, (1995): “Procedures for assessing the environmental fate and ecotoxicology of pesticides.”, SETAC; chapter 3.1. – Soil dissipation study;
- NAFTA Guidance Document for Conducting Terrestrial Field Dissipation Studies, 31 March 2006;
- US EPA Fate, Transport and Transformation Test Guidelines, OPPTS Guideline 835.6100 – Terrestrial Field Dissipation;

Additionally, in the area of the kinetic assessment of the results, it was evaluated for the compliance with the following Guidelines:

- FOCUS (2006): “Guidance Document on Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration.” Report of the FOCUS Work Group on Degradation Kinetics, EC Document Reference SANCO/10058/2005 version 2.0, 434 pp.;
- FOCUS, 2011: “Generic Guidance for Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration.” Version 1.0, Nov. 23, 2011.

The following deviations from the Guidelines cited above were stated:

- The history of the test fields over 5 years preceding the trials was not provided, therefore it is not possible to state whether flufenacet or other plant protection products belonging to the same group – oxyacetamides, acetamides or amides, were used there during that period;
- The analytical method used in the study was generally adequately characterised, with exception of the instrumental methods used for identification and quantitation of the test compounds. That was indicated solely to be HPLC-MS/MS. However, as the method was declared to be a validated method, it was probably very similar or the same as used in other studies aimed on the determination of the route of degradation of Flufenacet in soil;
- The characteristics of the trial plots was very limited – only the area was provided without the plot’s dimension (width, length) and other physical features usually required, such as the plot’s slope;
- The soil cores were sampled to the depth of 50 cm, while the relevant Guidelines recommend 1-metre deep sampling;
- The kinetic analysis of the results was performed according to Timme and Frehse, the method not compliant with the currently recommended procedure for kinetic evaluation of the data;

- The study report contains the weather data, but reported, for the first 30 days in 7-days intervals, and afterwards in ~30 days intervals; additionally average monthly values and average monthly values of many years are given, what may substantially complicate the normalisation procedure;
- The analysis in the area of degradation products was performed only for the metabolites formed by the degradation within the phenyl moiety – FOE Oxalate, FOE Alcohol, and FOE Sulfonic acid; the would-be fate of Flufenacet within the thiadiazole moiety was not examined.

Despite these deficiencies RMS found the study acceptable, and possible to be used for the regulatory purposes, at least as a source of the data characterising persistence of Flufenacet and its selected major soil degradation products in soil under field conditions. The study is summarised below.

Summary:

The aim of the study was to examine the dissipation of Flufenacet and formation and fate of its degradation products in soil under field conditions. The experiment was carried out on two trial locations in France – one in Northern France (Fresne-L'Archeveque) and another in Southern France (Saussay-la-Campagne). It was performed on cropped fields, covered with winter wheat. The characteristic of trial sites is presented below in the table B.8.1.1.2.2.1._CA-27.

Table B.8.1.2.2.1._CA-27: The characteristic of the trial sites.

Information			Trial:	
			<i>Saussay-la Campagne</i>	<i>Fresne-L'Archeveque</i>
Trial data	Trial code number		30254/6	30455/7
	Trial location		F-27150 Saussay-la-Campagne, Le Mont de Lisors, South France	F-27700 Fresne-L'Archeveque, La Marette, North France
	Size of the test plot [m ²]		312	312
	Duration of the field trial		242 days	240 days
	Soil cultivation and maintenance activities	Crop cover	Winter wheat var. Apollo	Winter wheat var. Scipion
		Date of sowing	14/10/1993	22/10/1993
		Date of harvest	05/08/1994	08/03/1994
		Sowing density	120 kg/ha	240 kg/ha
		Maintenance practices	Local agricultural practices, mechanical weed control, no irrigation, 7 PPP used	Local agricultural practices, mechanical weed control, no irrigation, 5 PPP used
	Data on application of the test compound	Test compound	Flufenacet	Flufenacet
		Formulation	FOE 5043 60 WG	FOE 5043 60 WG
		Application rate [g s.a./ ha]	240	240
		Number of Applications	1	1
		Type of application	Spraying	Spraying
		Application equipment	Knapsack Sprayer Pulval 00750	Knapsack Sprayer Pulval 00750
		Water rate [L/ha]	280	280
		Date of application	11/03/1994	28/03/1994
		Air temperature at application	10°C	11°C
Soil properties for the trial field	Soil textural class	DIN 19682	Weak loamy silt	Loamy silt
		USDA	Silt loam	Silt loam
	Particle size distribution (USDA)	Sand	9.6	8.8
		Silt	78.4	75.0
		Clay	12.0	16.2
	pH (in 0.01M CaCl ₂ aq)		7.4	6.6
	OC [%]		0.92	1.00
	OM [%]		1.58	1.72
	Soil moisture [g/100 g soil d.w.]		41.5	39.1
	N content [mg/100 g soil d.w.]		100	80

The information provided in the study report on the use of the Plant Protection Products other than the test compound in the trials is given below in the table B.8.1.1.2.2.1._CA-28.

Table B.8.1.1.2.2.1._CA-28: The information on the use of other Plant Protection Products in the trials.

Trial site	Pesticide applied	Parameter			
		Date of the treatment	PPP data		
			Name of the formulation	Type of formulation	Application rate of formulated product
<i>Saussay-la-Campagne (30254/6), Southern France</i>	Pesticide 1	26/03/1994	Cycocel	460 SL	2.0 [L/ha]
	Pesticide 2	15/04/1994	Sponsor	250+250 EC	1.5 [L/ha]
	Pesticide 3	29/04/1994	Terpal	305 + 155 SL	0.8 [L/ha]
	Pesticide 4	10/05/1994	Alto Mayor	80 + 350 EC	0.6 [L/ha]
	Pesticide 5	10/05/1994	Karate	80 EC	0.25 [L/ha]
	Pesticide 6	30/05/1994	Sirius	75 + 300 SC	2.0 [L/ha]
	Pesticide 7	30/05/1994	Tracker	108 EC	0.07 [L/ha]
<i>Fresne-L'Archeveque (30455/7); Northern France</i>	Pesticide 1	26/03/1994	Cycocel	460 SL	2.0 [L/ha]
	Pesticide 2	19/04/1994	Horizon	280 EW	0.6 [L/ha]
	Pesticide 3	31/05/1994	Opus	125 SC	0.4 [L/ha]
	Pesticide 4	31/05/1994	Planete Aster	250 SC	0.25 [L/ha]
	Pesticide 5	16/06/1994	Karate	80 EC	0.125 [L/ha]

The Test Substance – Flufenacet formulated as FOE 5043 60 WG, was applied in early spring to the soil covered with winter wheat sown on the previous autumn. Prior to the application from each trial site 50-cm soil cores were sampled for the characterisation of the soil on the test plot.

After application 50-cm soil cores were taken from each test field at pre-designated time point. The locations of sampling points were statistically distributed over the plot to get the representative samples. The cores were taken using a pushing sampling system – Wacker Hammer. The first samples – DAT 0 samples (DAT stands for “Days After Treatment”), were taken directly after application, immediately after drying of the spray film. For that time point, as well as for the last time point two types of soil cores were sampled for the further analysis – treated samples and control samples (from the non-treated plots). For the remaining time points only the cores from the treated plots were samples. At each sampling interval 20 cores were sampled from the treated plot and another 20 from the control. Additionally on DAT 0 samples were taken from the 0-10cm layer using the RA-piercer. The sampled cores were deep-frozen ($T < -18^{\circ}\text{C}$) on the sampling site on the day of sampling and in that state shipped to the laboratory for further analysis. The sampling protocol for each trial site is presented below, in the table B.8.1.1.2.2.1._CA-29. The deep-frozen samples were stored for up to ~500 days before being processed.

In the laboratory the cores were cut into 10 cm segments and segments of one layer, further called laboratory samples, were milled and homogenised. A part of such sample was used in the analysis, performed using the internal analytical method developed by Bachlechner and Allemendinger. It consisted of cold-solvent extraction followed by the quantitative analysis using HPLC-MS/MS technique.

The cold-solvent extraction looked as follows: soil samples were extracted by shaking for 60 minutes on mechanic shaker, with 100 mL of 0.1N HCl/CH₃CN (1:1) solution. The liquid phase was decanted and purified by filtration. 40 mL of filtrate was concentrated to 5 mL on TurboVap and brought to the volume of 10 mL with first 0.4 mL of 37% HCl_{aq} followed by the appropriate amount of distilled water. After centrifugation it was analysed by HPLC-MS/MS. RMS noticed that the used extraction method was almost identical to that described in the open-source publication by [Lam, McKinney and Clay; 2002], summarised as **Study 8** under the point B.8.1.1.1.1. of this Renewal Assessment Report. This may indicate that it may be considered fully appropriate for the purpose it was used for.

The identification and quantitation was performed using HPLC-MS/MS method in comparison to internal standards – deuterised derivatives of the analytes, added after extraction. The qualitative and quantitative analysis was performed for the following compounds: Flufenacet, FOE Alcohol, FOE Oxalate and FOE Sulfonic acid.

The method was validated and controlled by determining the procedural recoveries for each of the test compounds in range 10 – 600 µg/kg. They were following:

- for Flufenacet the mean recovery was 89.6% with RSD = 6.2%;
- for FOE Alcohol the mean recovery was 94.3% with RSD = 4.3%;
- for FOE Oxalate the mean recovery was 96.6% with RSD = 7.9%;
- for FOE Sulfonic acid the mean recovery was 102% with RSD = 3.8%.

The performance of the method was also determined in terms of LOD = 3 µg/kg and LOQ = 10 µg/kg. These values were relevant for all analytes.

Additionally were determined the recovery rates during analyses for each analysed compound and each trial site. The results are presented in the table B.8.1.1.2.2.1._CA-30. They were used to verify the integrity of the analysis of residues.

The verification of the application rate was performed for each trial site using 0-10 cm layers of sampled soil cores. The resulting values were the averages of four replicates. They were compared to the theoretical concentrations of Flufenacet in soil, calculated using the following assumptions: the compound was evenly distributed in 0-10cm layer and the soil density was 1.5 g/cm³. The theoretical concentration of the test compound, for the application rate of 240 g Flufenacet/ha was **160 µg/kg soil**.

The detailed results of the verification of application rate for each trial are provided in the table B.8.1.1.2.2.1._CA-31.

The results of the analysis are presented in tabularised form further down this summary (tables B.8.1.1.2.2.1._CA-32 – B.8.1.1.2.2.1._CA-34/34a). Finally, on figures B.8.1.1.2.2.1._CA-11 and B.8.1.1.2.2.1._CA-12 are presented the weather data as they were provided in the study report.

Table B.8.1.1.2.2.1._CA-29: The sampling data for the French trials Saussay-la-Campagne and Fresne-L'Archeveque.

Trial: Saussay-la-Campagne (30254/6), Southern France					Trial: Fresne-L'Archeveque (30455/7), Northern France				
Sampling point - DAT	Type of sample	Soil layer [cm]	Mass of the sample [kg]		Sampling point - DAT	Type of sample	Soil layer [cm]	Mass of the sample [kg]	
			Field sample	Laboratory sample				Field sample	Laboratory sample
0	Control	0-10	34.31	6.18	0 ¹⁾	Control	0-10	6.78	6.78
		10-20	34.31	6.47		Treated	0-10	6.58	6.58
		20-30	34.31	6.69	7	Treated	Samples not prepared because of damaging during transport		
		30-40	34.31	6.93			Samples not prepared because of damaging during transport		
		40-50	34.31	6.44	14	Treated	Samples not prepared because of damaging during transport		
	Treated	0-10	34.20	6.15			28	Treated	0-10
		10-20	34.20	6.27	10-20	36.0			7.18
		20-30	34.20	6.58	20-30	36.0			7.49
		30-40	34.20	6.91	30-40	36.0			7.45
		40-50	34.20	6.50	40-50	36.0			5.19
7	Treated	0-10	35.60	6.32	53	Treated	0-10	35.9	6.88
		10-20	35.60	6.61			10-20	35.9	7.13
		20-30	35.60	7.02			20-30	35.9	7.35
		30-40	35.60	7.31			30-40	35.9	7.15
		40-50	35.60	6.23			40-50	35.9	5.38
14	Treated	Samples not prepared because of damaging during transport			88	Treated	0-10	34.6	6.04
28	Treated	Samples not prepared because of damaging during transport					10-20	34.6	6.42
52	Treated	0-10	35.50	6.74			20-30	34.6	6.73
		10-20	35.50	6.86			30-40	34.6	7.07
		20-30	35.50	7.22			40-50	34.6	6.64
		30-40	35.50	7.59	120	Treated	0-10	37.0	7.04
		40-50	35.50	5.03			10-20	37.0	6.89
70	Treated	0-10	35.9	6.89			20-30	37.0	7.08
		10-20	35.9	6.93			30-40	37.0	7.01
		20-30	35.9	7.27			40-50	37.0	6.59
		30-40	35.9	7.39	178	Treated	0-10	40	7.13
		40-50	35.9	5.10			10-20	40	7.38
89	Treated	0-10	36.10	6.92			20-30	40	7.71
		10-20	36.10	6.93			30-40	40	7.63
		20-30	36.10	7.31			40-50	49	6.01
		30-40	36.10	7.53	240	Control	0-10	37.8	7.05
		40-50	36.10	5.46			10-20	37.8	7.14
116	Treated	0-10	33.00	5.68			20-30	37.8	7.48
		10-20	33.00	6.08			30-40	37.8	6.37
		20-30	33.00	6.37			40-50	37.8	6.75
		30-40	33.00	6.69	Treated	0-10	37.9	7.16	
		40-50	33.00	6.31		10-20	37.9	7.19	
180	Treated	0-10	40	6.66		20-30	37.9	7.43	
		10-20	40	6.97		30-40	37.9	7.25	
		20-30	40	7.38		40-50	37.9	6.83	
		30-40	40	7.57					
		40-50	40	5.92					
240	Control	0-10	37.60	7.14					
		10-20	37.60	7.01					
		20-30	37.60	7.19					
		30-40	37.60	7.39					
		40-50	37.60	6.86					
	Treated	0-10	37.30	6.86					
		10-20	37.30	6.94					
		20-30	37.30	7.14					
		30-40	37.30	7.34					
		40-50	37.30	6.91					

Footnotes to the table:

- 1) For this time point samples taken using RA-piercer were analysed, because the soil cores taken using Wacker Hammer were not available for the analysis – they were damaged during transport;

Next table – B.8.1.1.2.2.1._CA-30 provides the results of the determination of recovery rates for each analyte during analyses. It is followed by the table B.8.1.1.2.2.1._CA-31 presenting the results of the verification of the application rate for each trial site.

Table B.8.1.1.2.2.1._CA-30: The results of the verification of the recovery rates for each analyte during the analysis of the collected samples.

Compound	Parameter	Results for the trial:	
		Saussay-la-Campagne (30254/6), Southern France	Fresne-L'Archeveque (30455/7), Northern France
Flufenacet	Recovery rate [%]	92.8	88.0
	RSD [%]	8.2	13.9
FOE Alcohol	Recovery rate [%]	88.5	86.4
	RSD [%]	9.8	4.4
FOE Oxalate	Recovery rate [%]	97.2	96.3
	RSD [%]	8.1	7.5
FOE Sulfonic acid	Recovery rate [%]	88.5	93.9
	RSD [%]	5.3	15.9

Table B.8.1.1.2.2.1._CA-31: The results of the verification of the application rate for each trial site.

Trial	Application rate [g Flufenacet/ha]	Theoretical DAT-0 concentration of Flufenacet in top 10-cm soil layer [µg/kg soil]	Measured DAT-0 concentration of Flufenacet in top 10-cm soil layer [µg/kg soil]	Measured DAT-0 concentration of Flufenacet in top soil as % of Theoretical concentration
Saussay-la-Campagne (30254/6), Southern France	240	160	115	71.9
Fresne-L'Archeveque (30455/7), Northern France	240	160	93.0	58.1

Below are presented the results of the study – the concentrations in [µg/kg] of Flufenacet and its degradation products – FOE Alcohol, FOE Oxalate and FOE Sulfonic acid, in soil for each trial. The results are presented in three tables – table B.8.1.1.2.2.1._CA-32, summarising the values obtained in samples from the control plots, and then for the treated plots individually for each trial in tables B.8.1.1.2.2.1._CA-33/33a and B.8.1.1.2.2.1._CA-34/34a. The values are given for the the layers down to 50-cm depth.

In case of the degradation products – FOE Alcohol, FOE Oxalate and FOE Sulfonic acid, their residues, if detected, were found in the top 0-10 cm layer. In the lower layers – 10-20 cm, 20-30 cm, 30-40 cm and 40-50 cm, these compounds, if detected, were in amounts < LOQ (10 µg/kg). Additionally it was stated that in almost all cases they were < LOD (3 µg/kg), so in fact were not detected in deeper soil layers.

Table B.8.1.1.2.2.1._CA-32: The results of the determination of the concentrations of the test compounds in samples from control (untreated) plots obtained in the trials.

Results obtained for the trial: Saussay-la-Campagne (30254/6)					
Sampling point - DAT	Soil layer [cm]	Concentration [µg/kg] of:			
		Flufenacet	FOE Alcohol	FOE Oxalate	FOE Sulfonic acid
0	0-10	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
	10-20	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
	20-30	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
	30-40	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
	40-50	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
242	0-10	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
	10-20	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
	20-30	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
	30-40	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
	40-50	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
Results obtained for the trial: Fresne-L'Archeveque (30455/7)					
Sampling point - DAT	Soil layer [cm]	Concentration [µg/kg] of:			
		Flufenacet	FOE Alcohol	FOE Oxalate	FOE Sulfonic acid
0	0-10	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
240	0-10	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
	10-20	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
	20-30	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
	30-40	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
	40-50	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾

Footnotes to the table:

1) n. d. = not detectable – the values below the LOD = 3 µg/kg soil.

Table B.8.1.1.2.2.1_CA-33: The results of the determination of the concentrations of the test compounds in samples from treated plot obtained in the South French trial
Saussay-la-Campagne (30254/6).

Sampling point - DAT	Soil layer [cm]	Concentration of Flufenacet [µg/kg]					Concentration of FOE Alcohol [µg/kg]				
		Rep1	Rep 2	Rep 3	Rep 4	Mean	Rep1	Rep 2	Rep 3	Rep 4	Mean
0	0-10	115.2	113.4	113.1	119.8	115	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d.⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
8	0-10	75.98	76.31	83.58	67.18	75.8	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d.⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
52	0-10	10.87	10.53	---- ⁵⁾	---- ⁵⁾	10.7	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
70	0-10	< 10 ³⁾	< 10 ³⁾	---- ⁵⁾	---- ⁵⁾	< 10³⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
89	0-10	< 10 ³⁾	< 10 ³⁾	---- ⁵⁾	---- ⁵⁾	< 10³⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
116	0-10	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
180	0-10	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
242	0-10	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾

Footnotes to the table:

- 1) for that layer usually the values for two replicates were reported;
- 2) for these layers the values one replicate were reported;
- 3) <10 = values below the LOQ = 10 µg/kg soil;
- 4) n. d. = not detectable – the values below the LOD = 3 µg/kg soil.
- 5) No value.

Table B.8.1.1.2.2.1_CA-33a: The results of the determination of the concentrations of the test compounds in samples from treated plot obtained in the South French trial
Saussay-la-Campagne (30254/6) – continued.

Sampling point - DAT	Soil layer [cm]	Concentration of FOE Oxalate [$\mu\text{g/kg}$]					Concentration of FOE Sulfonic acid [$\mu\text{g/kg}$]				
		Rep1	Rep 2	Rep 3	Rep 4	Mean	Rep1	Rep 2	Rep 3	Rep 4	Mean
0	0-10	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
8	0-10	< 10 ³⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	< 10 ³⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
52	0-10	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
70	0-10	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
89	0-10	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
116	0-10	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
180	0-10	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
242	0-10	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾

Footnotes to the table:

- 1) for that layer usually the values for two replicates were reported;
- 2) for these layers the values one replicate were reported;
- 3) <10 = values below the LOQ = 10 $\mu\text{g/kg}$ soil;
- 4) n. d. = not detectable – the values below the LOD = 3 $\mu\text{g/kg}$ soil.
- 5) No value.

Table B.8.1.1.2.2.1_CA-34: The results of the determination of the concentrations of the test compounds in samples from treated plot obtained in the North French trial
Fresne-L'Archeveque (30455/7).

Sampling point - DAT	Soil layer [cm]	Concentration of Flufenacet [µg/kg]					Concentration of FOE Alcohol [µg/kg]				
		Rep1	Rep 2	Rep 3	Rep 4	Mean	Rep1	Rep 2	Rep 3	Rep 4	Mean
0	0-10	85.00	95.33	94.84	96.95	93.0	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d.⁴⁾
28	0-10	25.83	29.85	---- ⁵⁾	---- ⁵⁾	27.8	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
53	0-10	< 10 ³⁾	< 10 ³⁾	---- ⁵⁾	---- ⁵⁾	< 10³⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
88	0-10	< 10 ³⁾	< 10 ³⁾	---- ⁵⁾	---- ⁵⁾	< 10³⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
120	0-10	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
178	0-10	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
240	0-10	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾

Footnotes to the table:

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- 4) n. d. = not detectable – the values below the LOD = 3 µg/kg soil.
- 5) No value.

Table B.8.1.1.2.2.1_CA-34a: The results of the determination of the concentrations of the test compounds in samples from treated plot obtained in the North French trial
Fresne-L'Archeveque (30455/7) – continued.

Sampling point - DAT	Soil layer [cm]	Concentration of FOE Oxalate [$\mu\text{g/kg}$]					Concentration of FOE Sulfonic acid [$\mu\text{g/kg}$]				
		Rep1	Rep 2	Rep 3	Rep 4	Mean	Rep1	Rep 2	Rep 3	Rep 4	Mean
0	0-10	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	0-10	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
28	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	0-10	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
53	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	0-10	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
88	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	0-10	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
120	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	0-10	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
178	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	0-10	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
240	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	0-10	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾

Footnotes to the table:

- 1) for that layer usually the values for two replicates were reported;
- 2) for these layers the values one replicate were reported;
- 3) <10 = values below the LOQ = 10 $\mu\text{g/kg}$ soil;
- 4) n. d. = not detectable – the values below the LOD = 3 $\mu\text{g/kg}$ soil.
- 5) No value.

The weather data for each trial site provided by the study report are presented below on figures B.8.1.1.2.2.1._CA-11 and B.8.1.1.2.2.1._CA-12.

Study No.: 30254/6
Origin of Data: Meteo. France Station de Boos (76)
Test Location: 27150 Saussay La Campagne

Date/Period of Time	Remark	Mean Temp. (°C)	Rainfall (mm)	Sunshine (hours)
03/11/94 - 03/20/94		7	18	23
03/21/94 - 03/31/94		9	17	36
04/01/94 - 04/10/94		5	76	33
04/11/94 - 04/20/94		5	6	35
04/21/94 - 04/30/94		13	3	70
05/01/94 - 05/10/94		11	19	59
05/11/94 - 05/20/94		13	49	52
05/21/94 - 05/31/94		12	34	55
06/01/94 - 06/10/94		12	37	51
06/11/94 - 06/20/94		15	0	117
06/21/94 - 06/30/94		17	8	90
07/01/94 - 07/10/94		17	10	51
07/11/94 - 07/20/94		20	37	85
07/21/94 - 07/31/94		20	45	88
08/01/94 - 08/10/94		20	29	84
08/11/94 - 08/20/94		15	58	57
08/21/94 - 08/31/94		15	17	42
09/01/94 - 09/10/94		14	28	37
09/11/94 - 09/20/94		11	27	21
09/21/94 - 09/30/94		13	9	30
10/01/94 - 10/10/94		9	2	57
10/11/94 - 10/20/94		11	9	58
10/21/94 - 10/31/94		10	43	20
11/01/94 - 11/10/94		10	17	32
03/11/94	T, S	6	0	9
03/18/94	S	8	0	0
03/25/94	S	11	1	0
04/08/94	S	7	8	2
05/02/94	S	11	0	13
05/20/94	S	11	13	1
06/08/94	S	11	0	1
07/05/94	S	14	0	0
09/07/94	S	15	2	3
11/08/94	S	9	0	0

T: Treatment
S: Sampling

Figure B.8.1.1.2.2.1._CA-11: The weather data presented in the study report for the South French trial site Saussay-la Campagne (30254/6); copied from the study report.

Study No.: 304557
 Origin of Data: Meteo. France Station de Boos (76)
 Test Location: 27700 Fresno l'Archeveque

Date/Period of Time	Remark	Mean Temp. (°C)	Rainfall (mm)	Sunshine (hours)
03/11/94 - 03/20/94		7	18	23
03/21/94 - 03/31/94		9	17	36
04/01/94 - 04/10/94		5	76	33
04/11/94 - 04/20/94		5	6	35
04/21/94 - 04/30/94		13	3	70
05/01/94 - 05/10/94		11	19	59
05/11/94 - 05/20/94		13	49	52
05/21/94 - 05/31/94		12	34	55
06/01/94 - 06/10/94		12	37	51
06/11/94 - 06/20/94		15	0	117
06/21/94 - 06/30/94		17	8	90
07/01/94 - 07/10/94		17	10	51
07/11/94 - 07/20/94		20	37	85
07/21/94 - 07/31/94		20	45	88
08/01/94 - 08/10/94		20	29	84
08/11/94 - 08/20/94		15	58	57
08/21/94 - 08/31/94		15	17	42
09/01/94 - 09/10/94		14	28	37
09/11/94 - 09/20/94		11	27	21
09/21/94 - 09/30/94		13	9	30
10/01/94 - 10/10/94		9	2	57
10/11/94 - 10/20/94		11	9	58
10/21/94 - 10/31/94		10	43	20
11/01/94 - 11/10/94		10	17	32
11/11/94 - 11/20/94		11	44	6
11/21/94 - 11/30/94		9	4	7
03/28/94	T, S	10	0	0
04/05/94	S	5	9	3
04/11/94	S	6	0	8
04/25/94	S	10	0	8
05/20/94	S	11	13	1
06/24/94	S	22	2	13
07/26/94	S	20	0	6
09/22/94	S	13	0	2
11/23/94	S	9	0	6

T: Treatment
 S: Sampling

Figure B.8.1.1.2.2.1._CA-12: The weather data presented in the study report for the North French trial site Fresno-L'Archeveque (30455/7); copied from the study report.

The results of the study were kinetically examined. It was stated that due to the fact that for the degradation products – FOE Oxalate and FOE Sulfonic acid, only in few samples from the layer 0-10 cm the concentrations were above the LOQ = 10 µg/kg soil (d. w.), while for FOE Alcohol the values were generally < LOQ, it was not possible to perform the kinetic examination of the data. Therefore only for the data obtained for Flufenacet kinetic analysis was performed.

The kinetic examination of the data was carried out using Timme and Frehse method. As that method of the kinetic analysis is not any longer considered valid for the regulatory purposes in the EU, RMS decided not to present its results in the summary. Instead the results will be kinetically evaluated, in line with the recommendations of the FOCUS Kineitics Guidance Document [FOCUS; 2006], further down this Renewal Assessment Report.

Study 4:

Report: Sommer H., (1995): “Dissipation of FOE 5043 in Soil under Field Conditions (France, Italy).”; Bayer AG, Crop Protection Business Group, Crop Protection-Development, Institute for Metabolism Research & Residue Analysis, D-51368 Leverkusen-Baywerk, Germany (performing laboratory) *for* Bayer Corporation, Agriculture Division, P. O. Box 4913, Hawthorne Road, Kansas City, MO 64120-0013, USA; Study Report No. RA-2019/94; Bayer Report No. 107721; 23 November 1995; study reference number: M-002175-01-2;

Guidelines: The study was performed to comply with the following Guidelines:

- BBA Guideline IV-4.1, (1986);
- US. EPA Guidelines for Pesticide Registration, Subdivision N, Section 164-1, Terrestrial Field Dissipation (Supplemental).

GLP: Yes;

RMS comments: The study had been evaluated for the previous authorisation of Flufenacet in the EU, by inclusion of the compound into the Annex I of the Directive 91/414/EEC. Its brief summary can be found under the point B.7.1.2.2., in section B.7 of the Annex B to the Monograph prepared by the RMS – France, for Flufenacet. Assessing it, as well as other three similar studies, the RMS stated that it was acceptable, although at the same time indicated that the study was not triggered, and hence required, according to the provisions of the Commission Directive 95/36/EC of the 14th July 1994, amending the Council Directive 91/414/EEC. It was however required according to the provisions of the German BBA guideline for assessing Plant Protection Products, part IV, 4.1.

For the purpose of the current assessment the study was evaluated for its compliance with the following guidelines:

- Lynch M. R., editor, (1995): “Procedures for assessing the environmental fate and ecotoxicology of pesticides.”, SETAC; chapter 3.1. – Soil dissipation study;
- NAFTA Guidance Document for Conducting Terrestrial Field Dissipation Studies, 31 March 2006;
- US EPA Fate, Transport and Transformation Test Guidelines, OPPTS Guideline 835.6100 – Terrestrial Field Dissipation;

Additionally, in the area of the kinetic assessment of the results, it was evaluated for the compliance with the following Guidelines:

- FOCUS (2006): “Guidance Document on Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration.” Report of the FOCUS Work Group on Degradation Kinetics, EC Document Reference SANCO/10058/2005 version 2.0, 434 pp.;
- FOCUS, 2011: “Generic Guidance for Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration.” Version 1.0, Nov. 23, 2011.

The following deviations from the Guidelines cited above were stated:

- The history of the test fields over 5 years preceding the trials was not provided, therefore it is not possible to state whether flufenacet or other plant protection products belonging to the same group – oxyacetamides, acetamides or amides, were used there during that period;
- The analytical method used in the study was generally adequately characterised, with exception of the instrumental methods used for identification and quantitation of the test compounds. That was indicated solely to be HPLC-MS/MS. However, as the method was declared to be a validated method, it was probably very similar or the same as used in other studies aimed on the determination of the route of degradation of Flufenacet in soil;
- The characteristics of the trial plots was very limited – only the area was provided without the plot’s dimension (width, length) and other physical features usually required, such as the plot’s slope;
- The soil cores were sampled to the depth of 50 cm, while the relevant Guidelines recommend 1-metre deep sampling;
- The kinetic analysis of the results was performed according to Timme and Frehse, the method not compliant with the currently recommended procedure for kinetic evaluation of the data;

- The study report contains the weather data, but reported, for the first 30 days in 7-days intervals, and afterwards in ~30 days intervals; additionally average montly values and average monthly values of many years are given, what may substantially complicate the normalisation procedure;
- The analysis in the area of degradation products was performed only for the metabolites formed by the degradation within the phenyl moiety – FOE Oxalate, FOE Alcohol, and FOE Sulfonic acid; the would-be fate of Flufenacet within the thiadiazole moiety was not examined.

Despite these deficiencies RMS found the study acceptable, and possible to be used for the regulatory purposes, at least as a source of the data characterising persistence of Flufenacet and its selected major soil degradation products in soil under field conditions. The study is summarised below.

Summary:

The aim of the study was to examine the dissipation of Flufenacet and formation and fate of its degradation products in soil under field conditions. The experiment was carried out on four trial locations, in southern France (two locations) and in Italy (two locations). It was performed on cropped fields, covered with either sunflower (French trials) or soybean (Italian trials). The characteristic of trial sites is presented below in the table B.8.1.1.2.2.1._CA-35.

Table B.8.1.2.2.1._CA-35: The characteristic of the trial sites.

Information			Trial:			
			Laudun	St. Etienne du Gres	Ravenna	S. Romualdo
Trial data	Trial code number		40163/3	40164/1	40494/2	40495/0
	Trial location		F-30290 Laudun, France (South)	F-13103 St. Etienne du Gres, France (South)	I-48100 Ravenna, Italy	I-48020 S. Romulato, Italy
	Size of the test plot [m ²]		310	310	672	672
	Duration of the field trial		240 days	236 days	236 days	236 days
	Soil cultivation and maintenance activities	Crop cover	Sunflower, variety Lotus	Sunflower	Soybean, variety Azzurra	Soybean, variety Westfield
		Date of sowing	04/05/1994	16/04/1994	25/04/1994	26/04/1994
		Date of harvest	Not given	Not given	15/09/1994	16/09/1994
		Sowing density	110000 plants/ha	75000 plants/ha	50 [kg/ha]	50 [kg/ha]
		Maintenance practices	Local agricultural practices, mechanical weed control, no irrigation, no PPP used			
	Data on application of the test compound	Test compound	Flufenacet	Flufenacet	Flufenacet	Flufenacet
		Formulation – Test Substance	FOE 5043 60 WG	FOE 5043 60 WG	FOE 5043 60 WG	FOE 5043 60 WG
		Application rate [g a. s./ ha]	600	600	600	600
		Number of applications	1	1	1	1
		Type of application	Spraying	Spraying	Spraying	Spraying
		Application equipment	Knapsack sprayer	Knapsack sprayer	Wheelbarrow applicator	Wheelbarrow applicator
		Water rate [L/ha]	280	280	400	400
		Date of application	17/05/1994	22/04/1994	27/04/1994	27/04/1994
		Air temperature at application	19°C	16°C	19°C	19°C
Soil properties for the trial field (0-30 cm layer)	Soil textural class	DIN 19682	Silty clay loam	Silty loam	Sandy loamy silt	Loamy clay
		USDA	Clay loam	Silt loam	Silt loam	Silty clay
	Particle size distribution (USDA)	Sand	20.6	14.8	35.4	4.3
		Silt	48.0	62.3	51.5	47.1
		Clay	31.4	22.9	13.1	48.6
	pH (in 0.01M CaCl ₂ aq)		7.6	7.7	7.8	7.8
	OC [%]		1.28	0.96	0.98	1.11
	OM [%]		2.2	1.65	1.69	1.91
	CEC [meq/100 g soil d. w.]		19	10	9	18
	Soil moisture [g/100 g soil d.w.]		41.0	38.7	44.1	51.3
	N content [mg/100 g soil d.w.]		170	150	110	170

The Test Substance – Flufenacet formulated as FOE 5043 60 WG, was applied at spring, shortly after sowing of the crop. Prior to the application from each trial site 50-cm soil cores were sampled for the characterisation of the soil on the test plot.

After application 50-cm soil cores, having a diameter 49.0, 49.5 or 50 mm (depending on soil properties on sampling date) were taken from each test field at pre-designated time point. The locations of sampling points were statistically distributed over the plot to get the representative samples. The cores were taken using a pushing sampling system – Wacker Hammer. The first samples – DAT 0 samples (DAT stands for “Days After Treatment”), were taken directly after application, immediately after drying of the spray film. For that time point, as well as for the last time point two types of soil cores were sampled for the further analysis – treated samples and control samples (from the non-treated plots). For the remaining time points only the cores from the treated plots were samples. At each sampling interval 20 cores were sampled from the treated plot and 20 from the control, untreated, plot. The sampled cores were deep-frozen ($T < -18^{\circ}\text{C}$) on the sampling site on the day of sampling and in that state shipped to the laboratory for further analysis. The sampling protocol for each trial site is presented below, in tables B.8.1.1.2.2.1._CA-36 for French trials and B.8.1.1.2.2.1._CA-37 for Italian trials. The deep-frozen samples were stored for up to ~500 days, depending on the trial and sample, before being processed.

In the laboratory the cores were cut into 10 cm segments and segments of one layer, further called laboratory samples, milled and homogenised. A part of such sample was used in the analysis, performed using the internal analytical method developed by Bachlechner and Allemendinger. It consisted of cold-solvent extraction followed by the quantitative analysis using HPLC-MS/MS technique.

The cold-solvent extraction looked as follows: soil samples were extracted by shaking for 60 minutes on mechanic shaker, with 100 mL of 0.1N HCl/CH₃CN (1:1) solution. The liquid phase was decanted and purified by filtration. 40 mL of filtrate was concentrated to 5 mL on TurboVap and brought to the volume of 10 mL with first 0.4 mL of 37% HCl_{aq} followed by the appropriate amount of distilled water. After centrifugation it was analysed by HPLC-MS/MS. RMS noticed that the used extraction method was almost identical to that described in the open-source publication by [Lam, McKinney and Clay; 2002], summarised as **Study 8** under the point B.8.1.1.1.1. of this Renewal Assessment Report. This may indicate that it may be considered fully appropriate for the purpose it was used for.

The identification and quantitation was performed using HPLC-MS/MS method in comparison to internal standards – deuterised derivatives of the analytes, added after extraction. The qualitative and quantitative analysis was performed for the following compounds: Flufenacet, FOE Alcohol, FOE Oxalate and FOE Sulfonic acid.

The method was validated and controlled by determining the procedural recoveries for each of the test compounds in range 10 – 600 µg/kg. They were following:

- for Flufenacet the mean recovery was 89.6% with RSD = 6.2%;
- for FOE Alcohol the mean recovery was 94.3% with RSD = 4.3%;
- for FOE Oxalate the mean recovery was 96.6% with RSD = 7.9%;
- for FOE Sulfonic acid the mean recovery was 102% with RSD = 3.8%.

The performance of the method was also determined in terms of LOD = 3 µg/kg and LOQ = 10 µg/kg. These values were relevant for all analytes.

Additionally were determined the recovery rates during analyses for each analysed compound and each trial site. The results are presented in the table B.8.1.1.2.2.1._CA-38. They were used to verify the integrity of the analysis of residues.

The verification of the application rate was performed for each trial site using 0-10 cm layers of sampled soil cores. The resulting values were the averages of four replicates. They were compared to the theoretical concentrations of Flufenacet in soil calculated using the following assumptions: the compound was evenly distributed in 0-10cm layer and the soil density was 1.5 g/cm³. The theoretical concentration of the test compound, for the application rate of 600 g Flufenacet/ha was **400 µg/kg soil**. The detailed results of the verification of application rate for each trial are provided in the table B.8.1.1.2.2.1._CA-39.

The results of the analysis are presented in tabularised form further down this summary (tables B.8.1.1.2.2.1._CA-40 – B.8.1.1.2.2.1._CA-45/45a). Finally, on figures B.8.1.1.2.2.1._CA-13 – B.8.1.1.2.2.1._CA-16 are presented the weather data as they were provided in the study report.

Table B.8.1.1.2.2.1._CA-36: The sampling data for the French trials Laudun and St. Etienne du Gres.

Trial: Laudun (40163/3)					Trial: St. Etienne du Gres (40164/1)				
Sampling point - DAT	Type of sample	Soil layer [cm]	Mass of the sample [kg]		Sampling point - DAT	Type of sample	Soil layer [cm]	Mass of the sample [kg]	
			Field sample	Laboratory sample				Field sample	Laboratory sample
0	Control	0-10	36.0	6.47	0	Control	0-10	34.4	6.14
		10-20	36.0	6.95			10-20	34.4	6.79
		20-30	36.0	7.56			20-30	34.4	7.02
		30-40	36.0	7.46			30-40	34.4	7.27
		40-50	36.0	5.19			40-50	34.4	5.12
	Treated	0-10	35.3	6.59		Treated	0-10	34.4	6.53
		10-20	35.3	6.98			10-20	34.4	6.56
		20-30	35.3	7.23			20-30	34.4	6.87
		30-40	35.3	7.14			30-40	34.4	6.18
		40-50	35.3	5.31			40-50	34.4	5.08
8	Treated	0-10	36.2	6.62	7	Treated	0-10	35.5	6.38
		10-20	36.2	6.67			10-20	35.5	7.09
		20-30	36.2	7.24			20-30	35.5	7.15
		30-40	36.2	7.18			30-40	35.5	7.36
		40-50	36.2	6.43			40-50	35.5	5.51
14	Treated	0-10	35.7	6.15	14	Treated	0-10	34.3	6.14
		10-20	35.7	6.68			10-20	34.3	6.77
		20-30	35.7	7.30			20-30	34.3	6.97
		30-40	35.7	7.34			30-40	34.3	7.30
		40-50	35.7	6.35			40-50	34.3	5.17
28	Treated	0-10	31.8	5.58	28	Treated	0-10	35.9	6.16
		10-20	31.8	5.68			10-20	35.9	6.79
		20-30	31.8	6.18			20-30	35.9	7.06
		30-40	31.8	6.67			30-40	35.9	7.16
		40-50	31.8	6.15			40-50	35.9	6.46
57	Treated	0-10	29.8	5.09	56	Treated	0-10	34.5	6.22
		10-20	29.8	5.23			10-20	34.5	6.87
		20-30	29.8	5.83			20-30	34.5	7.03
		30-40	29.8	6.23			30-40	34.5	7.20
		40-50	29.8	5.68			40-50	34.5	5.23
91	Treated	0-10	35.0	5.45	90	Treated	0-10	35.3	5.64
		10-20	35.0	6.00			10-20	35.3	6.29
		20-30	35.0	6.22			20-30	35.3	6.28
		30-40	35.0	6.55			30-40	35.3	6.43
		40-50	35.0	5.79			40-50	35.3	6.08
125	Treated	0-10	34.72	6.13	123	Treated	0-10	23.54	4.46
		10-20	34.72	6.47			10-20	23.54	4.91
		20-30	34.72	6.84			20-30	23.54	4.67
		30-40	34.72	7.01			30-40	23.54	4.32
		40-50	34.72	6.51			40-50	23.54	4.12
182	Treated	0-10	36.05	6.38	180	Treated	0-10	36.84	6.56
		10-20	36.05	6.67			10-20	36.84	7.04
		20-30	36.05	7.23			20-30	36.84	7.20
		30-40	36.05	7.16			30-40	36.84	7.27
		40-50	36.05	6.74			40-50	36.84	6.81
240	Control	0-10	35.2	6.21	236	Control	0-10	37.0	6.64
		10-20	35.2	6.29			10-20	37.0	6.99
		20-30	35.2	6.92			20-30	37.0	7.13
		30-40	35.2	7.10			30-40	37.0	7.21
		40-50	35.2	6.75			40-50	37.0	6.92
	Treated	0-10	35.0	5.38		Treated	0-10	37.3	6.85
		10-20	35.0	6.16			10-20	37.3	6.95
		20-30	35.0	6.82			20-30	37.3	6.97
		30-40	35.0	7.22			30-40	37.3	7.02
		40-50	35.0	6.68			40-50	37.3	7.10

Table B.8.1.1.2.2.1._CA-37: The sampling data for the Italian trials Ravenna Monheim and S. Romualdo.

Trial: Ravenna (40494/2)					Trial: S. Romualdo (40495/0)				
Sampling point - DAT	Type of sample	Soil layer [cm]	Mass of the sample [kg]		Sampling point - DAT	Type of sample	Soil layer [cm]	Mass of the sample [kg]	
			Field sample	Laboratory sample				Field sample	Laboratory sample
0	Control	0-10	34.8	6.62	0	Control	0-10	35.0	6.34
		10-20	34.8	7.17			10-20	35.0	7.15
		20-30	34.8	6.91			20-30	35.0	7.11
		30-40	34.8	6.91			30-40	35.0	7.15
		40-50	34.8	5.09			40-50	35.0	5.47
	Treated	0-10	35.2	6.74		Treated	0-10	35.8	6.78
		10-20	35.2	7.27			10-20	35.8	7.40
		20-30	35.2	6.99			20-30	35.8	7.29
		30-40	35.2	6.83			30-40	35.8	7.26
		40-50	35.2	5.23			40-50	35.8	4.85
7	Treated	0-10	35.3	6.86	7	Treated	0-10	35.0	6.19
		10-20	35.3	7.30			10-20	35.0	7.25
		20-30	35.3	7.07			20-30	35.0	7.20
		30-40	35.3	7.01			30-40	35.0	7.15
		40-50	35.3	5.06			40-50	35.0	5.07
14	Treated	0-10	34.9	6.14	14	Treated	0-10	35.10	6.25
		10-20	34.9	7.08			10-20	35.10	7.36
		20-30	34.9	6.81			20-30	35.10	7.26
		30-40	34.9	6.68			30-40	35.10	7.14
		40-50	34.9	5.06			40-50	35.10	5.05
28	Treated	0-10	34.1	6.30	28	Treated	0-10	34.80	6.08
		10-20	34.1	7.05			10-20	34.80	7.15
		20-30	34.1	6.73			20-30	34.80	7.18
		30-40	34.1	6.73			30-40	34.80	7.10
		40-50	34.1	4.79			40-50	34.80	5.06
56	Treated	0-10	33.6	6.49	56	Treated	0-10	34.10	6.10
		10-20	33.6	6.86			10-20	34.10	7.04
		20-30	33.6	6.69			20-30	34.10	7.01
		30-40	33.6	6.64			30-40	34.10	7.10
		40-50	33.6	4.76			40-50	34.10	4.77
90	Treated	0-10	30.7	5.63	90	Treated	0-10	32.60	5.95
		10-20	30.7	5.92			10-20	32.60	6.36
		20-30	30.7	5.85			20-30	32.60	6.20
		30-40	30.7	5.54			30-40	32.60	6.29
		40-50	30.7	5.06			40-50	32.60	5.69
121	Treated	0-10	31.0	5.47	121	Treated	0-10	31.8	5.77
		10-20	31.0	5.95			10-20	31.8	6.34
		20-30	31.0	5.87			20-30	31.8	6.18
		30-40	31.0	5.52			30-40	31.8	6.11
		40-50	31.0	4.77			40-50	31.8	5.37
180	Treated	0-10	32.3	6.12	180	Treated	0-10	34.5	6.46
		10-20	32.3	6.47			10-20	34.5	6.96
		20-30	32.3	6.27			20-30	34.5	6.80
		30-40	32.3	6.64			30-40	34.5	6.37
		40-50	32.3	5.70			40-50	34.5	5.87
236	Control	0-10	34.35	6.41	236	Control	0-10	36.4	6.76
		10-20	34.35	6.79			10-20	36.4	7.04
		20-30	34.35	6.64			20-30	36.4	6.96
		30-40	34.35	6.45			30-40	36.4	6.88
		40-50	34.35	5.97			40-50	36.4	6.64
	Treated	0-10	33.65	6.37		Treated	0-10	36.7	6.86
		10-20	33.65	6.73			10-20	36.7	7.03
		20-30	33.65	6.51			20-30	36.7	6.96
		30-40	33.65	6.18			30-40	36.7	6.88
		40-50	33.65	5.74			40-50	36.7	6.64

Next table – B.8.1.1.2.2.1._CA-38 provides the results of the determination of recovery rates for each analyte during analyses. It is followed by the table B.8.1.1.2.2.1._CA-39 presenting the results of the verification of the application rate for each trial site.

Table B.8.1.1.2.2.1._CA-38: The results of the verification of the recovery rates for each analyte during the analysis of the collected samples.

Compound	Parameter	Results for the trial:			
		<i>Laudun (40163/3) South France</i>	<i>St. Etienne du Gres (40164/1) South France</i>	<i>Ravenna (40494/2) Italy</i>	<i>S. Romualdo (40495/0) Italy</i>
<i>Flufenacet</i>	Recovery rate [%]	85.8	83.3	92.2	84.7
	RSD [%]	9.11	7.94	4.03	9.33
	Number of experiments	10	8	8	10
<i>FOE Alcohol</i>	Recovery rate [%]	87.1	85.8	90.3	85.6
	RSD [%]	4.43	1.78	8.18	9.07
	Number of experiments	10	8	8	10
<i>FOE Oxalate</i>	Recovery rate [%]	97.8	97.4	101	99.1
	RSD [%]	5.22	4.74	5.54	6.48
	Number of experiments	10	8	8	10
<i>FOE Sulfonic acid</i>	Recovery rate [%]	96.2	95.0	112	103
	RSD [%]	7.57	4.86	7.04	4.44
	Number of experiments	10	8	8	10

Table B.8.1.1.2.2.1._CA-39: The results of the verification of the application rate for each trial site.

Trial	Application rate [g Flufenacet/ha]	Theoretical DAT-0 concentration of Flufenacet in top 10-cm soil layer [µg/kg soil]	Measured DAT-0 concentration of Flufenacet in top 10-cm soil layer [µg/kg soil]	Measured DAT-0 concentration of Flufenacet in top soil as % of Theoretical concentration
<i>Laudun (40163/3); South France</i>	600	400	202	50.5
<i>St. Etienne du Gres (40164/1); South France</i>	600	400	227	56.8
<i>Ravenna (40494/2) Italy</i>	600	400	345	86.3
<i>S. Romualdo (40495/0) Italy</i>	600	400	345	86.3

Below are presented the results of the study – the concentrations in [µg/kg] of Flufenacet and its degradation products – FOE Alcohol, FOE Oxalate and FOE Sulfonic acid, in soil for each trial. The results are presented in five tables – table B.8.1.1.2.2.1._CA-40, summarising the values obtained in samples from the control plots, and for then for the treated plots individually for each trial in tables: B.8.1.1.2.2.1._CA-41/41a for Laudun, B.8.1.1.2.2.1._CA-42/42a for St Etienne du Gres, B.8.1.1.2.2.1._CA-43/43a for Ravenna and B.8.1.1.2.2.1._CA-44/44a for S. Romualdo. The values are given for the the layers down to 50-cm depth.

In case of the degradation products – FOE Alcohol, FOE Oxalate and FOE Sulfonic acid, their residues, if detected, were found in the top 0-10 cm layer. In the lower layers – 10-20 cm, 20-30 cm, 30-40 cm and 40-50 cm, these compounds, if detected, were in amounts < LOQ (10 µg/kg). Additionally it was stated that in almost all cases they were < LOD (3 µg/kg), so in fact were not detected in deeper soil layers.

Table B.8.1.1.2.2.1_CA-40: The results of the determination of the concentrations of the test compounds in samples from control (untreated) plots.

Results obtained for the trial: Laudun (40163/3); South France					
Sampling point - DAT	Soil layer [cm]	Concentration [$\mu\text{g/kg}$] of:			
		Flufenacet	FOE Alcohol	FOE Oxalate	FOE Sulfonic acid
0	0-10	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
	10-20	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
	20-30	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
	30-40	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
	40-50	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
240	0-10	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
	10-20	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
	20-30	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
	30-40	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
	40-50	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
Results obtained for the trial: St. Etienne du Gres (40164/1); South France					
Sampling point - DAT	Soil layer [cm]	Concentration [$\mu\text{g/kg}$] of:			
		Flufenacet	FOE Alcohol	FOE Oxalate	FOE Sulfonic acid
0	0-10	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
	10-20	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
	20-30	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
	30-40	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
	40-50	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
236	0-10	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
	10-20	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
	20-30	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
	30-40	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
	40-50	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
Results obtained for the trial: Ravenna (40494/2); Italy					
Sampling point - DAT	Soil layer [cm]	Concentration [$\mu\text{g/kg}$] of:			
		Flufenacet	FOE Alcohol	FOE Oxalate	FOE Sulfonic acid
0	0-10	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
	10-20	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
	20-30	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
	30-40	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
	40-50	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
236	0-10	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
	10-20	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
	20-30	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
	30-40	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
	40-50	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
Results obtained for the trial: S. Romualdo (40495/0); Italy					
Sampling point - DAT	Soil layer [cm]	Concentration [$\mu\text{g/kg}$] of:			
		Flufenacet	FOE Alcohol	FOE Oxalate	FOE Sulfonic acid
0	0-10	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
	10-20	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
	20-30	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
	30-40	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
	40-50	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
236	0-10	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
	10-20	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
	20-30	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
	30-40	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
	40-50	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾

Footnotes to the table:1) n. d. = not detectable – the values below the LOD = 3 $\mu\text{g/kg}$ soil.

Table B.8.1.1.2.2.1_CA-41: The results of the determination of the concentrations of the test compounds in samples from treated plot obtained in the South French trial
Laudun (40163/3).

Sampling point - DAT	Soil layer [cm]	Concentration of Flufenacet [µg/kg]					Concentration of FOE Alcohol [µg/kg]				
		Rep1	Rep 2	Rep 3	Rep 4	Mean	Rep1	Rep 2	Rep 3	Rep 4	Mean
0	0-10	203.2	202.2	187.3	216.1	202	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
8	0-10	243.5	242.9	246.0	225.7	240	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
14	0-10	254.7	275.4	---- ⁵⁾	---- ⁵⁾	265	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
28	0-10	216.5	195.8	---- ⁵⁾	---- ⁵⁾	206 ⁶⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
57	0-10	136.2	139.1	---- ⁵⁾	---- ⁵⁾	138	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	10-20 ¹⁾	< 10 ³⁾	< 10 ³⁾	---- ⁵⁾	---- ⁵⁾	< 10 ³⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
91	0-10	84.95	81.56	---- ⁵⁾	---- ⁵⁾	83.3	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
125	0-10	n. d. ^{4, 6)}	n. d. ^{4, 6)}	n. d. ^{4, 6)}	n. d. ^{4, 6)}	n. d. ^{4, 6)}	n. d. ^{4, 6)}	n. d. ^{4, 6)}	n. d. ^{4, 6)}	n. d. ^{4, 6)}	n. d. ^{4, 6)}
	10-20 ¹⁾	31.45 ⁶⁾	29.79 ⁶⁾	31.78 ⁶⁾	31.62 ⁶⁾	31.2 ⁶⁾	n. d. ^{4, 6)}	n. d. ^{4, 6)}	n. d. ^{4, 6)}	n. d. ^{4, 6)}	n. d. ^{4, 6)}
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
182	0-10	< 10 ³⁾	< 10 ³⁾	---- ⁵⁾	---- ⁵⁾	< 10 ³⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
240	0-10	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾

Footnotes to the table:

- 1) for that layer usually the values for two replicates were reported;
- 2) for these layers the values one replicate were reported;
- 3) <10 = values below the LOQ = 10 µg/kg soil;
- 4) n. d. = not detectable – the values below the LOD = 3 µg/kg soil.
- 5) No value;
- 6) Due to the wrong labelling of samples after milling and homogenisation the samples from these two layers were mismatched – the residues from the layer 10-20 cm should be attributed to the layer 0-10 cm, while those for the layer 0-10 cm to the layer 10-20 cm.

Table B.8.1.1.2.2.1_CA-41a: The results of the determination of the concentrations of the test compounds in samples from treated plot obtained in the South French trial
Laudun (40163/3) – continued.

Sampling point - DAT	Soil layer [cm]	Concentration of FOE Oxalate [$\mu\text{g/kg}$]					Concentration of FOE Sulfonic acid [$\mu\text{g/kg}$]				
		Rep1	Rep 2	Rep 3	Rep 4	Mean	Rep1	Rep 2	Rep 3	Rep 4	Mean
0	0-10	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
8	0-10	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
14	0-10	< 10 ³⁾	< 10 ³⁾	---- ⁵⁾	---- ⁵⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	---- ⁵⁾	---- ⁵⁾	< 10 ³⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
28	0-10	< 10 ³⁾	< 10 ³⁾	---- ⁵⁾	---- ⁵⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	---- ⁵⁾	---- ⁵⁾	< 10 ³⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
57	0-10	11.56	11.41	---- ⁵⁾	---- ⁵⁾	11.5	< 10 ³⁾	< 10 ³⁾	---- ⁵⁾	---- ⁵⁾	< 10 ³⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
91	0-10	20.88	18.17	---- ⁵⁾	---- ⁵⁾	19.5	14.55	12.72	---- ⁵⁾	---- ⁵⁾	13.6
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
125	0-10	n. d. ^{4, 6)}	n. d. ^{4, 6)}	n. d. ^{4, 6)}	n. d. ^{4, 6)}	n. d. ^{4, 6)}	n. d. ^{4, 6)}	n. d. ^{4, 6)}	n. d. ^{4, 6)}	n. d. ^{4, 6)}	n. d. ^{4, 6)}
	10-20 ¹⁾	< 10 ^{3, 6)}	< 10 ^{3, 6)}	< 10 ^{3, 6)}	< 10 ^{3, 6)}	< 10 ^{3, 6)}	< 10 ^{3, 6)}	< 10 ^{3, 6)}	< 10 ^{3, 6)}	< 10 ^{3, 6)}	< 10 ^{3, 6)}
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
182	0-10	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
240	0-10	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾

Footnotes to the table:

- 1) for that layer usually the values for two replicates were reported;
- 2) for these layers the values one replicate were reported;
- 3) <10 = values below the LOQ = 10 $\mu\text{g/kg}$ soil;
- 4) n. d. = not detectable – the values below the LOD = 3 $\mu\text{g/kg}$ soil.
- 5) No value;
- 6) Due to the wrong labelling of samples after milling and homogenisation the samples from these two layers were mismatched – the residues from the layer 10-20 cm should be attributed to the layer 0-10 cm, while those for the layer 0-10 cm to the layer 10-20 cm.

Table B.8.1.1.2.2.1_CA-42: The results of the determination of the concentrations of the test compounds in samples from treated plot obtained in the South French trial St. Etienne du Gres (40164/1).

Sampling point - DAT	Soil layer [cm]	Concentration of Flufenacet [µg/kg]					Concentration of FOE Alcohol [µg/kg]				
		Rep1	Rep 2	Rep 3	Rep 4	Mean	Rep1	Rep 2	Rep 3	Rep 4	Mean
0	0-10	223.6	222.6	219.6	240.5	227	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
7	0-10	287.9	290.8	282.3	281.0	285	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
14	0-10	197.4	191.0	---- ⁵⁾	---- ⁵⁾	1947	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
28	0-10	229.6	242.9	---- ⁵⁾	---- ⁵⁾	236	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
56	0-10	140.5	147.7	---- ⁵⁾	---- ⁵⁾	144	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
90	0-10	74.85	72.09	---- ⁵⁾	---- ⁵⁾	73.5	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
123	0-10	59.19	62.86	---- ⁵⁾	---- ⁵⁾	61.0	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
180	0-10	11.18	12.75	---- ⁵⁾	---- ⁵⁾	12.0	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
236	0-10	< 10 ³⁾	< 10 ³⁾	---- ⁵⁾	---- ⁵⁾	< 10 ³⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾

Footnotes to the table:

- 1) for that layer usually the values for two replicates were reported;
- 2) for these layers the values one replicate were reported;
- 3) <10 = values below the LOQ = 10 µg/kg soil;
- 4) n. d. = not detectable – the values below the LOD = 3 µg/kg soil.
- 5) No value.

Table B.8.1.1.2.2.1_CA-42a: The results of the determination of the concentrations of the test compounds in samples from treated plot obtained in the South French trial
St. Etienne du Gres (40164/1) – continued.

Sampling point - DAT	Soil layer [cm]	Concentration of FOE Oxalate [$\mu\text{g/kg}$]					Concentration of FOE Sulfonic acid [$\mu\text{g/kg}$]				
		Rep1	Rep 2	Rep 3	Rep 4	Mean	Rep1	Rep 2	Rep 3	Rep 4	Mean
0	0-10	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	--- ⁵⁾	--- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	--- ⁵⁾	--- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	--- ⁵⁾	--- ⁵⁾	--- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	--- ⁵⁾	--- ⁵⁾	--- ⁵⁾	n. d. ⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	--- ⁵⁾	--- ⁵⁾	--- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	--- ⁵⁾	--- ⁵⁾	--- ⁵⁾	n. d. ⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	--- ⁵⁾	--- ⁵⁾	--- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	--- ⁵⁾	--- ⁵⁾	--- ⁵⁾	n. d. ⁴⁾
7	0-10	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	--- ⁵⁾	--- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	--- ⁵⁾	--- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	--- ⁵⁾	--- ⁵⁾	--- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	--- ⁵⁾	--- ⁵⁾	--- ⁵⁾	n. d. ⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	--- ⁵⁾	--- ⁵⁾	--- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	--- ⁵⁾	--- ⁵⁾	--- ⁵⁾	n. d. ⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	--- ⁵⁾	--- ⁵⁾	--- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	--- ⁵⁾	--- ⁵⁾	--- ⁵⁾	n. d. ⁴⁾
14	0-10	n. d. ⁴⁾	n. d. ⁴⁾	--- ⁵⁾	--- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	--- ⁵⁾	--- ⁵⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	--- ⁵⁾	--- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	--- ⁵⁾	--- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	--- ⁵⁾	--- ⁵⁾	--- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	--- ⁵⁾	--- ⁵⁾	--- ⁵⁾	n. d. ⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	--- ⁵⁾	--- ⁵⁾	--- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	--- ⁵⁾	--- ⁵⁾	--- ⁵⁾	n. d. ⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	--- ⁵⁾	--- ⁵⁾	--- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	--- ⁵⁾	--- ⁵⁾	--- ⁵⁾	n. d. ⁴⁾
28	0-10	< 10 ³⁾	< 10 ³⁾	--- ⁵⁾	--- ⁵⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	--- ⁵⁾	--- ⁵⁾	< 10 ³⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	--- ⁵⁾	--- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	--- ⁵⁾	--- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	--- ⁵⁾	--- ⁵⁾	--- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	--- ⁵⁾	--- ⁵⁾	--- ⁵⁾	n. d. ⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	--- ⁵⁾	--- ⁵⁾	--- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	--- ⁵⁾	--- ⁵⁾	--- ⁵⁾	n. d. ⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	--- ⁵⁾	--- ⁵⁾	--- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	--- ⁵⁾	--- ⁵⁾	--- ⁵⁾	n. d. ⁴⁾
56	0-10	< 10 ³⁾	< 10 ³⁾	--- ⁵⁾	--- ⁵⁾	< 10 ³⁾	10.89	10.69	--- ⁵⁾	--- ⁵⁾	10.8
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	--- ⁵⁾	--- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	--- ⁵⁾	--- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	--- ⁵⁾	--- ⁵⁾	--- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	--- ⁵⁾	--- ⁵⁾	--- ⁵⁾	n. d. ⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	--- ⁵⁾	--- ⁵⁾	--- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	--- ⁵⁾	--- ⁵⁾	--- ⁵⁾	n. d. ⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	--- ⁵⁾	--- ⁵⁾	--- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	--- ⁵⁾	--- ⁵⁾	--- ⁵⁾	n. d. ⁴⁾
90	0-10	< 10 ³⁾	< 10 ³⁾	--- ⁵⁾	--- ⁵⁾	< 10 ³⁾	10.88	11.08	--- ⁵⁾	--- ⁵⁾	11.0
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	--- ⁵⁾	--- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	--- ⁵⁾	--- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	--- ⁵⁾	--- ⁵⁾	--- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	--- ⁵⁾	--- ⁵⁾	--- ⁵⁾	n. d. ⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	--- ⁵⁾	--- ⁵⁾	--- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	--- ⁵⁾	--- ⁵⁾	--- ⁵⁾	n. d. ⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	--- ⁵⁾	--- ⁵⁾	--- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	--- ⁵⁾	--- ⁵⁾	--- ⁵⁾	n. d. ⁴⁾
123	0-10	< 10 ³⁾	< 10 ³⁾	--- ⁵⁾	--- ⁵⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	--- ⁵⁾	--- ⁵⁾	< 10 ³⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	--- ⁵⁾	--- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	--- ⁵⁾	--- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	--- ⁵⁾	--- ⁵⁾	--- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	--- ⁵⁾	--- ⁵⁾	--- ⁵⁾	n. d. ⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	--- ⁵⁾	--- ⁵⁾	--- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	--- ⁵⁾	--- ⁵⁾	--- ⁵⁾	n. d. ⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	--- ⁵⁾	--- ⁵⁾	--- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	--- ⁵⁾	--- ⁵⁾	--- ⁵⁾	n. d. ⁴⁾
180	0-10	n. d. ⁴⁾	n. d. ⁴⁾	--- ⁵⁾	--- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	--- ⁵⁾	--- ⁵⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	--- ⁵⁾	--- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	--- ⁵⁾	--- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	--- ⁵⁾	--- ⁵⁾	--- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	--- ⁵⁾	--- ⁵⁾	--- ⁵⁾	n. d. ⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	--- ⁵⁾	--- ⁵⁾	--- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	--- ⁵⁾	--- ⁵⁾	--- ⁵⁾	n. d. ⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	--- ⁵⁾	--- ⁵⁾	--- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	--- ⁵⁾	--- ⁵⁾	--- ⁵⁾	n. d. ⁴⁾
236	0-10	n. d. ⁴⁾	n. d. ⁴⁾	--- ⁵⁾	--- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	--- ⁵⁾	--- ⁵⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	--- ⁵⁾	--- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	--- ⁵⁾	--- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	--- ⁵⁾	--- ⁵⁾	--- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	--- ⁵⁾	--- ⁵⁾	--- ⁵⁾	n. d. ⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	--- ⁵⁾	--- ⁵⁾	--- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	--- ⁵⁾	--- ⁵⁾	--- ⁵⁾	n. d. ⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	--- ⁵⁾	--- ⁵⁾	--- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	--- ⁵⁾	--- ⁵⁾	--- ⁵⁾	n. d. ⁴⁾

Footnotes to the table:

- 1) for that layer usually the values for two replicates were reported;
- 2) for these layers the values one replicate were reported;
- 3) <10 = values below the LOQ = 10 $\mu\text{g/kg}$ soil;
- 4) n. d. = not detectable – the values below the LOD = 3 $\mu\text{g/kg}$ soil.
- 5) No value.

Table B.8.1.1.2.2.1_CA-43: The results of the determination of the concentrations of the test compounds in samples from treated plot obtained in the Italian trial Ravenna (40494/2).

Sampling point - DAT	Soil layer [cm]	Concentration of Flufenacet [µg/kg]					Concentration of FOE Alcohol [µg/kg]				
		Rep1	Rep 2	Rep 3	Rep 4	Mean	Rep1	Rep 2	Rep 3	Rep 4	Mean
0	0-10	373.0	356.2	334.7	315.7	345	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d.⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
7	0-10	278.4	298.9	288.3	285.1	288	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d.⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
14	0-10	223.8	229.8	---- ⁵⁾	---- ⁵⁾	227	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
28	0-10	280.2	274.5	---- ⁵⁾	---- ⁵⁾	277	< 10 ³⁾	< 10 ³⁾	---- ⁵⁾	---- ⁵⁾	< 10³⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
56	0-10	113.0	109.1	---- ⁵⁾	---- ⁵⁾	111	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
90	0-10	41.90	44.18	---- ⁵⁾	---- ⁵⁾	43.0	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
121	0-10	45.31	46.38	---- ⁵⁾	---- ⁵⁾	45.8	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
180	0-10	11.04	10.74	---- ⁵⁾	---- ⁵⁾	10.9	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
236	0-10	< 10 ³⁾	< 10 ³⁾	---- ⁵⁾	---- ⁵⁾	< 10³⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d.⁴⁾

Footnotes to the table:

- 1) for that layer usually the values for two replicates were reported;
- 2) for these layers the values one replicate were reported;
- 3) <10 = values below the LOQ = 10 µg/kg soil;
- 4) n. d. = not detectable – the values below the LOD = 3 µg/kg soil.
- 5) No value.

Table B.8.1.1.2.2.1_CA-43a: The results of the determination of the concentrations of the test compounds in samples from treated plot obtained in the Italian trial Ravenna (40494/2) – continued.

Sampling point - DAT	Soil layer [cm]	Concentration of FOE Oxalate [$\mu\text{g/kg}$]					Concentration of FOE Sulfonic acid [$\mu\text{g/kg}$]				
		Rep1	Rep 2	Rep 3	Rep 4	Mean	Rep1	Rep 2	Rep 3	Rep 4	Mean
0	0-10	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
7	0-10	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
14	0-10	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
28	0-10	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
56	0-10	< 10 ³⁾	< 10 ³⁾	---- ⁵⁾	---- ⁵⁾	< 10 ³⁾	10.36	10.24	---- ⁵⁾	---- ⁵⁾	10.3
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
90	0-10	< 10 ³⁾	< 10 ³⁾	---- ⁵⁾	---- ⁵⁾	< 10 ³⁾	12.83	14.47	---- ⁵⁾	---- ⁵⁾	13.7
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
121	0-10	< 10 ³⁾	< 10 ³⁾	---- ⁵⁾	---- ⁵⁾	< 10 ³⁾	21.19	20.43	---- ⁵⁾	---- ⁵⁾	20.8
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
180	0-10	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
236	0-10	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾

Footnotes to the table:

- 1) for that layer usually the values for two replicates were reported;
- 2) for these layers the values one replicate were reported;
- 3) <10 = values below the LOQ = 10 $\mu\text{g/kg}$ soil;
- 4) n. d. = not detectable – the values below the LOD = 3 $\mu\text{g/kg}$ soil.
- 5) No value.

Table B.8.1.1.2.2.1_CA-44: The results of the determination of the concentrations of the test compounds in samples from treated plot obtained in the Italian trial S. Romualdo (40495/0).

Sampling point - DAT	Soil layer [cm]	Concentration of Flufenacet [µg/kg]					Concentration of FOE Alcohol [µg/kg]				
		Rep1	Rep 2	Rep 3	Rep 4	Mean	Rep1	Rep 2	Rep 3	Rep 4	Mean
0	0-10	346.8	331.9	334.8	367.5	345	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
7	0-10	376.8	344.1	346.2	358.0	356	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
14	0-10	326.0	322.5	---- ⁵⁾	---- ⁵⁾	324	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
28	0-10	319.3	342.8	---- ⁵⁾	---- ⁵⁾	331	< 10 ³⁾	< 10 ³⁾	---- ⁵⁾	---- ⁵⁾	< 10 ³⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
56	0-10	155.6	171.1	---- ⁵⁾	---- ⁵⁾	163	< 10 ³⁾	< 10 ³⁾	---- ⁵⁾	---- ⁵⁾	< 10 ³⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
90	0-10	97.78	95.97	---- ⁵⁾	---- ⁵⁾	96.9	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
121	0-10	77.05	81.50	---- ⁵⁾	---- ⁵⁾	79.3	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
180	0-10	20.27	19.23	---- ⁵⁾	---- ⁵⁾	19.7	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
236	0-10	14.31	15.02	---- ⁵⁾	---- ⁵⁾	14.7	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾

Footnotes to the table:

- 1) for that layer usually the values for two replicates were reported;
- 2) for these layers the values one replicate were reported;
- 3) <10 = values below the LOQ = 10 µg/kg soil;
- 4) n. d. = not detectable – the values below the LOD = 3 µg/kg soil.
- 5) No value.

Table B.8.1.1.2.2.1_CA-44a: The results of the determination of the concentrations of the test compounds in samples from treated plot obtained in the Italian trial
S. Romualdo (40495/0) – continued.

Sampling point - DAT	Soil layer [cm]	Concentration of FOE Oxalate [$\mu\text{g/kg}$]					Concentration of FOE Sulfonic acid [$\mu\text{g/kg}$]				
		Rep1	Rep 2	Rep 3	Rep 4	Mean	Rep1	Rep 2	Rep 3	Rep 4	Mean
0	0-10	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
7	0-10	< 10 ³⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	< 10 ³⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
14	0-10	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
28	0-10	< 10 ³⁾	< 10 ³⁾	---- ⁵⁾	---- ⁵⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	---- ⁵⁾	---- ⁵⁾	< 10 ³⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
56	0-10	< 10 ³⁾	< 10 ³⁾	---- ⁵⁾	---- ⁵⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	---- ⁵⁾	---- ⁵⁾	< 10 ³⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
90	0-10	< 10 ³⁾	< 10 ³⁾	---- ⁵⁾	---- ⁵⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	---- ⁵⁾	---- ⁵⁾	< 10 ³⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
121	0-10	< 10 ³⁾	< 10 ³⁾	---- ⁵⁾	---- ⁵⁾	< 10 ³⁾	< 10 ³⁾	< 10 ³⁾	---- ⁵⁾	---- ⁵⁾	< 10 ³⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
180	0-10	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
236	0-10	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	10-20 ¹⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	30-40 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	40-50 ²⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾

Footnotes to the table:

- 1) for that layer usually the values for two replicates were reported;
- 2) for these layers the values one replicate were reported;
- 3) <10 = values below the LOQ = 10 $\mu\text{g/kg}$ soil;
- 4) n. d. = not detectable – the values below the LOD = 3 $\mu\text{g/kg}$ soil.
- 5) No value.

The weather data for each trial site provided by the study report are presented below on figures B.8.1.1.2.2.1_CA-13 – B.8.1.1.2.2.1_CA-16.

Study No. : 40163/3
 Origin of Data : Meteo France
 Test Location : F-30290 Laudun

Date/Period of Time	Remark	Mean Temp. (°C)	Rainfall (mm)	Sunshine (hours)
05/01/94 - 05/10/94		16	9	95
05/11/94 - 05/20/94		16	71	51
05/17/94	T,S	16	11	0
05/25/94	S	18	0	13
05/21/94 - 05/31/91		19	8	93
05/31/94	S	23	0	13
06/01/90 - 06/10/94		19	7	105
06/11/94 - 06/20/94		21	9	114
06/14/94	S	21	0	9
06/21/94 - 06/30/94		24	7	115
07/01/94 - 07/10/94		25	0	131
07/13/94	S	27	0	11
07/11/94 - 07/20/94		26	4	114
07/21/94 - 07/31/94		26	11	114
08/01/94 - 08/10/94		26	1	100
08/16/94	S	27	0	11
08/11/94 - 08/20/94		24	6	96
08/21/94 - 08/31/94		25	8	97
09/01/94 - 09/10/94		21	39	89
09/11/94 - 09/20/94		16	82	56
09/19/94	S	14	0	10
09/21/94 - 09/30/94		18	103	39
10/01/94 - 10/31/94		14	149	176
11/01/94 - 11/10/94		14	84	24
11/15/94	S	11	0	6
11/11/94 - 11/20/94		13	0	60
11/21/94 - 11/30/94		11	0	42
12/01/94 - 12/31/94		8	9	150
01/01/95 - 01/10/95		2	5	61
01/12/95	S	2	2	7
01/11/95 - 01/20/95		5	55	52

T : Treatment
 S : Sampling

Figure B.8.1.1.2.2.1_CA-13: The weather data presented in the study report for the South French trial site Laudun (40163/3); copied from the study report.

Study No. : 40164/1
 Origin of Data : Meteo France
 Test Location : F-13103 St. Etienne du Gres

Date/Period of Time	Remark	Mean Temp. (°C)	Rainfall (mm)	Sunshine (hours)
04/11/94 - 04/20/94		10	4	50
04/21/94 - 04/30/94		15	30	89
04/22/94	T, S	13	0	12
04/29/94	S	19	0	12
05/01/94 - 05/10/94		16	0	98
05/11/94 - 05/20/94		17	35	77
05/06/94	S	18	0	12
05/20/94	S	19	0	11
05/21/94 - 05/31/94		19	0	105
06/01/94 - 06/10/94		20	4	112
06/17/94	S	23	0	13
06/11/94 - 06/20/94		21	1	115
06/21/94 - 06/30/94		24	34	115
07/01/94 - 07/10/94		25	0	132
07/11/94 - 07/20/94		26	0	117
07/21/94	S	27	0	13
07/21/94 - 07/31/94		26	2	120
08/01/94 - 08/10/94		26	0	118
08/11/94 - 08/20/94		24	0	111
08/23/94	S	26	0	10
08/21/94 - 08/31/94		24	67	111
09/01/94 - 09/30/94		18	236	202
10/01/94 - 10/10/94		14	16	49
10/19/94	S	16	10	0
10/11/94 - 10/20/94		16	111	66
10/21/94 - 10/31/94		14	20	61
11/01/94 - 11/30/94		13	81	135
12/01/94 - 12/10/94		9	3	24
12/14/94	S	8	0	0
12/11/94 - 12/20/94		8	0	53

T : Treatment
 S : Sampling

Figure B.8.1.1.2.2.1. CA-14: The weather data presented in the study report for the Soth French trial site St. Etienne du Gres (40164/1); copied from the study report.

Study No. : 40494/2
 Origin of Data : Ar. Sperim. M.Marani/Ravenna
 Test Location : I-48100 Ravenna

Date/Period of Time	Remark	Mean Temp. (°C)	Rainfall (mm)	Sunshine (hours)
04/27/94	T,S	15	0	8
04/28/94 - 05/03/94		16	4	59
05/04/94	S	13	0	10
05/05/94 - 05/10/94		14	4	49
05/11/94	S	15	0	5
05/12/94 - 05/24/94		17	4	62
05/25/94	S	21	0	7
05/26/94 - 06/21/94		19	116	218
06/22/94	S	22	0	11
06/23/94 - 07/25/94		24	30	284
07/26/94	S	25	0	9
07/27/94 - 08/25/94		25	15	224
08/26/94	S	22	0	9
08/27/94 - 10/23/94		17	172	202
10/24/94	S	12	11	0
10/25/94 - 12/18/94		8	51	71
12/19/94	S	1	0	0

T : Treatment
 S : Sampling

Figure B.8.1.1.2.2.1_CA-15: The weather data presented in the study report for the Italian trial site Ravenna (40494/2); copied from the study report.

Study No. : 40495/0
 Origin of Data : Ar. Sperim. M.Marani/Ravenna
 Test Location : I-48020 S.Romualdo

Date/Period of Time	Remark	Mean Temp. (°C)	Rainfall (mm)	Sunshine (hours)
04/27/94	T,S	15	0	8
04/28/94 - 05/03/94		16	4	59
05/04/94	S	13	0	10
05/05/94 - 05/10/94		14	4	49
05/11/94	S	15	0	5
05/12/94 - 05/24/94		17	4	62
05/25/94	S	21	0	7
05/26/94 - 06/21/94		19	116	218
06/22/94	S	22	0	11
06/23/94 - 07/25/94		24	30	284
07/26/94	S	25	0	9
07/27/94 - 08/25/94		25	15	224
08/26/94	S	22	0	9
08/27/94 - 10/23/94		17	172	202
10/24/94	S	12	11	0
10/25/94 - 12/18/94		8	51	71
12/19/94	S	1	0	0

T : Treatment

S : Sampling

Figure B.8.1.1.2.2.1_CA-16: The weather data presented in the study report for the Italian trial site S. Romualdo (40495/0); copied from the study report.

The results of the study were kinetically examined. It was stated that due to the fact that for the degradation products – FOE Oxalate and FOE Sulfonic acid, only in few samples from the layer 0-10 cm the concentrations were above the LOQ = 10 µg/kg soil (d. w.), while for FOE Alcohol the values were generally < LOQ, it was not possible to perform the kinetic examination of the data. Therefore only for the data obtained for Flufenacet kinetic analysis was performed.

The kinetic examination of the data was carried out using Timme and Frehse method. As that method of the kinetic analysis is not any longer considered valid for the regulatory purposes in the EU, RMS decided not to present its results in the summary. Instead the results will be kinetically evaluated, in line with the recommendations of the FOCUS Kineitcs Guidance Document [FOCUS; 2006], further down this Renewal Assessment Report.

Study 5:

Report: Lin H, Green D. L., Fig P. S, (1995): “Freezer stability of [Phenyl-UL-¹⁴C]FOE 5043 in Soil.”; Agriculture Division, Miles Inc., Research and Development Department, P. O. Box 4913, Kansas City, Missouri 64120, USA; Miles Study No. F3132101, Miles Report No. 106231, 23 February 1995; study reference number: M-002201-01-1;

Guidelines: The study was performed to comply with the following Guidelines:

- US. EPA Guidelines for Pesticide Registration, Subdivision N, Section 164-1, Terrestrial Field Dissipation (Supplemental).

GLP: Yes;

RMS comments: The study had been evaluated for the previous authorisation of Flufenacet in the EU, by inclusion of the compound into the Annex I of the Directive 91/414/EEC.. Its brief summary can be found under the point B.7.1.2.2.4, in section B.7 of the Annex B to the Monograph prepared by the RMS – France, for Flufenacet. The study was then found acceptable. For the purpose of the current assessment RMS-Poland evaluated it and found it acceptable as a supplementary study to the studies on field dissipation summarised above as **Studies 1-4**, conforming the acceptability of the study in the area of handling the sampled soil cores before their processing. As such it is summarised below.

Summary:

The aim of the study was to examine the stability of Flufenacet in stored deep-frozen soil samples. That parameter was examined in soil samples stored frozen for up to 733 days (approx. two years). The experiment was performed with one soil – Howe, Iowa, Sandy loam soil, used in other experiments examining fate and behaviour of Flufenacet in soil. The characteristic of the test soil is provided below in the table B.8.1.1.2.2.1._CA-45.

Table B.8.1.1.2.2.1._CA-45: The characteristic of soil used in the study.

Parameter		Soil:	
		395	
Soil origin		Howe, Indiana, USA	
Soil type (USDA)		Sandy loam	
Particle size distribution	Sand [%]	72.5	
	Silt [%]	20.5	
	Clay [%]	7.5	
pH value (medium not reported)		6.1	
Organic matter content (OM) [%]		Not reported	
Organic carbon content (C _{org}) [%]		Not reported	
Cation Exchange Capacity – CEC [mEq/100g]		6.9	
Bulk density (disturbed) [g/cm ³]		1.31	
Moisture holding capacity at ½ bar [%]		14.8	
Available nutrients ¹⁾	Ca	1500 [lb/ac]	1680.929 [kg/ha]
	Mg	250 [lb/ac]	280.155 [kg/ha]
	Na	23 [lb/ac]	25.774 [kg/ha]
	K	156 [lb/ac]	174.817 [kg/ha]
	H	37 [lb/ac]	41.463 [kg/ha]
Percent base saturation	% Ca	54.3	
	% Mg	15.1	
	% Na	0.7	
	% K	2.9	
	% H	26.7	
Microbial activity [CPU/g soil]		3.1 E6	

Footnotes to the table:

1) In the study report only the values in [lb/ac] (US pound/US acre) were given. RMS recalculated them to kg/ha using the following assumptions:
1 kg = 0.4535 US pound and 1ha = 0.4046873 US acre.

The test soil was sieved through 2-mm sieve before being characterised.

At the beginning of the experiment 25-g (d.w.) aliquots of the test soil were weighed to fifty 2-oz (~59.14 mL) flint jars, serving as test vessels. Next, the moisture content of soil sample in each jar was adjusted to the level of 75% of 1/3 bar by addition of the appropriate amount of water. The amount of so prepared test vessels was such, to grant 25 samples treated with the test compound, 22 control samples and three blank samples. The treated

samples were used to examine the freezer storage stability and were treated at the beginning of the experiment with Flufenacet applied to each sample at the fortification level of 0.55 mg/kg soil. Control samples were stored alongside the treated samples, but unlike them were fortified with the test compound on sampling date, to provide the concurrent recovery data. Finally, blank samples were left untreated and were processed on DAT 0 (the beginning of the experiment) to check the background radioactivity in the test soil.

The treated samples were spiked with the test compound – [Phenyl-U-¹⁴C]Flufenacet, applied to each sample in form of a spiking acetonitrile-solution having a nominal concentration 110 ppm.

The test compound was radiolabelled flufenacet – [Phenyl-U-¹⁴C]Flufenacet having a specific activity of 66.5 mCi/mMole (406246 dpm/μg) and radiochemical purity of 99.5% when determined by HPLC (99.3% when determined by TLC). Its structural formula is presented below on figure B.8.1.1.2.2.1._CA-17. It was delivered as liquid sample in Vial C-584, further called a standard.

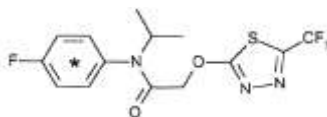


Figure B.8.1.1.2.2.1._CA-17: The structural formula of the test compound – [Phenyl-U-¹⁴C]Flufenacet; the asterisk denotes radiolabelling position (copied from the study report).

The spiking solution was prepared in a following way: first 84-μL of a standard was transferred from Vial C-584 and the original solvent evaporated under the gentle stream of N₂. Next the sample was reconstituted in 8.75 mL of acetonitrile (CH₃CN) to obtain a solution having a concentration 110 mg Flufenacet/L, further called **spiking solution**. Its radiochemical purity was verified by radio-HPLC and radio-TLC, while the concentration of the test compound by LSC.

On DAT-0 all treated samples were fortified with **spiking solution** applied in amount 0.125 mL to obtain the fortification level 0.55 mg Flufenacet/kg soil, and mixed thoroughly by shaking. In the study report it was stated that that fortification level corresponded to the maximum recommended application rate – 1 lb a. i./acre in the top 6-inch soil. When recalculated using standard assumptions – soil density $d = 1.5 \text{ g/cm}^3$ and the thickness of soil layer $l = 5 \text{ cm}$, that fortification level corresponded to the field application rate **A = 412.91 g Flufenacet/ha**.

After fortification all treated samples, except those labelled DAT-0 samples and blank samples which were both processed immediately after fortification of treated samples, and all control samples were placed in the walk-in freezer, set to the constant temperature $T = -23.9 \pm 2.5^\circ\text{C}$, and stored there for up to 733 days (24 months) of freezer storage, until being analysed. The sampling dates for treated samples were set to DAT (Days After Treatment) 0, 34, 92, 184, 365, 547 and 733. For the control samples the sampling intervals were set to 0 days, 1 month, 3 months, 6 months, 12 months 18 months and 24 months of freezer storage. At these sampling points triplicate samples of each type were removed from the freezer. Control samples were then treated with the test compound in exactly the same manner as described above for treated samples, to obtain the fortification level of 0.55 ppm. Next, all samples were processed by stir-extracting the whole soil aliquots with two 50-100 mL portions of CH₃CN/H₂O (9:1). Each extraction step lasted for 2-3 hours and was performed in a room temperature. The extracts were filtered, combined and concentrated to 10 mL by evaporation under vacuum at $T < 35^\circ\text{C}$. The concentrated extracts were analysed by LSC, HPLC and TLC.

Additionally, at 3-month intervals extracts of replicate samples were combined after routine LSC and chromatographic analyses and further analysed by GC-MS.

Extracted soil pellets were analysed, after combustion, for their radioactivity content.

The LSC analysis of sample extracts was performed using their 0.1 – 0.5 mL aliquots mixed with 15 mL of Ultima Gold liquid scintillation cocktail. It was used as quantitative analysis - to determine the radioactivity content in extracts.

The counting was performed using Packard Tricarb Scintillation Counter, model 4640. The performance parameters of the analysis were following:

- average volume of analysed sample was 0.2 mL,
- sample counting time was 5 minutes,
- the average background (BKGD) – 32 cpm,
- the minimum sensitivity was 4.15 E-4 ppm ,
- the Lowest Acceptable Gross Count Rate (LAGC) was 64 cpm,
- the Lowest Acceptable Net Count Rate (LANC) – 32 cpm,
- the greatest probable error GPE = 9.236%.

The analysis of extracted soil pellets was a quantitative analysis, aimed on the determination of the radioactivity retained by soil matrix. For that purpose 0.2-g aliquots of the extracted soil samples were oxidised. The formed $^{14}\text{CO}_2$ was absorbed in 15:5 mixture of Permafluor E and Carbo-sorb E and quantified using Packard Tricarb Scintillation Counter, model 4640. The performance parameters of the analysis were following:

- average mass of analysed sample was 0.2 g,
- sample counting time was 5 minutes,
- the average background (BKGD) – 32 cpm,
- the minimum sensitivity was 4.15 E-4 ppm ,
- the Lowest Acceptable Gross Count Rate (LAGC) was 64 cpm,
- the Lowest Acceptable Net Count Rate (LANC) – 32 cpm,
- the greatest probable error GPE = 9.236%.

Chromatographic analysis – HPLC and TLC was quantitative and qualitative analysis performed to identify the constituents of each extract and quantify them.

HPLC analysis was carried out using either Hewlett Packard 1090 or Shimadzu LC (SCL-6A) chromatographic station coupled with Raytest radioactivity detector (Ramona 90). Chromatographic separation was performed on 250 x 4.6 mm Zorbax ODS chromatographic column preceded by Spheri-5 guard column. It was carried out in a gradient mode presented below in the table B.8.1.1.2.2.1_CA-46. The flow rate of the mobile phase was set to 1.0 mL/min.

Table B.8.1.1.2.2.1_CA-46: The HPLC gradient mode used in the study.

Time [min]	Solvent ratio	
	<i>Solvent A – Water + 0.1% CH_3COOH</i>	<i>Solvent B – Acetonitrile + 0.1% CH_3COOH</i>
0	100	0
2	100	0
7	75	25
27	25	75
32	0	0
40	0	0

The identification was performed by comparison of the retention times with those of the known standards.

The TLC analysis was performed on 20 x 20 cm, 0.25-mm-thick silica-gel plates. They were developed in a following solvent system: hexane/ethyl acetate (1:1). The non-radiolabelled standard was co-chromatographed and visualised under UV light. The developed TLC plates were radiographed using Kodak X-Omat AR films and scanned for quantitation using Ramona Rita-6800 radio-TLC analyser.

The GC-MS analysis was carried out on Hewlett Packard 5890 GC station coupled with Finnigan INCOS 50 quadrupole MS detector. The chromatographic separation was performed on GC capillary column DB-5, 15-m long, 0.25-mm i. d., 0.25- μm film thickness. The carrier gas was He at flow rate 1 mL/min. The GC oven programme was following:

- initial T = 80°C ;
- gradual increase to T = 250°C at rate $20^\circ\text{C}/\text{min}$.

The MS operated in EI mode. Scanned range was 50-400 amu at a rate 0.5 sec/scan.

The method was used to confirm the identity of Flufenacet in standard and spiking solutions as well as in control and treatment samples.

The results of the study are presented below.

Results and their discussion:

The analysis of the blank samples performed on DAT 0 showed that they contained no radioactivity, hence the test soil was free of radioactive contamination prior to the treatment.

The radiochemical purity of the spiking solution determined on DAT 0 was 97.4% when determined by HPLC and 97.7% when determined by TLC. The actual level radioactivity added to each treated sample was 5546310 dpm, corresponding to the fortification level 0.55 mg/kg soil (d. w.).

The numerical results of the experiment are presented below in the table B.8.1.1.2.2.1._CA-47.

Table B.8.1.1.2.2.1._CA-47: The numerical results of the determination of the storage stability of Flufenacet in frozen soil.

Sampling point		Type of sample	Replicate	Radioactivity recovered [% AR]				
Month of freeze-storage	Day of freeze-storage (DAT)			Extracted			Bound	Total recovered
				Total	Identified as Flufenacet			
			By HPLC		By TLC			
0	0	Treated	Rep. 1	94.5	90.2	93.2	1.6	96.1
			Rep 2	98.2	93.9	96.1	1.7	99.9
			Rep 3	99.2	96.7	97.4	1.7	100.9
			Average	97.3	93.6	95.6	1.7	99.0
1	34	Control	Rep. 1	94.1	94.1	93.0	0.7	94.8
			Rep 2	103.3	103.3	102.5	0.7	104.0
			Rep 3	105.7	105.7	104.7	0.7	106.4
			Average	101.0	101.0	100.1	0.7	101.7
		Treated	Rep. 1	101.4	101.4	100.3	0.9	102.3
			Rep 2	95.5	95.5	94.7	1.0	96.5
			Rep 3	99.7	99.7	99.7	1.2	100.8
			Average	98.9	98.9	98.2	1.0	99.9
3	92	Control	Rep. 1	92.1	92.1	92.1	0.3	92.4
			Rep 2	96.1	96.1	96.1	0.2	96.3
			Rep 3	95.1	95.1	95.1	0.2	95.3
			Average	94.4	94.4	94.4	0.2	94.7
		Treated	Rep. 1	100.7	100.7	100.7	0.5	101.2
			Rep 2	98.2	98.2	98.2	0.3	98.5
			Rep 3	104.9	104.9	104.9	0.4	105.3
			Average	101.3	101.3	101.3	0.4	101.7
6	184	Control	Rep. 1	98.0	98.0	98.0	0.1	98.1
			Rep 2	97.1	97.1	97.1	0.1	97.2
			Rep 3	97.2	97.2	97.2	0.1	97.3
			Average	97.4	97.4	97.4	0.1	97.5
		Treated	Rep. 1	87.3	87.3	87.3	0.2	87.5
			Rep 2	96.4	96.4	96.4	0.2	96.6
			Rep 3	103.1	103.1	103.1	0.2	103.3
			Average	95.6	95.6	95.6	0.2	95.8
12	365	Control	Rep. 1	101.2	100.5	101.2	0.2	101.4
			Rep 2	102.9	102.3	102.9	0.3	103.2
			Rep 3	95.0	94.3	95.0	0.3	95.3
			Average	99.7	99.0	99.7	0.3	100.0
		Treated	Rep. 1	97.6	96.8	97.5	0.5	98.1
			Rep 2	98.0	97.4	98.0	0.7	98.7
			Rep 3	97.7	97.2	97.7	0.6	98.3
			Average	97.7	97.1	97.8	0.6	98.4
18	547	Control	Rep. 1	92.8	92.8	92.2	0.1	92.9
			Rep 2	82.3	82.3	82.0	0.1	82.4
			Rep 3	58.6	58.6	58.6	0.1	58.6
			Average	77.9	77.9	77.6	0.1	78.0
		Treated	Rep. 1	101.9	101.9	100.7	0.7	102.6
			Rep 2	102.0	102.0	101.2	0.6	102.6
			Rep 3	111.1	111.1	110.4	0.7	111.8
			Average	105.0	105.0	104.1	0.7	105.7
24	733	Control	Rep. 1	102.0	102.0	99.9	0.3	102.3
			Rep 2	101.7	98.3	101.7	0.3	102.0
			Rep 3	100.3	96.3	99.5	0.3	100.6
			Average	101.3	98.9	100.4	0.3	101.6
		Treated	Rep. 1	97.4	92.3	96.7	0.6	98.0
			Rep 2	96.1	91.8	96.1	0.7	96.8
			Rep 3	97.3	93.2	97.3	0.7	98.0
			Average	96.9	92.4	96.7	0.7	97.6

Additionally the obtained results – the concentrations of Flufenacet in treated soils in function of storage time, were presented in graphical form. For that purpose the concentrations of Flufenacet in extracts, determined using HPLC and TLC methods, were logarithmically transformed (by calculating Ln). Next, the trend line was plotted

using the linear regression. The results are presented below, on figure B.8.1.1.2.2.1._CA-18. These graphs clearly indicate no degradation of Flufenacet is stored frozen samples over the examined storage period.

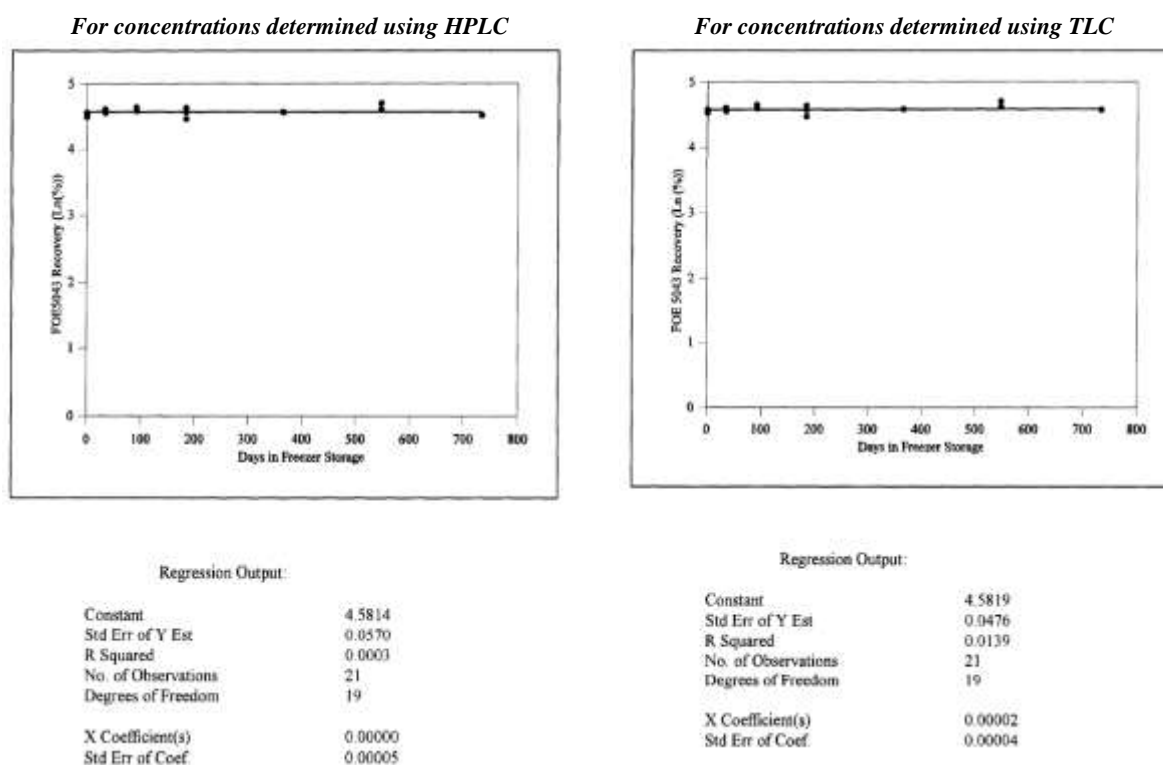


Figure B.8.1.1.2.2.1._CA-18: The results of the analysis of the change in concentration of Flufenacet in stored frozen soil samples in function of time (copied from the study report).

Conclusion:

On the basis of the obtained results it was stated that Flufenacet was stable in sandy loam soil stored in freezer conditions for at least two years.

Study 6:

Report: Lin H, Green D. L., Fig P. S, (1995): “Freezer stability of seven metabolites of [¹⁴C]FOE 5043 in Soil.”; Agriculture Division, Miles Inc., Research and Development Department, P. O. Box 4913, Kansas City, Missouri 64120, USA; Miles Study No. F3132102, Miles Report No. 106640, 26 June 1995; study reference number: M-002199-01-1;

Guidelines: The study was performed to comply with the following Guidelines:

- US. EPA Guidelines for Pesticide Registration, Subdivision N, Section 164-1, Terrestrial Field Dissipation (Supplemental).

GLP: Yes;

RMS comments: The study had been evaluated for the previous authorisation of Flufenacet in the EU, by inclusion of the compound into the Annex I of the Directive 91/414/EEC. Its brief summary can be found under the point B.7.1.2.2.4, in section B.7 of the Annex B to the Monograph prepared by the RMS – France, for Flufenacet. The study was then found acceptable. For the purpose of the current assessment RMS-Poland evaluated it and found it acceptable as a supplementary study to the studies on field dissipation summarised above as **Studies 1-4**, conforming the acceptability of the study in the area of handling the sampled soil cores before their processing. As such it is summarised below.

Summary:

The aim of the study was to examine the stability of seven degradation products of Flufenacet – FOE Alcohol, FOE Oxalate, FOE Sulfonic acid, FOE Methylsulfoxide, FOE Methylsulfone, FOE Thioglycolate sulfoxide and FOE Thiadone, in stored deep-frozen soil samples. That parameter was examined in soil samples stored frozen for up to 727 days (approx. two years). The experiment was performed with one soil – Howe, Iowa, Sandy loam soil, used in other experiments examining fate and behaviour of Flufenacet in soil. The characteristic of the test soil is provided below in the table B.8.1.1.2.2.1._CA-48.

Table B.8.1.1.2.2.1._CA-48: The characteristic of soil used in the study.

Parameter		Soil:	
		395	
Soil origin		Howe, Indiana, USA	
Soil type (USDA)		Sandy loam	
Particle size distribution	Sand [%]	70.7	
	Silt [%]	21.3	
	Clay [%]	8.0	
pH value (measured in water)		6.7	
Organic matter content (OM) [%]		1.8	
Organic carbon content (C _{org}) [%]		1.04	
Cation Exchange Capacity – CEC [mEq/100g]		9.9	
Bulk density (disturbed) [g/cm ³]		1.29	
Moisture holding capacity at ½ bar [%]		15.0	
Available nutrients ¹⁾	Ca	2300 [lb/ac]	2577.424 [kg/ha]
	Mg	370 [lb/ac]	414.629 [kg/ha]
	Na	26 [lb/ac]	29.136 [kg/ha]
	K	210 [lb/ac]	235.330 [kg/ha]
	H	46 [lb/ac]	51.548 [kg/ha]
	Olsen P	81 [lb/ac]	90.770
Percent base saturation	% Ca	57.9	
	% Mg	15.5	
	% Na	0.6	
	% K	2.7	
	% H	23.3	
Microbial activity [CPU/g soil]		3.0 E5	

Footnotes to the table:

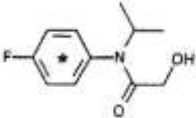
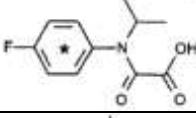
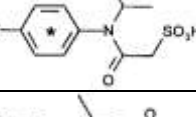
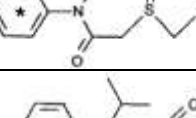
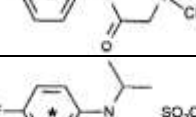
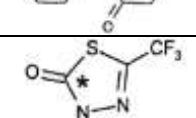
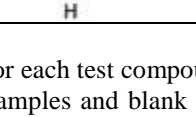
- 2) In the study report only the values in [lb/ac] (US pound/US acre) were given. RMS recalculated them to kg/ha using the following assumptions:
1 kg = 0.4535 US pound and 1ha = 0.4046873 US acre.

The test soil was kept in a bulk pit at the test facility, covered with alfalfa crop, until being used. Before being used the test soil was sieved through 2-mm sieve and its 25-g (d.w.) portions were weighed into fifty 2-oz (~59.14 mL) flint jars equipped with the Teflon-lined lids, serving as test vessels. Next, moisture content of soil

sample in each jar was adjusted to the level of 75% of 1/3 bar (11.25%) by addition of the appropriate amount of water. The amount of so prepared test vessels was such, to grant three replicates of treated samples for each test compound per each sampling point, the same number of the control samples and three blank samples.

Samples designated to be treated samples were fortified with the spiking solutions of the seven already listed radiolabelled test compounds. The spiking solutions were prepared individually for each of the test compounds, by dissolving the appropriate amount of the standard in acetonitrile/water (1:1) to obtain 11 mL of a solution having a concentration 62.5 ppm. The characteristic of each test compound – its structural formula with radiolabelling position marked by asterisk, radiochemical purity and specific activity determined by LSC for 0.2 ml of the spiking solution, is presented below in the table B.8.1.1.2.2.1._CA-49.

Table B.8.1.1.2.2.1._CA-49: The characteristic of the test compounds used in the study (structural formulas copied from their study report).

Compound	Structural formula	Sample code	Specific activity [mCi/mMole]	Radiochemical purity (measured) [%]
<i>FOE Alcohol</i>		C-581	11.8	97.6
<i>FOE Oxalate</i>		C-596	18.4	100.0
<i>FOE Sulfonic acid</i>		C-606	21	100.0
<i>FOE Thioglycolate sulfoxide</i>		C-608	21	100.0
<i>FOE Methylsulfoxide</i>		C-612	21	98.9
<i>FOE Methylsulfone</i>		C-613	21	98.4
<i>FOE Thiadone</i>		C-595	57	97.0

The fortification level for each test compound was set to 0.5 ppm. For each test compound an individual set of treated samples, control samples and blank samples was prepared. The treated samples were fortified with the given test compound, applied as a spiking solution in amount 0.2 mL, on DAT 0 (first day of storage period; DAT stands for Days After Treatment). The treated samples, except DAT 0 samples which were treated and analysed at application, were stored frozen – at $T = -25.2 \pm 0.4^\circ\text{C}$, for up to 24 months (DAT 715). At designated time points – on the 3rd, 6th, 12th, 18th and 24th month of frozen storage triplicate treated samples for each test compound were removed for further analysis. The exact sampling time points (DAT) may differ for each test compound. At the same time points for each test compound triplicate control samples were removed from freezer. These were treated with the given test compound, in exactly the same manner as treated samples, on the day of sampling. The control samples were not sampled on DAT 0. Instead the triplicate blank samples, set to determine the background soil radioactivity level were processed together with DAT-0 treated samples.

The samples collected at the given time point were processed in the following manner:

- firstly all samples were extracted with two 25-30 mL portions of $\text{CH}_3\text{CN}/0.1\text{N HCl}$ (1:1) in stir extraction carried out at room temperature; the extracts were combined and their 0.1-0.5 mL aliquots analysed for radioactivity content by LSC;

- extracts of samples treated with FOE Alcohol were directly analysed by HPLC because of the high specific activity ;
- extracts of samples treated with FOE Sulfonic acid were azeotropically concentrated (that was due to the fact that that compound is readily soluble in water, but its concentration in extract did not enable direct HPLC analysis); next the 20-mL aliquots of each concentrated extract were mixed with 90 mL of CH₃CN and the mixture was rotary-evaporated to approx. 1mL under vacuum and at T = 30-35⁰C; the so concentrated extracts were then analysed by HPLC;
- extracts from samples treated with remaning five test compounds were partitioned with two 20-mL portions of CH₂Cl₂ and radioactivity in aqueous and organosoluble (DCM) phases was quantified by LSC; next the DCM phase was dried under the gentle stream of nitrogen and reconstituted in 2 mL of either CH₃CN/H₂O (1:1) or water prior to HPLC analysis; in case of DCM phase from extracts of samples treated with FOE Thiadone in order to limit potential losses due to volatilisation 0.02 mL of 5% C₁₀H₁₁OH was added before solvent evaporation.

Extracted soil pellets were analysed, after combustion, for their radioactivity content by LSC.

The LSC analysis of sample extracts was performed using their 0.2 mL aliquots mixed with 15 mL of Ultima Gold liquid scintillation cocktail. It was used as quantitative analysis - to determine the radioactivity content in extracts.

The counting was performed using Packard Tricarb Scintillation Counter, model 4640. The performance parameters of the analysis were following:

- average volume of analysed sample was 0.2 mL,
- sample counting time was 5 minutes,
- the average background (BKGD) – 32 cpm,
- the minimum sensitivity was a compound-specific parameter and is provided further down the report,
- the Lowest Acceptable Gross Count Rate (LAGC) was 64 cpm,
- the Lowest Acceptable Net Count Rate (LANC) – 32 cpm,
- the greatest probable error GPE = 9.2%.

The minimum sensitivity determined for each test compound was following:

- for FOE Alcohol – 1.38 E-4 ppm;
- for FOE Oxalate – 9.68 E-4 ppm;
- for FOE Sulfonic acid – 9.93 E-4 ppm;
- for FOE Thioglycolate sulfoxide – 1.09 E-3 ppm;
- for FOE Methylsulfoxide – 9.28 E-4 ppm;
- for FOE Methylsulfone – 9.86 E-4 ppm;
- for FOE Thiadone – 2.26 E-4 ppm.

The analysis of extracted soil pellets was a quantitative analysis aimed on the determination of the radioactivity retained by soil matrix. For that purpose 0.2-g aliquots of the extracted soil samples were oxidised. The formed ¹⁴CO₂ was absorbed in a mixture of 15 mL Permafluor E and 5 mL Carbo-sorb E and quantified using Packard Tricarb Scintillation Counter, model 4640. The performance parameters of the analysis were following:

- average mass of analysed sample was 0.2 g,
- sample counting time was 5 minutes,
- the average background (BKGD) – 32 cpm,
- the minimum sensitivity was a compound-specific parameter, identical to the values presented above for liquid samples,
- the Lowest Acceptable Gross Count Rate (LAGC) was 64 cpm,
- the Lowest Acceptable Net Count Rate (LANC) – 32 cpm,
- the greatest probable error GPE = 9.2%.

Chromatographic – HPLC analysis was quantitative and qualitative analysis performed to identify the constituents of each extract and quantify them.

It was carried out using either Helwett Packard 1090 or Shimadzu LC (SCL-6A) chromatographic station coupled with Raytest radioactivity detector (Ramona 90). Chromatographic separation was performed on 305 x 7 mm Hamilton PRP-1 chromatographic column preceded by Hamilton PRP-1 guard column. It was carried out in a gradient mode presented below in the table B.8.1.1.2.2.1._CA-50. The flow rate of the mobile phase was set to 1.5 mL/min.

Table B.8.1.1.2.2.1._CA-50: The HPLC gradient mode used in the study.

Time [min]	Solvent ratio	
	<i>Solvent A – Water + 0.1% CH₃COOH</i>	<i>Solvent B – Acetonitrile + 0.1% CH₃COOH</i>
0	90	10
10	75	25
20	75	25
35	0	100
40	0	100

The identification was performed by comparison of the retention times with those of the known standards.

Additionally, for fractionated HPLC-eluates of the processed extracts of treated and control samples collected on the 18th month of freezer-storage, the LC-MS analysis was performed in order to identify the constituents. It was carried out on Varian 5040 HPLC coupled in-series to LB 505 Berthold flow-through radioactivity detector and Finnigan MAT 90 MS detector. The chromatographic separation was performed in a gradient mode on Hamilton PRP-1 (150 x 4.1 mm) HPLC column. The mobile phase consisted of CH₃OH – **Solvent 1**, and water – **Solvent 2**. Its composition changed linearly from 20% to 100% of **Solvent 1** during 20-minutes lasting elution. The flow rate of the mobile phase was 0.8 mL/min. 0.2 M CH₃COONH₄ was added post-column at a rate 0.2 mL/min. The MS detector operated in either positive- or negative-ion mode. The fragmentaric ions used for each test compound as identification factor are presented below in the table B.8.1.1.2.2.1._CA-51.

Table B.8.1.1.2.2.1._CA-51: LC/MS identification of the test compounds in the study.

Compound	Representative signals used in identification	
	<i>Position – m/z</i>	<i>Description</i>
FOE Alcohol	212	Protonated molecular ion [M+H] ⁺
FOE Sulfonic acid	274	Negative molecular ion [M – H] ⁻
FOE Oxalate	240	Protonated molecular ion [M+H] ⁺
	257	Ammonia adduct [M + NH ₄] ⁺
FOE Methylsulfoxide	258	Protonated molecular ion [M+H] ⁺
	275	Ammonia adduct [M + NH ₄] ⁺
FOE Methylsulfone	274	Protonated molecular ion [M+H] ⁺
	291	Ammonia adduct [M + NH ₄] ⁺
FOE Thioglycolate sulfoxide	316	Protonated molecular ion [M+H] ⁺
	333	Ammonia adduct [M + NH ₄] ⁺
FOE Thiadone	171	Negative molecular ion [M – H] ⁻

The results of the study are presented below.

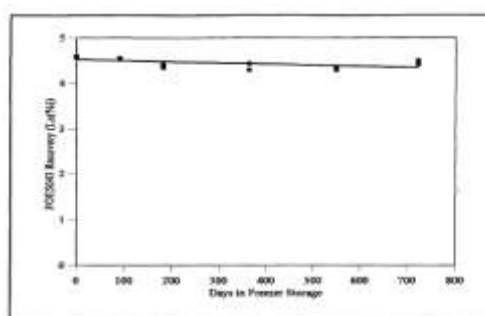
Results and their discussion:

The analysis of the blank samples performed on DAT 0 showed that they contained no radioactivity, hence the test soil was free of radioactive contamination prior to the treatment.

The numerical results of the experiment are presented below, individually for each test compound, in tables B.8.1.1.2.2.1._CA-52 – B.8.1.1.2.2.1._CA-58. The measured concentrations were logarithmically transformed (in form of ln) in order to determine the trend of decline in recovery and by that the rate of would-be degradation in stored frozen soil. These results are presented in graphical form individually for each compound, immediately after corresponding table, on figures B.8.1.1.2.2.1._CA-50 – B.8.1.1.2.2.1._CA-56.

Table B.8.1.1.2.2.1_CA-52: The numerical results of the determination of the storage stability of FOE Alcohol in frozen soil.

Sampling point		Type of sample	Replicate	Radioactivity recovered [% AR]				
Month of freeze-storage	Day of freeze-storage (DAT)			Extracted			Bound	Total recovered
				Total	Identified as FOE Alcohol (HPLC)			
					%	ln %		
0	0	Treated	Rep. 1	99.5	97.3	4.578	0.8	100.3
			Rep 2	100.0	98.9	4.594	0.7	100.7
			Rep 3	100.0	97.9	4.584	0.9	100.9
			Average	99.8	98.0	----	0.8	100.6
3	91	Control	Rep. 1	100.5	98.9	----	0.4	100.9
			Rep 2	101.4	99.2	----	0.4	101.8
			Average	101.0	99.0	----	0.4	101.3
		Treated	Rep. 1	102.3	94.8	4.552	1.2	103.4
			Rep 2	101.9	93.0	4.532	1.3	103.2
			Average	102.1	93.9	----	1.2	103.3
6	182	Control	Rep. 1	104.0	100.1	----	0.2	104.3
			Rep 2	103.1	98.8	----	0.4	103.5
			Average	103.6	99.5	----	0.3	103.9
		Treated	Rep. 1	99.7	83.2	4.422	2.0	101.7
			Rep 2	100.0	78.0	4.298	1.2	101.2
			Average	99.8	80.6	----	1.6	101.5
12	364	Control	Rep. 1	92.9	88.2	----	0.3	93.1
			Rep 2	89.7	86.0	----	0.3	90.0
			Average	91.3	87.1	----	0.3	91.6
		Treated	Rep. 1	100.4	84.3	4.434	2.5	102.9
			Rep 2	92.7	73.6	4.298	2.9	95.6
			Average	96.6	78.9	----	2.7	99.3
18	549	Control	Rep. 1	126.3	126.3	----	0.8	127.3
			Rep 2	112.7	112.7	----	0.5	113.2
			Average	119.5	119.5	----	0.6	120.32
		Treated	Rep. 1	97.3	76.5	4.337	2.6	99.9
			Rep 2	93.0	73.4	4.296	3.7	96.6
			Average	95.1	74.9	----	3.2	98.2
24	723	Control	Rep. 1	103.1	103.1	----	0.3	103.1
			Rep 2	102.5	99.3	----	0.5	103.0
			Average	102.8	101.2	----	0.4	103.2
		Treated	Rep. 1	100.4	89.2	4.491	1.7	102.1
			Rep 2	102.3	82.7	4.415	2.5	104.9
			Average	101.4	85.9	----	2.1	103.5



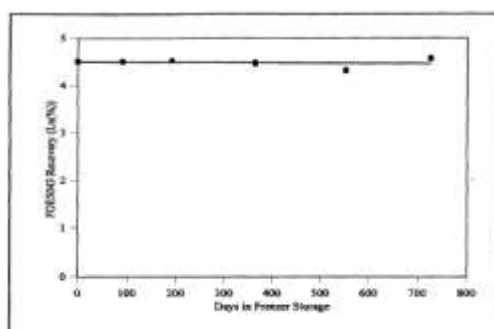
Regression Output:

Constant	4.5270
Std. Err. of Y Est.	0.0898
R Squared	0.3855
No. of Observations	13
Degrees of Freedom	11
X Coefficient(s)	-0.00025
Std. Err. of Coef.	0.000096

Figure B.8.1.1.2.2.1_CA-50: The graphical results of the determination of the storage stability of FOE Alcohol in frozen soil (copied from the study report).

Table B.8.1.1.2.2.1_CA-53: The numerical results of the determination of the storage stability of FOE Oxalate in frozen soil.

Sampling point		Type of sample	Replicate	Radioactivity recovered [% AR]				
Month of freeze-storage	Day of freeze-storage (DAT)			Extracted			Bound	Total recovered
				Total	Identified as FOE Oxalate (HPLC)			
					%	ln %		
0	0	Treated	Rep. 1	95.3	92.8	4.531	2.2	97.4
			Rep 2	92.9	89.6	4.495	3.3	96.1
			Rep 3	93.1	90.1	4.501	4.5	97.7
			Average	93.7	90.8	----	3.3	97.1
3	91	Control	Rep. 1	90.5	89.6	----	1.7	92.2
			Rep 2	94.5	93.6	----	2.7	97.2
			Average	92.5	91.6	----	2.2	94.7
		Treated	Rep. 1	90.8	90.0	4.500	3.1	93.9
			Rep 2	93.9	92.8	4.531	2.9	96.8
			Average	92.4	91.4	----	3.0	95.4
6	192	Contol	Rep. 1	99.0	98.1	----	3.4	102.4
			Rep 2	100.8	99.9	----	3.0	103.8
			Average	99.9	99.0	----	3.2	103.1
		Treated	Rep. 1	93.5	92.5	4.527	3.6	97.0
			Rep 2	95.0	94.1	4.544	4.7	99.8
			Average	94.3	93.3	----	4.2	98.4
12	364	Control	Rep. 1	97.7	96.8	----	3.2	100.9
			Rep 2	96.5	92.1	----	2.6	99.1
			Average	97.1	94.4	----	2.9	100.0
		Treated	Rep. 1	91.7	85.9	4.453	3.7	95.4
			Rep 2	90.9	90.0	4.499	4.0	94.9
			Average	91.3	87.9	----	3.8	95.1
18	552	Control	Rep. 1	89.0	73.9	----	2.2	91.0
			Rep 2	97.2	76.6	----	3.5	100.8
			Average	93.1	75.3	----	2.8	95.9
		Treated	Rep. 1	79.0	64.6	4.168	5.1	83.3
			Rep 2	93.1	74.2	4.307	5.2	98.3
			Average	86.1	69.4	----	5.2	90.8
24	727	Control	Rep. 1	99.2	97.6	----	1.7	101.0
			Rep 2	97.4	95.5	----	3.2	100.6
			Average	93.8	96.5	----	2.5	100.8
		Treated	Rep. 1	96.6	95.7	4.561	3.6	100.2
			Rep 2	99.7	98.2	4.587	3.8	103.7
			Average	98.2	96.9	----	3.7	102.0



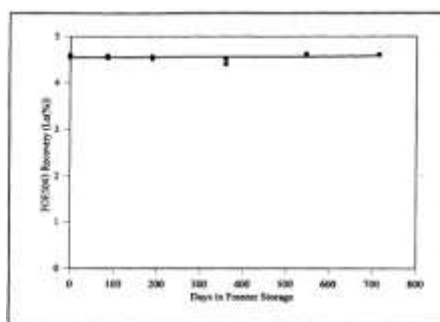
Regression Output:

Constant	4.5078
Std Err of Y Est	0.0860
R Squared	0.0403
No. of Observations	13
Degrees of Freedom	11
X Coefficient(s)	-0.00006
Std Err of Coef.	0.000092

Figure B.8.1.1.2.2.1_CA-51: The graphical results of the determination of the storage stability of FOE Oxalate in frozen soil (copied from the study report).

Table B.8.1.1.2.2.1_CA-54: The numerical results of the determination of the storage stability of FOE Sulfonic acid in frozen soil.

Sampling point		Type of sample	Replicate	Radioactivity recovered [% AR]				
Month of freeze-storage	Day of freeze-storage (DAT)			Extracted			Bound	Total recovered
				Total	Identified as FOE Sulfonic acid (HPLC)			
					%	ln %		
0	0	Treated	Rep. 1	98.9	98.4	4.589	0.3	99.2
			Rep 2	100.6	99.8	4.603	0.4	101.0
			Rep 3	96.4	95.1	4.555	0.3	96.8
			Average	98.7	97.8	----	0.3	99.0
3	86	Control	Rep. 1	104.8	101.5	----	0.3	105.1
			Rep 2	105.1	102.8	----	0.2	105.3
			Average	105.0	102.1	----	0.3	105.2
		Treated	Rep. 1	98.2	94.7	4.550	0.3	98.5
			Rep 2	98.6	98.6	4.591	0.4	98.9
			Average	98.4	96.6	----	0.4	98.7
6	189	Contol	Rep. 1	101.8	101.8	----	0.3	102.2
			Rep 2	102.0	102.0	----	0.3	102.3
			Average	101.9	101.9	----	0.3	102.3
		Treated	Rep. 1	96.4	96.4	4.569	0.4	96.8
			Rep 2	92.9	92.9	4.532	0.6	93.5
			Average	94.7	94.7	----	0.5	95.2
12	360	Control	Rep. 1	110.7	110.7	----	0.2	110.9
			Rep 2	110.3	110.3	----	0.2	110.5
			Average	110.5	110.5	----	0.2	110.7
		Treated	Rep. 1	82.1	82.1	4.407	0.3	82.4
			Rep 2	91.0	91.0	4.511	0.3	91.3
			Average	86.5	86.5	----	0.3	86.8
18	547	Control	Rep. 1	100.5	100.5	----	0.3	100.8
			Rep 2	98.3	98.3	----	0.5	98.8
			Average	99.4	99.4	----	0.4	99.8
		Treated	Rep. 1	102.1	102.1	4.626	0.5	102.6
			Rep 2	99.2	99.2	4.597	0.9	100.1
			Average	100.6	100.6	----	0.7	101.4
24	715	Control	Rep. 1	98.0	98.0	----	0.2	98.1
			Rep 2	101.3	100.1	----	0.2	101.5
			Average	99.6	99.0	----	0.2	99.8
		Treated	Rep. 1	99.9	99.9	4.604	0.5	100.3
			Rep 2	100.6	100.6	4.611	0.4	101.0
			Average	100.2	100.2	----	0.4	100.7



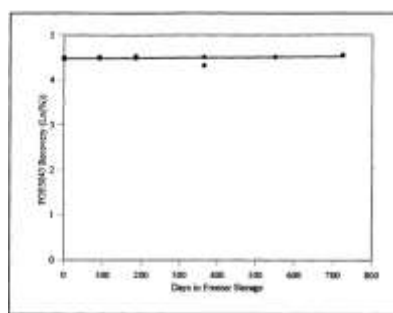
Regression Output:

Constant	4.5545
Std Err of Y Est	0.0597
R Squared	0.0274
No. of Observations	13
Degrees of Freedom	11
X Coefficient(s)	0.000036
Std Err of Coef.	0.000064

Figure B.8.1.1.2.2.1_CA-52: The graphical results of the determination of the storage stability of FOE Sulfonic acid in frozen soil (copied from the study report).

Table B.8.1.1.2.2.1._CA-55: The numerical results of the determination of the storage stability of FOE Thioglycolate sulfoxide in frozen soil.

Sampling point		Type of sample	Replicate	Radioactivity recovered [% AR]				
Month of freeze-storage	Day of freeze-storage (DAT)			Extracted			Bound	Total recovered
				Total	Identified as FOE TGS (HPLC)			
					%	ln %		
0	0	Treated	Rep. 1	94.6	89.3	4.492	0.7	95.2
			Rep 2	93.4	87.1	4.467	0.5	93.9
			Rep 3	93.8	90.5	4.506	0.9	94.7
			Average	93.9	89.0	----	0.7	94.6
3	90	Control	Rep. 1	100.9	96.6	----	0.7	101.6
			Rep 2	101.9	97.1	----	1.1	102.9
			Average	101.4	96.9	----	0.9	102.3
		Treated	Rep. 1	94.3	91.3	4.514	0.9	95.2
			Rep 2	92.1	88.9	4.488	0.8	92.9
			Average	93.2	90.1	----	0.9	94.1
6	185	Control	Rep. 1	101.7	98.7	----	1.0	102.6
			Rep 2	91.4	88.6	----	0.7	92.1
			Average	96.6	93.7	----	0.8	97.4
		Treated	Rep. 1	96.3	93.2	4.535	0.9	97.2
			Rep 2	92.0	89.1	4.490	0.8	92.8
			Average	94.1	91.2	----	0.9	95.0
12	363	Control	Rep. 1	102.4	95.8	----	0.9	103.2
			Rep 2	103.7	100.5	----	0.7	104.4
			Average	104.0	98.1	----	0.8	103.8
		Treated	Rep. 1	81.6	75.2	4.320	1.0	82.5
			Rep 2	93.9	90.9	4.509	0.8	94.7
			Average	87.7	83.0	----	0.9	88.6
18	549	Control	Rep. 1	99.5	96.7	----	1.3	100.8
			Rep 2	100.4	97.0	----	1.4	101.8
			Average	100.0	96.9	----	1.3	101.3
		Treated	Rep. 1	94.4	91.2	4.513	1.9	96.3
			Rep 2	94.3	91.3	4.514	1.5	95.8
			Average	94.4	91.2	----	1.7	96.1
24	724	Control	Rep. 1	105.8	101.6	----	0.6	106.3
			Rep 2	108.8	105.6	----	0.8	109.7
			Average	107.3	103.6	----	0.7	108.0
		Treated	Rep. 1	98.4	94.1	4.545	0.9	99.3
			Rep 2	98.9	95.3	4.557	1.0	99.9
			Average	98.7	94.7	----	0.9	99.6



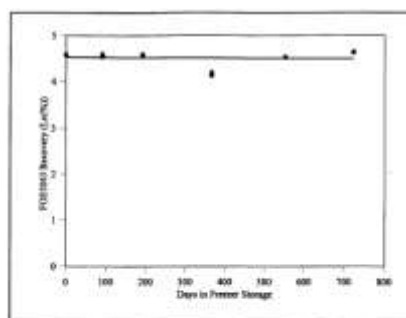
Regression Output:

Constant	4.4885
Std Err of Y Est	0.0593
R Squared	0.0593
No. of Observations	13
Degrees of Freedom	11
X Coefficient(s)	0.00005
Std Err of Coef.	0.00006

Figure B.8.1.1.2.2.1._CA-53: The graphical results of the determination of the storage stability of FOE Thioglycolate sulfoxide in frozen soil (copied from the study report).

Table B.8.1.1.2.2.1_CA-56: The numerical results of the determination of the storage stability of FOE Methylsulfoxide in frozen soil.

Sampling point		Type of sample	Replicate	Radioactivity recovered [% AR]				
Month of freeze-storage	Day of freeze-storage (DAT)			Extracted			Bound	Total recovered
				Total	Identified as FOE Methylsulfoxide (HPLC)			
					%	ln %		
0	0	Treated	Rep. 1	98.6	98.5	4.590	0.2	98.8
			Rep 2	98.4	98.3	4.588	0.2	98.6
			Rep 3	98.6	98.5	4.590	0.2	98.8
			Average	98.5	98.4	----	0.2	98.7
3	91	Control	Rep. 1	102.2	102.0	----	0.2	102.3
			Rep 2	104.2	98.3	----	0.2	104.4
			Average	103.2	100.1	----	0.2	103.4
		Treated	Rep. 1	99.0	98.9	4.594	0.5	99.4
			Rep 2	98.2	94.2	4.545	0.4	98.6
			Average	98.6	96.5	----	0.4	99.0
6	192	Control	Rep. 1	101.2	101.1	----	0.4	101.6
			Rep 2	104.1	104.0	----	0.3	104.4
			Average	102.7	102.6	----	0.3	103.0
		Treated	Rep. 1	99.1	99.0	4.595	0.4	99.4
			Rep 2	98.5	98.4	4.589	0.5	98.9
			Average	98.8	98.7	----	0.4	99.2
12	367	Control	Rep. 1	93.7	63.1	----	0.2	94.0
			Rep 2	92.9	65.5	----	0.42	93.3
			Average	93.3	64.8	----	0.3	93.6
		Treated	Rep. 1	96.5	62.2	4.130/.	0.4	96.9
			Rep 2	94.1	66.3	4.194	0.4	94.5
			Average	95.3	64.3	----	0.4	95.7
18	552	Control	Rep. 1	100.9	96.2	----	0.4	101.2
			Rep 2	96.2	92.6	----	0.6	96.7
			Average	98.5	94.4	----	0.5	99.0
		Treated	Rep. 1	96.9	92.8	4.530	0.4	97.4
			Rep 2	98.7	93.2	4.535	0.4	99.1
			Average	97.8	93.0	----	0.4	98.2
24	727	Control	Rep. 1	101.1	100.0	----	0.2	101.3
			Rep 2	100.5	99.1	----	0.2	100.7
			Average	100.8	99.5	----	0.2	101.0
		Treated	Rep. 1	102.5	102.4	4.629	0.4	102.9
			Rep 2	103.6	103.6	4.640	0.3	104.0
			Average	103.1	103.0	----	0.4	103.4



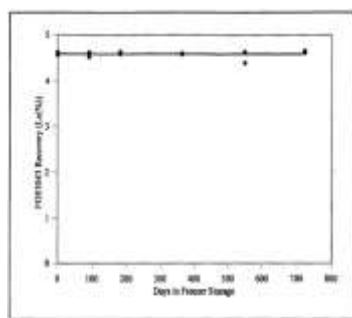
Regression Output:

Constant	4.5333
Std Err of Y Est.	0.1687
R Squared	0.0067
No. of Observations	12
Degrees of Freedom	11
X Coefficient(s)	-0.000015
Std Err of Coef.	0.00018

Figure B.8.1.1.2.2.1_CA-54: The graphical results of the determination of the storage stability of FOE Methylsulfoxide in frozen soil (copied from the study report).

Table B.8.1.1.2.2.1_CA-57: The numerical results of the determination of the storage stability of FOE Methylsulfone in frozen soil.

Sampling point		Type of sample	Replicate	Radioactivity recovered [% AR]				
Month of freeze-storage	Day of freeze-storage (DAT)			Extracted			Bound	Total recovered
				Total	Identified as FOE Methylsulfone (HPLC)			
					%	ln %		
0	0	Treated	Rep. 1	98.4	97.2	4.578	0.2	98.7
			Rep 2	103.9	103.0	4.594	0.3	104.2
			Rep 3	102.1	101.1	4.584	0.4	102.4
			Average	101.5	100.5	----	0.3	101.8
3	91	Control	Rep. 1	97.6	96.2	----	0.2	97.8
			Rep 2	99.1	97.0	----	0.2	99.3
			Average	98.4	96.6	----	0.2	98.6
		Treated	Rep. 1	103.9	102.4	4.552	0.4	104.3
			Rep 2	94.6	93.3	4.532	0.7	95.3
			Average	99.2	97.8	----	0.5	99.8
6	182	Contol	Rep. 1	105.0	104.7	----	0.3	105.3
			Rep 2	98.8	98.7	----	0.3	99.1
			Average	101.9	101.7	----	0.3	102.2
		Treated	Rep. 1	103.1	103.0	4.422	0.5	103.6
			Rep 2	99.2	99.1	4.356	0.6	99.8
			Average	101.2	101.1	----	0.5	101.7
12	364	Control	Rep. 1	104.8	104.8	----	0.1	104.9
			Rep 2	101.3	101.2	----	0.1	101.4
			Average	103.1	103.0	----	0.1	103.2
		Treated	Rep. 1	98.8	98.7	4.434	0.5	99.3
			Rep 2	100.1	100.0	4.298	0.5	100.6
			Average	99.4	99.4	----	0.5	99.9
18	549	Control	Rep. 1	74.0	73.9	----	1.1	74.9
			Rep 2	109.9	109.7	----	0.5	110.5
			Average	92.0	91.8	----	0.8	92.7
		Treated	Rep. 1	81.1	81.0	4.337	1.3	82.2
			Rep 2	103.0	102.9	4.296	0.4	103.4
			Average	92.0	92.0	----	0.9	92.8
24	723	Control	Rep. 1	106.3	106.2	----	0.2	106.5
			Rep 2	103.2	101.9	----	0.2	103.4
			Average	104.7	104.1	----	0.2	104.9
		Treated	Rep. 1	105.9	105.8	4.661	0.5	106.4
			Rep 2	103.8	102.0	4.625	0.6	104.5
			Average	104.8	103.9	----	0.6	105.4



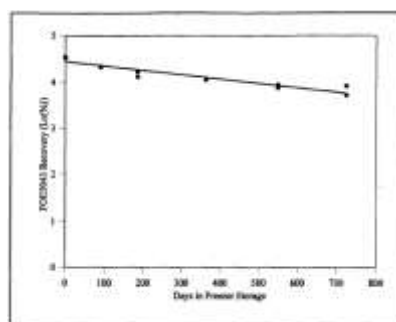
Regression Output:

Constant	4.5989
Std Err of Y Est	0.0710
R Squared	0.0028
No. of Observations	13
Degrees of Freedom	11
X Coefficient(s)	-0.00000
Std Err of Coef.	0.000004

Figure B.8.1.1.2.2.1_CA-55: The graphical results of the determination of the storage stability of FOE Methylsulfone in frozen soil (copied from the study report).

Table B.8.1.1.2.2.1_CA-58: The numerical results of the determination of the storage stability of FOE Thiadone in frozen soil.

Sampling point		Type of sample	Replicate	Radioactivity recovered [% AR]				
Month of freeze-storage	Day of freeze-storage (DAT)			Extracted			Bound	Total recovered
				Total	Identified as FOE Thiadone (HPLC)			
					%	ln %		
0	0	Treated	Rep. 1	94.2	93.9	4.542	0.8	95.0
			Rep 2	94.7	94.4	4.547	0.9	95.6
			Rep 3	93.6	93.2	4.534	0.8	94.4
			Average	94.1	93.8	----	0.8	95.0
3	90	Control	Rep. 1	102.0	101.4	----	1.8	103.9
			Rep 2	102.3	101.4	----	1.5	103.8
			Average	102.2	101.4	----	1.7	103.8
		Treated	Rep. 1	78.0	76.8	4.341	9.0	87.0
			Rep 2	77.9	76.6	4.338	9.1	87.0
			Average	78.0	76.7	----	9.1	87.0
6	185	Control	Rep. 1	96.1	96.1	----	0.3	96.5
			Rep 2	108.0	108.0	----	0.4	108.4
			Average	102.1	102.1	----	0.3	102.4
		Treated	Rep. 1	62.3	62.3	4.131	0.3	62.6
			Rep 2	69.6	69.6	4.243	0.5	70.1
			Average	65.9	65.9	----	0.4	66.3
12	363	Control	Rep. 1	150.4	143.2	----	6.1	156.5
			Rep 2	116.0	115.5	----	2.5	118.5
			Average	133.0	129.3	----	4.3	137.5
		Treated	Rep. 1	63.0	59.5	4.086	15.6	78.9
			Rep 2	59.6	58.0	4.060	19.9	79.5
			Average	61.3	58.7	----	17.9	79.2
18	549	Control	Rep. 1	106.8	104.1	----	1.4	108.2
			Rep 2	104.8	100.2	----	2.7	107.6
			Average	105.8	102.2	----	2.1	107.9
		Treated	Rep. 1	51.2	48.6	3.884	18.8	69.9
			Rep 2	56.4	51.9	3.950	18.0	74.4
			Average	53.8	50.3	----	18.4	72.2
24	724	Control	Rep. 1	100.2	99.8	----	2.5	102.7
			Rep 2	99.8	99.3	----	3.1	102.8
			Average	100.0	99.5	----	2.8	102.7
		Treated	Rep. 1	52.6	50.8	3.928	24.7	77.4
			Rep 2	43.9	41.6	3.728	24.1	68.0
			Average	48.3	46.2	----	24.4	72.7



Regression Output:

Constant	4.6589
Std Err of Y Est	0.0055
R Squared	0.9086
No. of Observations	13
Degrees of Freedom	11
X Coefficient(s)	-0.0010
Std Err of Coef.	0.00009

Figure B.8.1.1.2.2.1_CA-56: The graphical results of the determination of the storage stability of FOE Thiadone in frozen soil (copied from the study report).

Conclusions

On the basis of the obtained results following conclusions were drawn from the study:

- FOE Oxalate, FOE Sulfonic acid, FOE Thioglycolate sulfoxide, FOE Methylsulfoxide and FOE Methylsulfone were stable in stored frozen sandy loam soil throughout the 24-month test period;
- FOE Alcohol degraded slightly during the storage period, forming three unknown products; its extrapolated half-life in stored frozen sandy loam soil was 2748 days;
- In case of FOE Thiadone a significant decrease in concentration was observed during the storage period; it was attributed mainly to loss through volatilization and formation of bound residues; the extrapolated half-life for that compound in stored frozen sandy loam soil was 725 days.

In the Assessment Report for Flufenacet prepared by the RMS – France for the first authorisation of that compound in the EU, it was stated that the results of that study indicated that FOE Oxalate and FOE Sulfonic acid were stable in soil under frozen conditions for at least two years. No definitive conclusions were made with regard to the other degradation products undergoing that examination, but it may be stated that for all tested degradation products, except FOE Thiadone, their high stability in stored frozen soil for the period of two years was confirmed.

That also conforms that the results of the four field dissipation studies summarised above as **Studies 1-4** are fully reliable.

Kinetic examination of the obtained results

The results obtained in **Studies 1-4** were kinetically examined and the outcome of that examination was presented as an integral part of each study report. It was also presented in the Assessment Report prepared for the first authorisation of Flufenacet in the EU (by its inclusion into the Annex I of the Council Directive 91/414/EEC) by the then-RMS – France. Analysing that assessment the present RMS – Poland, stated that it did not comply with the current standards set for the kinetic evaluation of the data by the FOCUS Kineitics Guidance Document [FOCUS, 2006]. In all four study reports the kinetic analysis was declared to be performed in line with the method developed by Timme and Frehse. Additionally the best-fit kinetic model was determined only for the parent compound, while the data for the degradation products were not subjected to such analysis.

For the purpose of the present evaluation the Applicant focused on the kinetic analysis of the results aimed on the determination of the kinetic endpoints suitable for modelling exposure assessment for GW and SW compartments. It was presented in one study report summarised below as **Study 7**.

However no attempt was made by the Applicant to identify the best-fit model and to determine persistence endpoints for each trial. To fill that gap the RMS performed own kinetic analysis of the data obtained in field trials, in line with the recommendations given by FOCUS Workgroup on Degradation Kinetics [FOCUS 2006; FOCUS 2011]. At the same time the analysis was performed in such way to be compliant, as far as possible, with the kinetic evaluation of the data performed by the Applicant. That concerned mainly the pre-processing of the raw results in order to obtain the values subsequently used as input data for kinetic modelling tool.

The kinetic analysis of the data obtained in the field trials was a multi-step procedure, consisting of the following activities:

- **Step 1:** preliminary analysis of the data-sets obtained for each trial in order to determine for which compounds the kinetic analysis was possible;
- **Step 2:** pre-processing of the data identified as suitable for further kinetic assessment (detailed examination of the data sets for their suitability for kinetic assessment, calculation of the residue values for each sampling point, identification and elimination of the clear outliers, etc.);
- **Step 3:** kinetic examination of the pre-processed data sets following the recommendations given by FOCUS Workgroup on Degradation Kinetics [FOCUS 2006; FOCUS 2011];
- **Step 4:** presentation of the obtained results and conclusions.

The first step consisted on the preliminary analysis of the data obtained for each study and trial in order to identify those suitable for the kinetic examination. The general information on each study is provided below.

In the study No. 107724 [Sommer; 1995] the dissipation of Flufenacet was examined on eight trial sites – four located in Germany and another four in France. Each trial is briefly characterised below:

- **trial 30159/0, Breitenfelde:** performed in Germany, on bare soil, application rate 480 g Flufenacet/ha, spring application of the test compound in 1993;
- **trial 30162/0, Kirchlauter:** performed in Germany, on bare soil, application rate 480 g Flufenacet/ha, spring application of the test compound in 1993;
- **trial 30163/9, Monheim:** performed in Germany, on bare soil, application rate 480 g Flufenacet/ha, spring application of the test compound in 1993;
- **trial 30164/7, Burscheid:** performed in Germany, on bare soil, application rate 480 g Flufenacet/ha, spring application of the test compound in 1993;
- **trial 30248/1, Fresne-L'Archeveque:** performed in Northern France, on cropped soil (Maize), application rate 600 g Flufenacet/ha, spring application of the test compound in 1993;
- **trial 30250/3, Fresne-L'Archeveque 1:** performed in Northern France, on cropped soil (Maize), application rate 600 g Flufenacet/ha, spring application of the test compound in 1993;
- **trial 30251/1, Laudun:** performed in Southern France, on cropped soil (Sunflower), application rate 600 g Flufenacet/ha, spring application of the test compound in 1993;
- **trial 30253/8, St. Etienne du Gres:** performed in southern France, on cropped soil (Sunflower), application rate 600 g Flufenacet/ha, spring application of the test compound in 1993.

In the study No. 107722 [Sommer; 1995a] the dissipation of Flufenacet was examined on two trial sites, both located in Germany. Each trial is briefly characterised below:

- **trial 30499/9, Burscheid:** performed in Germany, on bare soil, application rate 240 g Flufenacet/ha, autumn application of the test compound in 1993;
- **trial 30500/6, Monheim:** performed in Germany, on bare soil, application rate 240 g Flufenacet/ha, autumn application of the test compound in 1993.

In the study No. 107723 [Sommer; 1995b] the dissipation of Flufenacet was examined on two trial sites, both located in France. Each trial is briefly characterised below:

- **trial 30254/6, Saussay-la-Campagne:** performed in Southern France, on cropped soil (winter wheat), application rate 240 g Flufenacet/ha, early spring application of the test compound in 1994;
- **trial 30455/7, Fresne-L'Archeveque:** performed in Northern France, on cropped soil (winter wheat), application rate 240 g Flufenacet/ha, early spring application of the test compound in 1994.

In the study No. 107721 [Sommer; 1995c] the dissipation of Flufenacet was examined on four trial sites – two located in France and another two in Italy. Each trial is briefly characterised below:

- **trial 40163/3, Laudun:** performed in Southern France, on cropped soil (Sunflower), application rate 600 g Flufenacet/ha, spring application of the test compound in 1994;
- **trial 40164/1, St. Etienne du Gres:** performed in Southern France, on cropped soil (Sunflower), application rate 600 g Flufenacet/ha, spring application of the test compound in 1994;
- **trial 40494/2, Ravenna:** performed in Italy, on cropped soil (Soybean), application rate 600 g Flufenacet/ha, spring application of the test compound in 1994;
- **trial 40495/0, S. Romualdo:** performed in Italy, on cropped soil (Soybean), application rate 600 g Flufenacet/ha, spring application of the test compound in 1994;

The results of the preliminary examination of the data sets from each trial are presented below, individually for each trial. RMS, deciding on the suitability of the data set for the given compound for kinetic analysis, used the criterion of whether it contained for at least one time point the values >LOQ. Therefore, if for the given compound in the given trial all values were <LOQ, even though some of them were still >LOD, such data sets were considered not suitable for further kinetic analysis, as the results of it would bear too high level of uncertainty (the results would be artificially set to pre-defined level without any guarantee that they may appropriately represent the real situation).

For the trial **30159/0, Breitenfelde** it was stated that:

- the residue data were provided for the soil layers down to 30 cm;
- the results were given for nine time points;
- for Flufenacet the measured values >LOQ were provided for seven of nine time points, while for the remaining two they were <LOQ, but still >LOD;
- for FOE Alcohol there was no values >LOD;
- for FOE Oxalate there was no values >LOQ and only for two time points >LOD;
- for FOE Sulfonic acid values >LOQ were recorded for two time points and >LOD for additional two time points;
- on that basis RMS stated that for this trial it was possible to perform the kinetic analysis for Flufenacet and it may be possible to perform such analysis also for FOE Sulfonic acid.

For the trial **30162/0, Kirchlauter** it was stated that:

- the residue data were provided for the soil layers down to 30 cm;
- the results were given for nine time points;
- for Flufenacet the measured values >LOQ were provided all nine time points;
- for FOE Alcohol there was no values >LOD;
- for FOE Oxalate there was no values >LOQ and for four time points were recorded those >LOD;
- for FOE Sulfonic acid there was no values >LOQ and for five time points were recorded those >LOD;
- on that basis RMS stated that for this trial it was possible to perform the kinetic analysis for Flufenacet only.

For the trial **30163/9, Monheim** it was stated that:

- the residue data were provided for the soil layers down to 30 cm;
- the results were given for nine time points;
- for Flufenacet the measured values >LOQ were provided for all nine time points;
- for FOE Alcohol there was no values >LOQ and only for two time points the values >LOD were recorded;
- for FOE Oxalate there was no values >LOQ and only for two time points the values >LOD were recorded;
- for FOE Sulfonic acid there was no values >LOQ and only for four time points the values >LOD were recorded;
- on that basis RMS stated that for this trial it was possible to perform the kinetic analysis for Flufenacet only.

For the trial **30164/7, Burscheid** it was stated that:

- the residue data were provided for the soil layers down to 30 cm;
- the results were given for nine time points;
- for Flufenacet the measured values >LOQ were provided for five of nine time points and additionally those >LOD but <LOQ were given for two time points;
- for FOE Alcohol the values >LOD were recorded for two time points and there was no results >LOQ;
- for FOE Oxalate there was no values >LOD;
- for FOE Sulfonic acid values there was no values >LOQ and only for two time points were recorded the values >LOD;
- on that basis RMS stated that for this trial it was possible to perform the kinetic analysis for Flufenacet only.

For the trial **30248/1, Fresne-L'Archeveque** it was stated that:

- the residue data were provided for the soil layers down to 30 cm;
- the results were given for nine time points;
- for Flufenacet the measured values >LOQ were provided for all nine time points;
- for FOE Alcohol there was no values >LOD;
- for FOE Oxalate there was no values >LOQ and for five time points were recorded those >LOD;
- for FOE Sulfonic acid values >LOQ were recorded for four time points and additionally those >LOD for three time points; it shall be noted that in case of one of the time points with values >LOD recorded, one of them was >LOQ;
- on that basis RMS stated that for this trial it was possible to perform the kinetic analysis for Flufenacet and it might be possible to do that for FOE Sulfonic acid as well.

For the trial **30250/3, Fresne-L'Archeveque 1** it was stated that:

- the residue data were provided for the soil layers down to 30 cm;
- the results were given for nine time points;
- for Flufenacet the measured values >LOQ were provided for all nine time points, while for the remaining two they were below LOQ, but still above LOD;
- for FOE Alcohol there was no values >LOD;
- for FOE Oxalate three time points the values were > LOQ and additionally for two two time points they were >LOD;
- for FOE Sulfonic acid values the values >LOQ were recorded for two time points and those >LOD for additional three time points, it shall be noted that for one of them, with the values predominantly > LOD, in one replicate the concentration was >LOQ;
- on that basis RMS stated that it was possible to perform the kinetic analysis for Flufenacet and it might be possible to perform such analysis also for FOE Oxalate and FOE Sulfonic acid.

For the trial **30251/1, Laudun** it was stated that:

- the residue data were provided for the soil layers down to 30 cm;
- the results were given for nine time points;
- for Flufenacet the measured values >LOQ were recorded for seven of nine time points, while for the remaining two they were <LOQ, but still >LOD;
- for FOE Alcohol for only one time point the residue values were >LOD, for the remaining eight being below that level;
- for FOE Oxalate for one time point the residue values were > LOQ and for additional three were reported as being <LOQ but >LOD;
- for FOE Sulfonic acid values >LOQ were recorded for three time points and those >LOD for additional two time points;
- on that basis RMS stated that it was possible to perform the kinetic analysis for Flufenacet and it might be possible to perform such analysis also for FOE Oxalate and FOE Sulfonic acid.

For the trial **30253/8, St. Etienne du Gres** it was stated that:

- the residue data were provided for the soil layers down to 30 cm;
- the results were given for nine time points;
- for Flufenacet the measured values >LOQ were provided for seven of nine time points, while for the remaining two they were below LOQ, but still above LOD;
- for FOE Alcohol there were no values >LOQ and only for one time points the values >LOD were recorded;
- for FOE Oxalate there was no values >LOQ, but for five consecutive time points the values >LOD were recorded;
- for FOE Sulfonic acid values >LOQ were recorded for only one time point, but for the two time points preceding it and two immediately after it were recorded the values >LOD;
- on that basis RMS stated that it was possible to perform the kinetic analysis for Flufenacet and it might be possible to perform such analysis also for FOE Sulfonic acid.

For the trial **30499/9, Burscheid** it was stated that:

- the residue data were provided for the soil layers down to 30 cm;
- the results were given for nine time points;
- for Flufenacet the measured values >LOQ were provided for seven of nine time points and for one additional time points the recorded residue concentrations were >LOD;
- for FOE Alcohol there was no values >LOD;
- for FOE Oxalate there was no values > LOD;
- for FOE Sulfonic acid there was no values >LOQ, but for four consecutive time points the values >LOD were recorded;
- on that basis RMS stated that it was possible to perform the kinetic analysis for Flufenacet only.

For the trial **30500/6, Monheim** it was stated that:

- the residue data were provided for the soil layers down to 30 cm;
- the results were given for nine time points;
- for Flufenacet the measured values >LOQ were recorded provided for eight of nine time points;
- for FOE Alcohol there was no values >LOD;
- for FOE Oxalate there was no values >LOD;
- for FOE Sulfonic acid there was no values >LOD;
- on that basis RMS stated that it was possible to perform the kinetic analysis for Flufenacet only.

For the trial **30254/6, Saussay-la-Campagne** it was stated that:

- the residue data were provided for the soil layers down to 50 cm, but for the layers 20-30cm, 30-40 cm and 40-50 cm the values were provided for a single replicate and all were >LOD – for that reason, and also to maintain the consistency of the pre-processed data sets RMS decided to present the non-processed data only to the depth of 30 cm;
- the results were given for eight time points;
- for Flufenacet the measured values >LOQ were recorded only for three time points and additionally for the two following time points they were >LOD;
- for FOE Alcohol there was no values >LOD;
- for FOE Oxalate there was no values >LOD;
- for FOE Sulfonic acid there was no values >LOD;
- on that basis RMS stated that it was possible to perform the kinetic analysis for Flufenacet only.

For the trial **30455/7, Fresne-L'Archeveque** it was stated that:

- the residue data were provided for the soil layers down to 50 cm, but for the layers 20-30cm, 30-40 cm and 40-50 cm the values were provided for a single replicate and all were >LOD – for that reason, and also to maintain the consistency of the pre-processed data sets RMS decided to present the non-processed data only to the depth of 30 cm;
- the results were given for seven time points;
- for Flufenacet the measured values >LOQ were recorded for only two time points and additionally for the two following time points the recorded residue values were >LOD;
- for FOE Alcohol there was no values >LOD;
- for FOE Oxalate there was no values >LOD;
- for FOE Sulfonic acid there was no values >LOD;
- on that basis RMS stated that it might be possible to perform the kinetic analysis for Flufenacet, but even for that compound, due to very limited amount of data points, it would bear a significant level of uncertainty.

For the trial **40163/3, Laudun**, it was stated that:

- the residue data were provided for the soil layers down to 50 cm, but for the layers 20-30cm, 30-40 cm and 40-50 cm the values were provided for a single replicate and all were >LOD – for that reason, and also to maintain the consistency of the pre-processed data sets RMS decided to present the non-processed data only to the depth of 30 cm;
- the results were given for nine time points;
- for Flufenacet the measured values >LOQ were recorded for seven of nine time points and additionally one following point had residue concentrations >LOD;
- for FOE Alcohol there was no values >LOD;
- for FOE Oxalate there were two time points with residue values >LOQ and additional four with those >LOD;
- for FOE Sulfonic acid there was one time point with values >LOQ and additional four with those >LOD;
- on that basis RMS stated that it was possible to perform the kinetic analysis for Flufenacet and it might be possible to perform such analysis also for FOE Oxalate and FOE Sulfonic acid.

For the trial **40164/1, St. Etienne du Gres** it was stated that:

- the residue data were provided for the soil layers down to 50 cm, but for the layers 20-30cm, 30-40 cm and 40-50 cm the values were provided for a single replicate and all were >LOD – for that reason, and also to maintain the consistency of the pre-processed data sets RMS decided to present the non-processed data only to the depth of 30 cm;
- the results were given for nine time points;
- for Flufenacet the measured values >LOQ were recorded for eight time points and additionally for the last time point they were >LOD;
- for FOE Alcohol there was no values >LOD;
- for FOE Oxalate there was no values >LOQ, but for five time points the values >LOD were recorded;
- for FOE Sulfonic acid the values >LOQ were recorded for two time points and those >LOD for additional two time points;
- on that basis RMS stated that it was possible to perform the kinetic analysis for Flufenacet and it might be possible to perform such analysis also for FOE Sulfonic acid.

For the trial **40494/2, Ravenna** it was stated that:

- the residue data were provided for the soil layers down to 50 cm, but for the layers 20-30cm, 30-40 cm and 40-50 cm the values were provided for a single replicate and all were >LOD – for that reason, and also to maintain the consistency of the pre-processed data sets RMS decided to present the non-processed data only to the depth of 30 cm;
- the results were given for nine time points;
- for Flufenacet the measured values >LOQ were recorded for eight time points and additionally for the last time point they were >LOD;
- for FOE Alcohol there was no values >LOQ and for only one time point the values >LOD were recorded;
- for FOE Oxalate there was no values >LOQ, but for three consecutive time points the values >LOD were recorded;
- for FOE Sulfonic acid the values >LOQ were recorded for three consecutive time points only and no other values >LOD were reported;
- on that basis RMS stated that it was possible to perform the kinetic analysis for Flufenacet and it might be possible to perform such analysis also for FOE Sulfonic acid.

For the trial **40495/0, S. Romualdo** it was stated that:

- the residue data were provided for the soil layers down to 50 cm, but for the layers 20-30cm, 30-40 cm and 40-50 cm the values were provided for a single replicate and all were >LOD – for that reason, and also to maintain the consistency of the pre-processed data sets RMS decided to present the non-processed data only to the depth of 30 cm;
- the results were given for nine time points;
- for Flufenacet the measured values >LOQ were recorded for all nine time points;
- for FOE Alcohol there was no values >LOQ, but for the two consecutive time points there were values >LOD;
- for FOE Oxalate there was no values >LOQ, but for four consecutive time points there were values >LOD;
- for FOE Sulfonic acid was no values >LOQ, but for four consecutive time points there were values >LOD;
- on that basis RMS stated that it was possible to perform the kinetic analysis for Flufenacet only.

The resulting data-sets determined for each trial site and subsequently used in the procedure of pre-processing the data are presented below in tables B.8.1.1.2.2.1._CA-59 – B.8.1.1.2.2.1._CA-68. For clarity the values were grouped into three sets:

- **set 1** presenting the results of eight trials identified as those for which it was possible to do the kinetic analysis solely for Flufenacet (tables B.8.1.1.2.2.1._CA-59 – B.8.1.1.2.2.1._CA-62);
- **set 2** presenting the results of four trials identified as those for which it was possible to perform the kinetic analysis of the data for Flufenacet and FOE Sulfonic acid (tables B.8.1.1.2.2.1._CA-63 and B.8.1.1.2.2.1._CA-65);
- **set 3** presenting the results of four trials identified as those for which it was possible to perform the kinetic analysis of the data for Flufenacet, FOE Oxalate and FOE Sulfonic acid (tables B.8.1.1.2.2.1._CA-66 – B.8.1.1.2.2.1._CA-68).

Table B.8.1.1.2.2.1._CA-59: The not processed residue data appropriate to be used in the kinetic analysis obtained in the trials: **30162/0 Kirchlauter** and **30163/9 Monheim**.

The not processed data set for the trial 30162/0, Kirchlauter (study [Sommer; 1995])						
Sampling point - DAT	Soil layer [cm]	Concentration of Flufenacet [µg/kg]				
		Rep1	Rep 2	Rep 3	Rep 4	Mean
0	0-10	242.4	232.4	249.5	232.5	239
	10-20	20.98	21.59	----	----	21.3
	20-30	n. d.	----	----	----	n. d.
7	0-10	202.5	214.3	200.9	211.6	207
	10-20	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.
14	0-10	215.4	215.1	207.8	212.9	213
	10-20	< 10	< 10	----	----	< 10
	20-30	n. d.	----	----	----	n. d.
28	0-10	295.9	257.3	279.5	276.2	277
	10-20	< 10	< 10	----	----	< 10
	20-30	n. d.	----	----	----	n. d.
56	0-10	102.0	11.5	111.3	113.0	110
	10-20	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.
90	0-10	82.41	80.21	84.91	78.32	81.5
	10-20	n. d.	n. d. ⁴⁾	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.
120	0-10	46.58	43.15	45.90	45.36	45.2
	10-20	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.
181	0-10	25.80	25.49	24.52	25.63	25.4
	10-20	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.
237	0-10	12.74	11.95	11.93	12.11	12.2
	10-20	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.
The not processed data set for the trial 30163/9, Monheim(study [Sommer; 1995])						
Sampling point - DAT	Soil layer [cm]	Concentration of Flufenacet [µg/kg]				
		Rep1	Rep 2	Rep 3	Rep 4	Mean
0	0-10	144.5	152.9	149.6	162.1	152
	10-20	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.
7	0-10	168.6	177.6	165.9	174.3	172
	10-20	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.
14	0-10	173.8	187.0	164.3	165.7	173
	10-20	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.
28	0-10	145.9	149.4	149.7	151.9	149
	10-20	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.
56	0-10	69.29	67.80	64.83	64.04	66.7
	10-20	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.
90	0-10	28.77	29.25	29.94	29.12	29.3
	10-20	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.
122	0-10	21.77	21.43	23.01	23.33	22.1
		22.03	21.43	21.97	21.84	
	10-20	n. d.	n. d.	----	----	n. d.
180	0-10	15.74	17.27	15.87	15.68	16.1
	10-20	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.
231	0-10	11.68	11.92	10.98	12.11	11.7
	10-20	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.

Table B.8.1.1.2.2.1._CA-60: The not processed residue data appropriate to be used in the kinetic analysis obtained in the trials: **30164/7 Burscheid** and **30499/9 Burscheid**.

The not processed data set for the trial 30164/7, Burscheid (study [Sommer; 1995])						
Sampling point - DAT	Soil layer [cm]	Concentration of Flufenacet [µg/kg]				
		Rep1	Rep 2	Rep 3	Rep 4	Mean
0	0-10	323.3	313.0	363.7	322.5	331
	10-20	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.
7	0-10	211.6	209.8	219.7	205.5	212
	10-20	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.
14	0-10	169.7	160.8	181.1	183.6	174
	10-20	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.
27	0-10	108.1	11.01	102.2	109.8	108
	10-20	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.
60	0-10	26.56	26.54	25.38	25.57	26.0
	10-20	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.
90	0-10	< 10	< 10	< 10	< 10	< 10
	10-20	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.
120	0-10	< 10	< 10	< 10	< 10	< 10
	10-20	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.
180	0-10	n. d.	n. d.	n. d.	n. d.	n. d.
	10-20	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.
239	0-10	n. d.	n. d.	n. d.	n. d.	n. d.
	10-20	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.
The not processed data set for the trial 30499/9, Burscheid (study [Sommer; 1995a])						
Sampling point - DAT	Soil layer [cm]	Concentration of Flufenacet [µg/kg]				
		Rep1	Rep 2	Rep 3	Rep 4	Mean
0	0-10	142.6	134.0	150.5	137.6	141
	10-20	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.
8	0-10	94.44	93.42	94.62	94.11	94.1
	10-20	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.
14	0-10	82.98	90.99	99.88	84.75	89.6
	10-20	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.
29	0-10	79.68	83.69	75.00	81.23	79.9
	10-20	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.
56	0-10	52.89	48.67	54.94	53.99	52.6
	10-20	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.
90	0-10	21.08	21.72	19.16	19.34	20.3
	10-20	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.
120	0-10	12.39	11.76	12.74	12.08	12.2
	10-20	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.
180	0-10	< 10	n. d.	< 10	< 10	< 10
	10-20	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.
240	0-10	n. d.	n. d.	n. d.	n. d.	n. d.
	10-20	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.

Table B.8.1.1.2.2.1._CA-61: The not processed residue data appropriate to be used in the kinetic analysis obtained in the trials: **30500/6 Monheim** and **30254/6 Saussay-la-Campagne**.

The not processed data set for the trial 30500/6, Monheim (study [Sommer; 1995a])						
Sampling point -DAT	Soil layer [cm]	Concentration of Flufenacet [µg/kg]				
		Rep1	Rep 2	Rep 3	Rep 4	Mean
0	0-10	105.0	102.3	98.99	97.76	101
	10-20	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.
8	0-10	97.87	100.5	101.8	104.8	101
	10-20	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.
14	0-10	90.34	90.34	89.65	85.19	88.9
	10-20	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.
28	0-10	111.7	110.2	106.7	107.0	109
	10-20	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.
52	0-10	66.64	66.32	68.23	67.11	67.1
	10-20	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.
98	0-10	36.29	35.76	36.15	34.88	35.8
	10-20	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.
120	0-10	26.74	28.56	29.24	30.69	27.6
	10-20	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.
181	0-10	12.74	12.95	12.63	12.90	12.8
	10-20	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.
240	0-10	n. d.	n. d.	n. d.	n. d.	n. d.
	10-20	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.
The not processed data set for the trial 30254/7, Saussay-la-Campagne(study [Sommer; 1995b])						
Sampling point -DAT	Soil layer [cm]	Concentration of Flufenacet [µg/kg]				
		Rep1	Rep 2	Rep 3	Rep 4	Mean
0	0-10	115.2	113.4	113.1	119.8	115
	10-20	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.
8	0-10	75.98	76.31	83.58	67.18	75.8
	10-20	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.
52	0-10	10.87	10.53	----	----	10.7
	10-20	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.
70	0-10	< 10	< 10	----	----	< 10
	10-20	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.
89	0-10	< 10	< 10	----	----	< 10
	10-20	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.
116	0-10	n. d.	n. d.	----	----	n. d.
	10-20	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.
180	0-10	n. d.	n. d.	----	----	n. d.
	10-20	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.
242	0-10	n. d.	n. d.	----	----	n. d.
	10-20	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.

Table B.8.1.1.2.2.1._CA-62: The not processed residue data appropriate to be used in the kinetic analysis obtained in the trials: **30455/7 Fresne-L'Archeveque** and **40495 S. Romualdo**.

The not processed data set for the trial 30455/7, Fresne-L'Archeveque (study [Sommer; 1995b])						
Sampling point -DAT	Soil layer [cm]	Concentration of Flufenacet [µg/kg]				
		Rep1	Rep 2	Rep 3	Rep 4	Mean
0	0-10	85.00	95.33	94.84	96.95	93.0
	10-20	----	----	----	----	----
	20-30	----	----	----	----	----
28	0-10	25.83	29.85	----	----	27.8
	10-20	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.
53	0-10	< 10	< 10	----	----	< 10
	10-20	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.
88	0-10	< 10	< 10	----	----	< 10
	10-20	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.
120	0-10	n. d.	n. d.	----	----	n. d.
	10-20	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.
178	0-10	n. d.	n. d.	----	----	n. d.
	10-20	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.
240	0-10	n. d.	n. d.	----	----	n. d.
	10-20	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.
The not processed data set for the trial 40495/0, S. Romualdo (study [Sommer; 1995c])						
Sampling point -DAT	Soil layer [cm]	Concentration of Flufenacet [µg/kg]				
		Rep1	Rep 2	Rep 3	Rep 4	Mean
0	0-10	346.8	331.9	334.8	367.5	345
	10-20	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.
7	0-10	376.8	344.1	346.2	358.0	356
	10-20	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.
14	0-10	326.0	322.5	----	----	324
	10-20	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.
28	0-10	319.3	342.8	----	----	331
	10-20	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.
56	0-10	155.6	171.1	----	----	163
	10-20	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.
90	0-10	97.78	95.97	----	----	96.9
	10-20	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.
121	0-10	77.05	81.50	----	----	79.3
	10-20	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.
180	0-10	20.27	19.23	----	----	19.7
	10-20	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.
236	0-10	14.31	15.02	----	----	14.7
	10-20	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.

Table B.8.1.1.2.2.1_CA-63: The not processed residue data appropriate to be used in the kinetic analysis obtained in the trials: **30159/0 Breitenfelde** and **30248/1 Fresne-L'Archeveque**.

The not processed data set for the trial 30159/0, Breitenfelde (study [Sommer; 1995])											
Sampling point - DAT	Soil layer [cm]	Concentration of Flufenacet [µg/kg]					Concentration of FOE Sulfonic acid [µg/kg]				
		Rep1	Rep 2	Rep 3	Rep 4	Mean	Rep1	Rep 2	Rep 3	Rep 4	Mean
0	0-10	237.8	240.0	231.0	236.9	236	n. d.	n. d.	n. d.	n. d.	n. d.
	10-20	< 10	< 10	----	----	< 10	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.	n. d.	----	----	----	n. d.
7	0-10	247.2	265.1	262.8	250.1	256	n. d.	n. d.	n. d.	n. d.	n. d.
	10-20	n. d.	n. d.	----	----	n. d.	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.	n. d.	----	----	----	n. d.
14	0-10	155.7	154.8	157.7	156.9	156	n. d.	n. d.	n. d.	< 10	< 10
	10-20	< 10	< 10	----	----	< 10	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.	n. d.	----	----	----	n. d.
28	0-10	145.4	131.5	138.8	133.9	137	< 10	< 10	< 10	< 10	< 10
	10-20	< 10	< 10	----	----	< 10	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.	n. d.	n. d.	----	----	n. d.
56	0-10	89.46	89.82	88.04	84.95	88.1	13.62	15.81	14.72	13.63	14.5
	10-20	n. d.	n. d.	----	----	n. d.	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	n. d.	----	----	n. d.	n. d.	n. d.	----	----	n. d.
90	0-10	33.29	32.80	31.65	31.57	32.3	12.05	12.19	13.70	13.18	12.8
	10-20	n. d.	n. d.	----	----	n. d.	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	n. d.	----	----	n. d.	n. d.	n. d.	----	----	n. d.
120	0-10	11.08	11.77	11.48	11.63	11.5	n. d.	n. d.	n. d.	n. d.	n. d.
	10-20	n. d.	n. d.	----	----	n. d.	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	n. d.	----	----	n. d.	n. d.	n. d.	----	----	n. d.
180	0-10	< 10	< 10	< 10	< 10	< 10	n. d.	n. d.	n. d.	n. d.	n. d.
	10-20	n. d.	n. d.	----	----	n. d.	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	n. d.	----	----	n. d.	n. d.	n. d.	----	----	n. d.
240	0-10	< 10	< 10	< 10	< 10	< 10	n. d.	n. d.	n. d.	n. d.	n. d.
	10-20	n. d.	n. d.	----	----	n. d.	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	n. d.	----	----	n. d.	n. d.	n. d.	----	----	n. d.
The not processed data set for the trial 30250/3, Fresne-L'Archeveque (study [Sommer; 1995])											
Sampling point - DAT	Soil layer [cm]	Concentration of Flufenacet [µg/kg]					Concentration of FOE Sulfonic acid [µg/kg]				
		Rep1	Rep 2	Rep 3	Rep 4	Mean	Rep1	Rep 2	Rep 3	Rep 4	Mean
0	0-10	370.9	367.8	335.4	374.5	362	n. d.	n. d.	n. d.	n. d.	n. d.
	10-20	n. d.	n. d.	----	----	n. d.	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.	n. d.	----	----	----	n. d.
14	0-10	200.2	200.8	221.4	212.3	209	n. d.	n. d.	n. d.	n. d.	n. d.
	10-20	n. d.	n. d.	----	----	n. d.	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.	n. d.	----	----	----	n. d.
28	0-10	232.7	229.4	232.9	233.5	232	14.44	13.33	14.50	13.30	13.9
	10-20	n. d.	n. d.	----	----	n. d.	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.	n. d.	----	----	----	n. d.
56	0-10	124.5	132.9	119.0	121.3	124	< 10	< 10	10.8	< 10	< 10
	10-20	n. d.	n. d.	----	----	n. d.	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.	n. d.	----	----	----	n. d.
90	0-10	92.41	90.94	95.29	92.68	92.8	10.51	11.31	11.88	11.30	11.3
	10-20	n. d.	n. d.	----	----	n. d.	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.	n. d.	----	----	----	n. d.
120	0-10	54.47	57.12	56.83	57.47	56.5	11.45	11.02	10.39	< 10	< 10
	10-20	n. d.	n. d.	----	----	n. d.	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.	n. d.	----	----	----	n. d.
181	0-10	29.91	28.91	31.41	30.46	30.2	< 10	n. d.	< 10	n. d.	< 10
	10-20	n. d.	n. d.	----	----	n. d.	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.	n. d.	----	----	----	n. d.
303	0-10	22.67	24.92	24.01	23.24	23.7	n. d.	n. d.	n. d.	n. d.	n. d.
	10-20	n. d.	n. d.	----	----	n. d.	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.	n. d.	----	----	----	n. d.

Table B.8.1.1.2.2.1_CA-64: The not processed residue data appropriate to be used in the kinetic analysis obtained in the trials: **30253/8 St. Etienne du Gres** and **40164/1 St. Etienne du Gres**.

The not processed data set for the trial 30253/8, St . Etienne du Gres (study [Sommer; 1995])											
Sampling point - DAT	Soil layer [cm]	Concentration of Flufenacet [µg/kg]					Concentration of FOE Sulfonic acid [µg/kg]				
		Rep1	Rep 2	Rep 3	Rep 4	Mean	Rep1	Rep 2	Rep 3	Rep 4	Mean
0	0-10	286.6	277.2	273.3	283.0	280	n. d.	n. d.	n. d.	n. d.	n. d.
	10-20	< 10	< 10	----	----	< 10	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.	n. d.	----	----	----	n. d.
7	0-10	< 10	n. d.	n. d.	n. d.	< 10	n. d.	n. d.	n. d.	n. d.	n. d.
	10-20	n. d.	n. d.	----	----	n. d.	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.	n. d.	----	----	----	n. d.
15	0-10	209.1	205.5	204.2	201.0	205	< 10	< 10	< 10	< 10	< 10
	10-20	< 10	< 10	----	----	< 10	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.	n. d.	----	----	----	n. d.
28	0-10	203.9	188.8	181.7	182.7	189	< 10	< 10	< 10	10.16	< 10
	10-20	n. d.	n. d.	----	----	n. d.	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.	n. d.	----	----	----	n. d.
56	0-10	102.3	94.59	89.26	95.79	95.5	10.39	10.73	< 10	10.15	< 10
	10-20	n. d.	n. d.	----	----	n. d.	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.	n. d.	----	----	----	n. d.
87	0-10	56.30	55.49	59.44	57.50	57.2	< 10	< 10	< 10	< 10	< 10
	10-20	n. d.	n. d.	----	----	n. d.	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.	n. d.	----	----	----	n. d.
119	0-10	52.66	47.14	52.63	51.18	50.9	< 10	< 10	< 10	< 10	< 10
	10-20	n. d.	n. d.	----	----	n. d.	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.	n. d.	----	----	----	n. d.
182	0-10	< 10	< 10	< 10	< 10	< 10	n. d.	n. d.	n. d.	n. d.	n. d.
	10-20	n. d.	n. d.	----	----	n. d.	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.	n. d.	----	----	----	n. d.
260	0-10	< 10	< 10	< 10	n. d.	< 10	n. d.	n. d.	n. d.	n. d.	n. d.
	10-20	n. d.	n. d.	----	----	n. d.	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.	n. d.	----	----	----	n. d.
The not processed data set for the trial 40164/1, Etienne du Gres (study [Sommer; 1995c])											
Sampling point - DAT	Soil layer [cm]	Concentration of Flufenacet [µg/kg]					Concentration of FOE Sulfonic acid [µg/kg]				
		Rep1	Rep 2	Rep 3	Rep 4	Mean	Rep1	Rep 2	Rep 3	Rep 4	Mean
0	0-10	223.6	222.6	219.6	240.5	227	n. d.	n. d.	n. d.	n. d.	n. d.
	10-20	n. d.	n. d.	----	----	n. d.	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.	n. d.	----	----	----	n. d.
78	0-10	287.9	290.8	282.3	281.0	285	n. d.	n. d.	n. d.	n. d.	n. d.
	10-20	n. d.	n. d.	----	----	n. d.	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.	n. d.	----	----	----	n. d.
14	0-10	197.4	191.0	----	----	194.7	n. d.	n. d.	----	----	n. d.
	10-20	n. d.	n. d.	----	----	n. d.	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.	n. d.	----	----	----	n. d.
28	0-10	229.6	242.9	----	----	236	< 10	< 10	----	----	< 10
	10-20	n. d.	n. d.	----	----	n. d.	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.	n. d.	----	----	----	n. d.
56	0-10	140.5	147.7	----	----	144	10.89	10.69	----	----	10.8
	10-20	n. d.	n. d.	----	----	n. d.	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.	n. d.	----	----	----	n. d.
90	0-10	74.85	72.09	----	----	73.5	10.88	11.08	----	----	11.0
	10-20	n. d.	n. d.	----	----	n. d.	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.	n. d.	----	----	----	n. d.
123	0-10	59.19	62.86	----	----	61.0	< 10	< 10	----	----	< 10
	10-20	n. d.	n. d.	----	----	n. d.	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.	n. d.	----	----	----	n. d.
180	0-10	11.18	12.75	----	----	12.0	n. d.	n. d.	----	----	n. d.
	10-20	n. d.	n. d.	----	----	n. d.	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.	n. d.	----	----	----	n. d.
236	0-10	< 10	< 10	----	----	< 10	n. d.	n. d.	----	----	n. d.
	10-20	n. d.	n. d.	----	----	n. d.	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.	n. d.	----	----	----	n. d.

Table B.8.1.1.2.2.1_CA-65: The not processed residue data appropriate to be used in the kinetic analysis obtained in the trial: **40494/2 Ravenna**.

The not processed data set for the trial 40494/2, Ravenna (study [Sommer; 1995c])											
Sampling point - DAT	Soil layer [cm]	Concentration of Flufenacet [µg/kg]					Concentration of FOE Oxalate [µg/kg]				
		Rep1	Rep 2	Rep 3	Rep 4	Mean	Rep1	Rep 2	Rep 3	Rep 4	Mean
0	0-10	373.0	356.2	334.7	315.7	345	n. d.	n. d.	n. d.	n. d.	n. d.
	10-20	n. d.	n. d.	----	----	n. d.	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.	n. d.	----	----	----	n. d.
7	0-10	278.4	298.9	288.3	285.1	288	n. d.	n. d.	n. d.	n. d.	n. d.
	10-20	n. d.	n. d.	----	----	n. d.	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.	n. d.	----	----	----	n. d.
14	0-10	223.8	229.8	----	----	227	n. d.	n. d.	----	----	n. d.
	10-20	n. d.	n. d.	----	----	n. d.	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.	n. d.	----	----	----	n. d.
28	0-10	280.2	274.5	----	----	277	n. d.	n. d.	----	----	n. d.
	10-20	n. d.	n. d.	----	----	n. d.	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.	n. d.	----	----	----	n. d.
56	0-10	113.0	109.1	----	----	111	10.36	10.24	----	----	10.3
	10-20	n. d.	n. d.	----	----	n. d.	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.	n. d.	----	----	----	n. d.
90	0-10	41.90	44.18	----	----	43.0	12.83	14.47	----	----	13.7
	10-20	n. d.	n. d.	----	----	n. d.	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.	n. d.	----	----	----	n. d.
121	0-10	45.31	46.38	----	----	45.8	21.19	20.43	----	----	20.8
	10-20	n. d.	n. d.	----	----	n. d.	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.	n. d.	----	----	----	n. d.
180	0-10	11.04	10.74	----	----	10.9	n. d.	n. d.	----	----	n. d.
	10-20	n. d.	n. d.	----	----	n. d.	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.	n. d.	----	----	----	n. d.
236	0-10	< 10	< 10	----	----	< 10	n. d.	n. d.	----	----	n. d.
	10-20	n. d.	n. d.	----	----	n. d.	n. d. ⁴⁾	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾
	20-30	n. d.	----	----	----	n. d.	n. d. ⁴⁾	---- ⁵⁾	---- ⁵⁾	---- ⁵⁾	n. d. ⁴⁾

Table B.8.1.1.2.2.1._CA-66: The not processed residue data appropriate to be used in the kinetic analysis obtained in the trial: **30250/3 Fresne-L'Archeveque 1.**

The not processed data set for the trial 30250/3, Fresne-L'Archeveque 1 (study [Sommer; 1995])											
Sampling point - DAT	Soil layer [cm]	Concentration of Flufenacet [µg/kg]					Concentration of FOE Oxalate [µg/kg]				
		Rep1	Rep 2	Rep 3	Rep 4	Mean	Rep1	Rep 2	Rep 3	Rep 4	Mean
0	0-10	258.2	273.4	283.3	278.7	273	n. d.	n. d.	n. d.	n. d.	n. d.
	10-20	< 10	< 10	----	----	< 10	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.	n. d.	----	----	----	n. d.
8	0-10	300.9	293.7	303.7	287.9	297	n. d.	n. d.	n. d.	n. d.	n. d.
	10-20	n. d.	n. d.	----	----	n. d.	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.	n. d.	----	----	----	n. d.
28	0-10	183.9	186.6	183.8	172.7	182	< 10	< 10	< 10	< 10	< 10
	10-20	< 10	n. d.	----	----	< 10	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.	n. d.	----	----	----	n. d.
56	0-10	116.4	114.1	109.6	108.2	112	11.35	10.70	< 10	10.65	< 10
	10-20	n. d.	n. d.	----	----	n. d.	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.	n. d.	----	----	----	n. d.
91	0-10	80.72	78.14	81.93	83.23	81.0	12.22	12.77	12.19	12.15	12.3
	10-20	n. d.	n. d.	----	----	n. d.	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.	n. d.	----	----	----	n. d.
120	0-10	67.78	64.23	65.05	61.77	64.7	10.48	11.18	11.05	10.53	10.8
	10-20	n. d.	n. d.	----	----	n. d.	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.	n. d.	----	----	----	n. d.
193	0-10	39.86	37.95	38.05	39.54	38.9	< 10	< 10	< 10	< 10	< 10
	10-20	n. d.	n. d.	----	----	n. d.	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.	n. d.	----	----	----	n. d.
287	0-10	16.58	17.30	18.04	17.18	17.3	n. d.	n. d.	n. d.	n. d.	n. d.
	10-20	n. d.	n. d.	----	----	n. d.	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.	n. d.	----	----	----	n. d.
Sampling point - DAT	Soil layer [cm]	Concentration of FOE Sulfonic acid [µg/kg]									
		Rep1	Rep 2	Rep 3	Rep 4	Mean					
0	0-10	n. d.	n. d.	n. d.	n. d.	n. d.					
	10-20	n. d.	n. d.	----	----	n. d.					
	20-30	n. d.	----	----	----	n. d.					
8	0-10	n. d.	n. d.	n. d.	n. d.	n. d.					
	10-20	n. d.	n. d.	----	----	n. d.					
	20-30	n. d.	----	----	----	n. d.					
28	0-10	< 10	< 10	< 10	< 10	< 10					
	10-20	n. d.	n. d.	----	----	n. d.					
	20-30	n. d.	----	----	----	n. d.					
56	0-10	10.54	< 10	< 10	< 10	< 10					
	10-20	n. d.	n. d.	----	----	n. d.					
	20-30	n. d.	----	----	----	n. d.					
91	0-10	11.61	13.23	10.09	12.91	12.0					
	10-20	n. d.	n. d.	----	----	n. d.					
	20-30	n. d.	----	----	----	n. d.					
120	0-10	11.72	10.42	11.37	12.34	11.5					
	10-20	n. d.	n. d.	----	----	n. d.					
	20-30	n. d.	----	----	----	n. d.					
193	0-10	< 10	< 10	< 10	< 10	< 10					
	10-20	n. d.	n. d.	----	----	n. d.					
	20-30	n. d.	----	----	----	n. d.					
287	0-10	n. d.	n. d.	n. d.	n. d.	n. d.					
	10-20	n. d.	n. d.	----	----	n. d.					
	20-30	n. d.	----	----	----	n. d.					

Table B.8.1.1.2.2.1_CA-67: The not processed residue data appropriate to be used in the kinetic analysis obtained in the trial: **30251/1 Laudun.**

The not processed data set for the trial 30251/1, Laudun (study [Sommer; 1995])											
Sampling point - DAT	Soil layer [cm]	Concentration of Flufenacet [µg/kg]					Concentration of FOE Oxalate [µg/kg]				
		Rep1	Rep 2	Rep 3	Rep 4	Mean	Rep1	Rep 2	Rep 3	Rep 4	Mean
0	0-10	360.5	366.1	388.7	390.4	376	n. d.	n. d.	n. d.	n. d.	n. d.
	10-20	< 10	< 10	----	----	< 10	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.	n. d.	----	----	----	n. d.
7	0-10	282.6	288.2	294.4	288.9	289	n. d.	n. d.	n. d.	n. d.	n. d.
	10-20	< 10	< 10	----	----	< 10	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.	n. d.	----	----	----	n. d.
15	0-10	320.8	295.7	303.8	321.0	310	n. d.	n. d.	n. d.	n. d.	n. d.
	10-20	n. d.	n. d.	----	----	n. d.	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.	n. d.	----	----	----	n. d.
28	0-10	214.7	183.8	211.1	197.0	202	< 10	< 10	< 10	< 10	< 10
	10-20	n. d.	n. d.	----	----	n. d.	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.	n. d.	----	----	----	n. d.
55	0-10	76.92	69.82	89.27	83.17	79.8	< 10	10.03	10.79	< 10	< 10
	10-20	n. d.	n. d.	----	----	n. d.	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.	n. d.	----	----	----	n. d.
87	0-10	40.41	44.61	45.50	39.23	42.4	< 10	< 10	< 10	< 10	< 10
	10-20	< 10	n. d.	----	----	< 10	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.	n. d.	----	----	----	n. d.
119	0-10	28.26	28.65	29.45	25.43	27.9	10.94	11.17	11.58	11.08	11.2
	10-20	n. d.	n. d.	----	----	n. d.	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.	n. d.	----	----	----	n. d.
182	0-10	< 10	< 10	< 10	< 10	< 10	n. d.	n. d.	n. d.	n. d.	n. d.
	10-20	n. d.	n. d.	----	----	n. d.	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.	n. d.	----	----	----	n. d.
255	0-10	< 10	< 10	< 10	< 10	< 10	n. d.	n. d.	n. d.	n. d.	n. d.
	10-20	n. d.	n. d.	----	----	n. d.	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.	n. d.	----	----	----	n. d.
Sampling point - DAT	Soil layer [cm]	Concentration of FOE Sulfonic acid [µg/kg]									
		Rep1	Rep 2	Rep 3	Rep 4	Mean					
0	0-10	n. d.	n. d.	n. d.	n. d.	n. d.					
	10-20	n. d.	n. d.	----	----	n. d.					
	20-30	n. d.	----	----	----	n. d.					
7	0-10	n. d.	n. d.	n. d.	n. d.	n. d.					
	10-20	n. d.	n. d.	----	----	n. d.					
	20-30	n. d.	----	----	----	n. d.					
15	0-10	n. d.	n. d.	n. d.	n. d.	n. d.					
	10-20	n. d.	n. d.	----	----	n. d.					
	20-30	n. d.	----	----	----	n. d.					
28	0-10	< 10	< 10	< 10	< 10	< 10					
	10-20	n. d.	n. d.	----	----	n. d.					
	20-30	n. d.	----	----	----	n. d.					
55	0-10	12.91	13.39	13.11	13.76	13.3					
	10-20	n. d.	n. d.	----	----	n. d.					
	20-30	n. d.	----	----	----	n. d.					
87	0-10	15.18	14.72	14.31	15.09	14.8					
	10-20	n. d.	n. d.	----	----	n. d.					
	20-30	n. d.	----	----	----	n. d.					
119	0-10	15.67	16.38	15.93	16.30	16.1					
	10-20	n. d.	n. d.	----	----	n. d.					
	20-30	n. d.	----	----	----	n. d.					
182	0-10	n. d.	n. d.	< 10	n. d.	< 10					
	10-20	n. d.	n. d.	----	----	n. d.					
	20-30	n. d.	----	----	----	n. d.					
255	0-10	n. d.	n. d.	n. d.	n. d.	n. d.					
	10-20	n. d.	n. d.	----	----	n. d.					
	20-30	n. d.	----	----	----	n. d.					

Table B.8.1.1.2.2.1_CA-68: The not processed residue data appropriate to be used in the kinetic analysis obtained in the trial: **40163/3 Laudun.**

The not processed data set for the trial 40163/3, Laudun (study [Sommer; 1995c])											
Sampling point - DAT	Soil layer [cm]	Concentration of Flufenacet [µg/kg]					Concentration of FOE Oxalate [µg/kg]				
		Rep1	Rep 2	Rep 3	Rep 4	Mean	Rep1	Rep 2	Rep 3	Rep 4	Mean
0	0-10	203.2	202.2	187.3	216.1	202	n. d.	n. d.	n. d.	n. d.	n. d.
	10-20	n. d.	n. d.	----	----	n. d.	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.	n. d.	----	----	----	n. d.
8	0-10	243.5	242.9	246.0	225.7	240	< 10	< 10	< 10	< 10	< 10
	10-20	n. d.	n. d.	----	----	n. d.	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.	n. d.	----	----	----	n. d.
14	0-10	254.7	275.4	----	----	265	< 10	< 10	----	----	< 10
	10-20	n. d.	n. d.	----	----	n. d.	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.	n. d.	----	----	----	n. d.
28	0-10	216.5	195.8	----	----	206	< 10	< 10	----	----	< 10
	10-20	n. d.	n. d.	----	----	n. d.	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.	n. d.	----	----	----	n. d.
57	0-10	136.2	139.1	----	----	138	11.56	11.41	----	----	11.5
	10-20	< 10	< 10	----	----	< 10	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.	n. d.	----	----	----	n. d.
91	0-10	84.95	81.56	----	----	83.3	20.88	18.17	----	----	19.5
	10-20	n. d.	n. d.	----	----	n. d.	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.	n. d.	----	----	----	n. d.
125	0-10	31.45	29.79	31.78	31.62	31.2	< 10	< 10	< 10	< 10	< 10
	10-20	n. d.	n. d.	n. d.	n. d.	n. d.	n. d.	n. d.	n. d.	n. d.	n. d.
	20-30	n. d.	----	----	----	n. d.	n. d.	----	----	----	n. d.
182	0-10	< 10	< 10	----	----	< 10	n. d.	n. d.	----	----	n. d.
	10-20	n. d.	n. d.	----	----	n. d.	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.	n. d.	----	----	----	n. d.
240	0-10	n. d.	n. d.	----	----	n. d.	n. d.	n. d.	----	----	n. d.
	10-20	n. d.	n. d.	----	----	n. d.	n. d.	n. d.	----	----	n. d.
	20-30	n. d.	----	----	----	n. d.	n. d.	----	----	----	n. d.
Sampling point - DAT	Soil layer [cm]	Concentration of FOE Sulfonic acid [µg/kg]									
		Rep1	Rep 2	Rep 3	Rep 4	Mean					
0	0-10	n. d.	n. d.	n. d.	n. d.	n. d.					
	10-20	n. d.	n. d.	----	----	n. d.					
	20-30	n. d.	----	----	----	n. d.					
8	0-10	< 10	< 10	< 10	< 10	< 10					
	10-20	n. d.	n. d.	----	----	n. d.					
	20-30	n. d.	----	----	----	n. d.					
14	0-10	< 10	< 10	----	----	< 10					
	10-20	n. d.	n. d.	----	----	n. d.					
	20-30	n. d.	----	----	----	n. d.					
28	0-10	< 10	< 10	----	----	< 10					
	10-20	n. d.	n. d.	----	----	n. d.					
	20-30	n. d.	----	----	----	n. d.					
57	0-10	< 10	< 10	----	----	< 10					
	10-20	n. d.	n. d.	----	----	n. d.					
	20-30	n. d.	----	----	----	n. d.					
91	0-10	14.55	12.72	----	----	13.6					
	10-20	n. d.	n. d.	----	----	n. d.					
	20-30	n. d.	----	----	----	n. d.					
125	0-10	< 10	< 10	< 10	< 10	< 10					
	10-20	n. d.	n. d.	n. d.	n. d.	n. d.					
	20-30	n. d.	----	----	----	n. d.					
182	0-10	n. d.	n. d.	----	----	n. d.					
	10-20	n. d.	n. d.	----	----	n. d.					
	20-30	n. d.	----	----	----	n. d.					
240	0-10	n. d.	n. d.	----	----	n. d.					
	10-20	n. d.	n. d.	----	----	n. d.					
	20-30	n. d.	----	----	----	n. d.					

As a next step, the data were pre-processed in order to be used as input in kinetic assessment. The pre-processing procedure used here is the same as that used by the Applicant to prepare the input data for the kinetic assessment performed to derive modelling endpoints and presented immediately after this evaluation as **Study 7**.

For all trials were available the data obtained for the soil layers 0-10 cm, 10-20 cm and 20-30 cm. Additionally, for six trials, in which the active substance was applied in 1994 ([Sommer; 1995b], study report No. 107723, and [Sommer; 1995c], study report No. 107721) the values for two additional layers – 30-40 cm and 40-50 cm, were reported. However, in order to maintain the consistency of the assessment, only the layers down to 30 cm were analysed.

The Applicant analysing the obtained data sets with aim to derive from them modelling kinetic endpoints for Flufenacet and FOE sulfonic acid stated that the quantifiable residues - > LOQ (10 µg/kg soil d. w.), were found predominantly in the uppermost soil layer – 0-10 cm. As a result, the subsequent analysis focused on that layer.

For the pre-processing of the data two crucial experimental parameters were used: LOD = 3 µg/kg soil and LOQ = 10 µg/kg soil. The procedure, according to the Applicant, followed the recommendations given by FOCUS Work Group on Degradation Kinetics [Focus; 2005].

The following solutions were adopted:

- All values < LOQ (in the tables presenting the results they are given as “< 10”) were set to $\frac{1}{2}$ (LOD + LOQ) = 6.5 µg/kg soil – the value representing the mean of the interval between LOD and LOQ;
- All values < LOD (in the tables presenting the results given as “n. d.”), appearing immediately before or after either the measured concentrations, or the concentrations being <LOQ, were set to $\frac{1}{2}$ LOD = 1.5 µg/kg soil; in case of the the second and next appearances of the values <LOD, they were set to 0, unless they were followed by either the value < LOQ or a quantifiable residue concentration, or else, for the same time point, the residues in deeper layer were either at the level < LOQ or quantifiable;
- For the degradation products the DAT-0 concentrations were set to zero;
- Finally, the kinetic curve was cut off after the first value <LOD, unless it was followed by the value <LOQ or a quantifiable residue concentration.

For the deeper layers – 10-20 cm and 20-30 cm, for which the residue concentrations in the topmost layer were determined to be a quantifiable value or that <LOQ or else <LOD, but in course of subsequent pre-processing described above set to $\frac{1}{2}$ LOD = 1.5 µg/kg soil, the values <LOD were also set to that level – $\frac{1}{2}$ LOD = **1.5 µg/kg soil**. Such approach was considered by the Applicant to be conservative – the residues were expected to be overestimated.

As a next step for each layer the average values were calculated and then summed up to represent the concentration in 0-10 cm layer. These values were subjected to the kinetic analysis. The additional step was the analysis of the data in search of the outliers. That was done for the parent compound. In case the value that was a probable outlier was initially identified, it was further examined, by comparing it to its immediate predecessor. In case the difference between the two was greater than 20%, the preceding and following data points were also analysed in order to determine the general distribution of the data points. Additionally the value supposed to be an outlier was compared to the theoretical DAT-0 concentration of the test compound in the top soil. When the value was conformed to be a potential outlier, it was not used in the kinetic evaluation of the data set. In case of the data sets consisting of parent – Flufenacet, and degradation products – either only FOE Sulfonic acid or FOE Oxalate and FOE Sulfonic acid, when for Flufenacet the given data point was identified as outlier also the corresponding value(s) for degradation product(s) was/were not used in the kinetic assessment as being uncertain.

The resulting data sets for each trial site are presented below in the table(s) B.8.1.1.2.2.1._CA-69 – B.8.1.1.2.2.1._CA-71. The outliers were reported for completeness, but marked italics and not used in the kinetic assessment.

Table B.8.1.1.2.2.1._CA-69: The pre-processed data obtained in the study by [Sommer; 1995], used in the kinetic assessment.

Results obtained for the trial: <i>Breitenfelde, 30159/0, Germany</i>			Results obtained for the trial: <i>Kirchlauter, 30162/0, Germany</i>		Results obtained for the trial: <i>Monheim, 30163/9, Germany</i>		Results obtained for the trial: <i>Burscheid, 30164/7, Germany</i>	
Time point – DAT [days]	Concentration [µg/kg] in 0-10 cm layer of:		Time point – DAT [days]	Concentration [µg/kg] of Flufenacet in 0-10 cm layer	Time point – DAT [days]	Concentration [µg/kg] of Flufenacet in 0-10 cm layer	Time point – DAT [days]	Concentration [µg/kg] of Flufenacet in 0-10 cm layer
	Flufenacet	FOE Sulfonic acid						
0	244.4	0.0	0	262.0	0	155.3	0	333.6
7	259.3	0.0	7	210.3	7	174.6	7	214.7
14	159.3	4.5	14	220.8	14	175.7	14	176.8
28	140.4	9.5	28	285.2	28	152.2	27	110.0
56	91.1	17.4	56	112.5	56	69.5	60	29.0
90	36.3	15.8	90	84.5	90	32.2	90	9.5
120	14.5	4.5	120	48.2	122	25.1	120	0.0
180	9.5	0.0	181	28.4	180	19.1	180	0.0
240	4.5	0.0	237	15.2	231	14.7	239	0.0

Results obtained for the trial: <i>Fresne-L'Archeveque, 30248/1, North France</i>			Results obtained for the trial: <i>Fresne-L'Archeveque 1, 30250/3, North France</i>			
Time point – DAT [days]	Concentration [µg/kg] in 0-10 cm layer of:		Time point – DAT [days]	Concentration [µg/kg] in 0-10 cm layer of:		
	Flufenacet	FOE Sulfonic acid		Flufenacet	FOE Oxalate	FOE Sulfonic acid
0	365.2	0.0	0	281.4	0.0	0.0
14	211.7	4.5	8	299.6	4.5	4.5
28	235.1	16.9	28	187.3	9.5	9.5
56	127.4	10.6	56	115.1	12.8	10.5
90	91.1	14.2	91	84.0	15.3	15.0
120	14.5	12.8	120	67.7	13.8	14.5
181	9.5	7.0	193	41.9	9.5	9.5
303	4.5	4.5	287	20.3	4.5	4.5

Results obtained for the trial: <i>St. Etienne du Gres, 30253/8, South France</i>			Results obtained for the trial: <i>Laudun, 30251/1, South France</i>			
Time point – DAT [days]	Concentration [µg/kg] in 0-10 cm layer of:		Time point – DAT [days]	Concentration [µg/kg] in 0-10 cm layer of:		
	Flufenacet	FOE Sulfonic acid		Flufenacet	FOE Oxalate	FOE Sulfonic acid
0	288.0	0.0	0	384.4	0.0	0.0
15	213.0	9.5	7	296.5	0.0	0.0
28	192.2	10.4	15	313.3	4.5	4.5
56	98.5	12.4	28	204.7	9.5	9.5
87	60.2	9.5	55	82.8	11.5	16.3
119	53.9	9.5	87	47.9	9.5	17.8
182	9.5	4.5	119	30.9	14.2	19.1
260	8.3	0.0	182	9.5	4.5	5.8
			255	9.5	0.0	4.5

Table B.8.1.1.2.2.1._CA-70: The pre-processed data obtained in the studies by [Sommer; 1995a] and [Sommer; 1995b], used in the kinetic assessment.

Study: [Sommer; 1995a]				Study: [Sommer; 1995b]			
Results obtained for the trial: Burscheid, 30499/9, Germany		Results obtained for the trial: Monheim, 30500/6, Germany		Results obtained for the trial: Saussay-la-Campagne, 30254/6, South France		Results obtained for the trial: Fresne-L'Archeveque, 30455/7, North France	
Time point – DAT [days]	Concentration [µg/kg] of Flufenacet in 0-10 cm layer	Time point – DAT [days]	Concentration [µg/kg] of Flufenacet in 0-10 cm layer	Time point – DAT [days]	Concentration [µg/kg] of Flufenacet in 0-10 cm layer	Time point – DAT [days]	Concentration [µg/kg] of Flufenacet in 0-10 cm layer
0	144.2	0	104.0	0	118.4	0	93.0
8	97.1	8	104.2	8	78.8	28	30.8
14	92.7	14	91.9	52	13.7	53	9.5
29	82.9	28	111.9	70	9.5	88	4.5
56	55.6	52	70.1	89	4.5	120	0.0
90	23.3	98	38.8	116	0.0	178	0.0
120	15.2	120	31.8	180	0.0	240	0.0
180	8.3	181	15.8	242	0.0		
240	4.5	240	4.5				

Table B.8.1.1.2.2.1._CA-71: The pre-processed data obtained in the study by [Sommer; 1995c], used in the kinetic assessment.

Results obtained for the trial: Laudun, 40163/3, South France				Results obtained for the trial: St. Etienne du Gres, 40164/1, South France		
Time point – DAT [days]	Concentration [µg/kg] in 0-10 cm layer of:			Time point – DAT [days]	Concentration [µg/kg] in 0-10 cm layer of:	
	Flufenacet	FOE Oxalate	FOE Sulfonic acid		Flufenacet	FOE Sulfonic acid
0	205.2	0.0	0.0	0	229.6	0.0
8	242.2	0.0	0.0	7	288.5	0.0
14	268.1	9.5	9.5	14	197.2	0.0
28	209.2	9.5	9.5	28	239.3	4.5
57	148.8	14.5	9.5	56	147.1	9.5
91	86.3	22.5	16.6	90	76.5	13.8
125	34.2	9.5	9.5	123	64.0	14.0
182	9.5	4.5	4.5	180	15.0	9.5
240	4.5	0.0	0.0	236	9.5	4.5
0.0						
	Results obtained for the trial: Ravenna, 40494/2, Italy			Results obtained for the trial: S. Romualdo, 40495/0, Italy		
	Time point – DAT [days]	Concentration [µg/kg] in 0-10 cm layer of:		Time point – DAT [days]	Concentration [µg/kg] of Flufenacet in 0-10 cm layer	
		Flufenacet	FOE Sulfonic acid			
	0	347.9	0.0	0	348.3	
	7	290.7	0.0	7	359.3	
	14	229.8	0.0	14	327.3	
	28	280.4	4.5	28	334.1	
	56	114.1	13.3	56	166.4	
	90	46.0	16.7	90	99.9	
	121	48.8	23.8	121	82.3	
	180	13.9	4.5	180	22.8	
	236	9.5	0.0	236	17.7	

The data presented above in above in the tables B.8.1.1.2.2.1._CA-69 – B.8.1.1.2.2.1._CA-71 were then subjected to the kinetic analysis similar to that used for the determination of the persistence kinetic endpoints for the laboratory studies and described in section B.8.1.1.2.1.1., eg. in the summary of the **Study 3** on page 203. It is presented, with necessary modifications, below.

The whole assessment was carried out as a multistep procedure, presented below.

It consisted of the following steps:

- **Step 1:** the data for the parent compound were fitted using two kinetic models: SFO and FOMC and verified for passing the acceptance criteria (χ^2 -error and distribution of residuals); in case the SFO fit was found visually acceptable and statistically more appropriate than FOMC, it was selected as the best-fit model;
- **Step 2:** in case the SFO model was found not to be more appropriate than FOMC, it was refined in three-step procedure, by removing the outliers, fixing model parameters and data weighing, until the best fit was achieved;
- **Step 3:** if the **Step-2** fitting for SFO model still failed the χ^2 -error test, and FOMC was demonstrated to be more appropriate, the DFOP model was tested in order to determine if bi-phasic model is acceptable and if so, which one should be selected as returning the best fit;
- **Step 4:** once the best-fit model was identified, the data for the degradation products, if available were added to the data set and the kinetic analysis repeated using the identified best-fit model for Flufenacet (parent compound) and SFO for the degradation products.

The obtained results of the kinetic analysis were evaluated by means of a detailed statistical analysis comprising the following components:

- visual assessment of the fit;
- χ^2 -error statistics;
- t-test significance;
- correlation analysis.

It was carried out in line with the approach characterised in section B.8.1.1.2.1.1. in the summary of the **Study 2**, presented on page 169.

In the visual assessment of the fit the following elements were taken into consideration:

- the conformity of the fitted decline curve with measured residue concentrations;
- the distribution of the residuals, which should be random and not systematic;
- level of residuals, which should be as small as possible – in such case even if their distribution is rather systematic, the fit may be still qualified as acceptable.

Based on these criteria the obtained fit was classified as:

- **good fit**, when the conformity of the kinetic curve and measured residues was good, levels of residuals were low, they were randomly scattered and no obvious systematic deviation in residual plot was visible;
- **acceptable fit**, when the conformity of the kinetic curve and measured residues was acceptable, levels of residuals were medium and they were more-or-less randomly scattered, and the absolute level of residuals was low;
- **poor fit**, when the fitted decline curve significantly deviated from the measured residues and did not match the observed pattern, the level of residuals was high and they were clearly not randomly scattered around zero line.

The next component of the assessment is χ^2 -error statistics, for which the threshold value is set by the relevant Guidelines to 15%. However, as it was for the laboratory studies, it should not be considered to be an absolute cut-off criterion in case of the field dissipation studies, especially in case of the degradation products. That is due to the fact that that threshold value is strictly appropriate for optimal experimental conditions only, which are hardly expected to occur in case of field dissipation studies. For that reason in some cases, even though χ^2 -error >15%, the fit may be acceptable. Additionally, for degradation products it shall be pointed out that for them usually measurements in comparison to the mean of all measurements are low, what strongly influences the χ^2 test.

Another element of that analysis is the t-test. It is recommended that the t-test probability of 0.05, as sufficiently small, should be used as acceptability criterion. In case however of degradation products, or the results of field dissipation studies (as it is in this case), the *prob > t* value of 0.10 or even higher may be still acceptable.

In case of FOMC fit the additional acceptability criterion was the range of Confidence Intervals (CI). Whenever it passed through zero, such fit was considered unreliable. Such approach is consistently used by the RMS – Poland, in all kinetic evaluations performed.

All that was taken into account when the goodness of fit was assessed.

The processed data were kinetically examined using CAKE ver. 3.1 modelling tool, developed by Tessella. The optimisation was performed using IRLS (Iteratively Reweighed Nonlinear Least Squares) algorithm. The settings of the optimiser were the defaults of the tool:

- maximum iterations: 100,
- maximum reweighing: 10,
- SANN maximum iterations: 10000,
- convergence tolerance: 1 E-5,
- error variance tolerance: 1 E-5,
- extra solver: yes, if required.

The results of the fitting are presented below, individually for each trial.

1) Results of the kinetic examination of the data obtained in the trial *Breitenfelde, 30159/0, Germany* (Study No 107724, [Sommer; 1995]):

The analysis for this data-set was a two-step analysis. Its results are presented below, individually for each step.

a) Results obtained at **Step 1** – fitting of the data for the parent compound (Flufenacet) alone:

The results of the kinetic analysis are presented below, in graphical form on figure B.8.1.1.2.2.1._CA-57 and in numerical form in the table B.8.1.1.2.2.1._CA-72. Additionally the table B.8.1.1.2.2.1._CA-73 provides the kinetic endpoints obtained with each of the kinetic models tested.

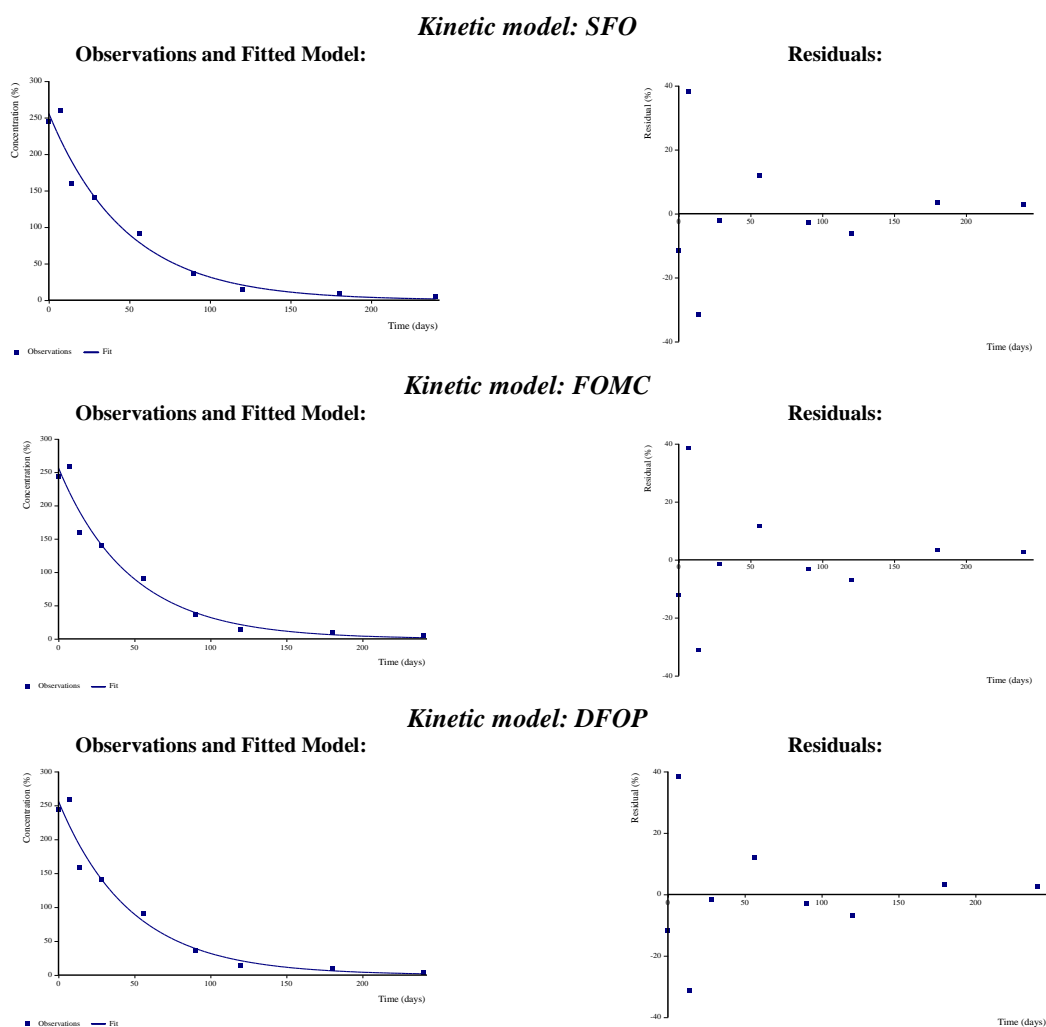


Figure B.8.1.1.2.2.1._CA-57: The graphical results of the kinetic analysis.

Table B.8.1.1.2.2.1._CA-72: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment
				Lower	Upper			
SFO	M_0	255.8	14.81	227.7	283.8	-----	13.3	0.9648; Acceptable fit
	k	0.02092	0.003042	0.01516	0.02669	1.18 E-4		
FOMC	M_0	256.1	18.09	221.0	291.3	-----	14.0	0.9648; Acceptable fit
	α	64.32	1510	-2866	3000	-----		
	β	3040	72100	-137000	143000	-----		
DFOP	M_0	256.5	22.7	210.7	302.2	-----	14.9	0.9648; Acceptable fit
	k_1	0.05167	2.135	-4.25	4.353	0.4908		
	k_2	0.02046	0.0246	-0.02911	0.0700	0.2217		
	g	0.0332	2.551	-5.107	5.174	not given		

Table B.8.1.1.2.2.1._CA-73: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested		
		SFO	FOMC	DFOP
Flufenacet	DT ₅₀ [days]	33.1	32.9	32.8
	DT ₉₀ [days]	110.0	111.0	111.0

The examination of the results showed that all three kinetic models returned visually and statistically acceptable fits, very similar one to another. The visual fit, although displaying good conformity with the experimental results, may be classified only as acceptable, because of the high level of residuals, which on the other hand are distributed randomly. However, neither the FOMC fit nor that obtained using DFOP model may be considered acceptable because of the lack of reliability of the kinetic parameters – in case of FOMC fit for both α and β the CI passes through zero, while for DFOP for both k_1 and k_2 the $prob > t$ was significantly higher than 0.1.

Only SFO returned visually and statistically acceptable fit with fully reliable kinetic parameters, hence it should be considered as the best-fit model for the parent compound – Flufenacet, and as such was used at the next stage of analysis.

- b) Results obtained at **Step 2** – fitting of the data for the parent compound (Flufenacet) and its degradation products:

The results of the kinetic analysis are presented below, in graphical form on figure B.8.1.1.2.2.1_CA-58 and in numerical form in the table B.8.1.1.2.2.1_CA-74. The fitting was performed for combination SFO-SFO.

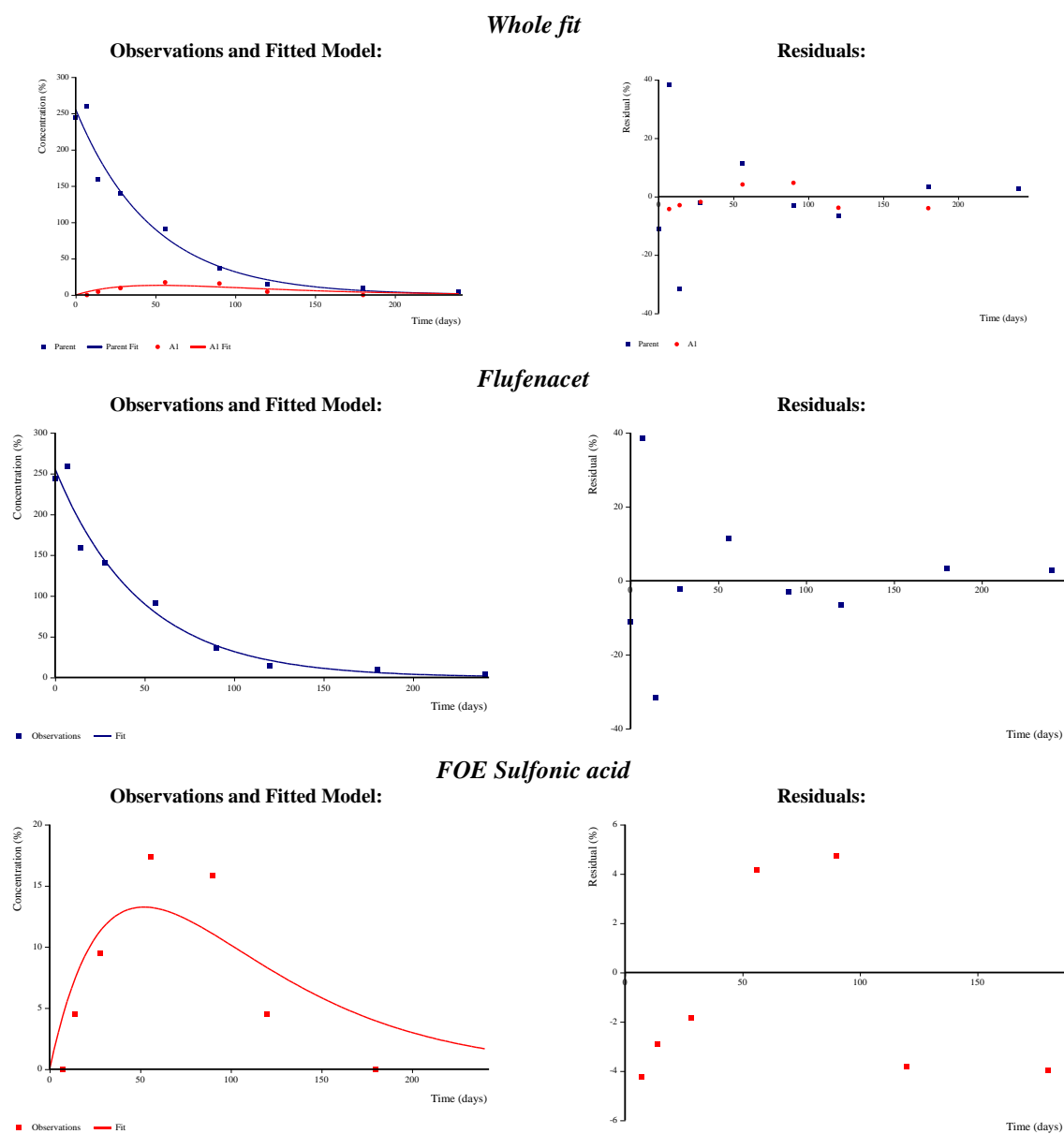


Figure B.8.1.1.2.2.1_CA-58: The graphical results of the kinetic examination of the data for Flufenacet and FOE Sulfonic acid obtained in the trial Breitenfelde, 30159/0.

Table B.8.1.1.2.2.1._CA-74: The numerical results of the kinetic examination of the data for Flufenacet and FOE Sulfonic acid obtained in the trial Breitenfelde, 30159/0.

Compound	Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
			Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment
					Lower	Upper			
Flufenacet	SFO	M ₀	255.5	15.06	228.7	282.3	-----	13.3	0.9648; Acceptable fit
		k	0.02082	0.003083	0.01533	0.02632	1.02 E-5		
FOE Sulfonic acid	SFO	M ₀	0.0	-----	-----	-----	-----	40.6	0.8898; Poor fit
		k	0.0177	0.008983	0.001686	0.03371	0.03618		
		ff	0.1304	0.0495	0.04216	0.2186	-----		

The kinetic endpoints derived from the study are presented below in the table B.8.1.1.2.2.1._CA-75.

Table B.8.1.1.2.2.1._CA-75: The kinetic endpoints determined in the experiment.

Determined parameter	Compound	
	Flufenacet	FOE Sulfonic acid
DT ₅₀ [days]	33.3	39.2
DT ₉₀ [days]	111.0	130
Kinetic formation fraction ff	Not applicable – parent compound	0.1304 ± 0.049
Precursor	Not applicable – parent compound	Flufenacet
Kinetic model	SFO	SFO

The kinetic fit obtained for Flufenacet may be classified as statistically and visually acceptable. Also the calculated kinetic parameters and derived from them kinetic endpoints are reliable.

The kinetic fit obtained for FOE Sulfonic acid cannot be considered acceptable, because of the high χ^2 error – 40.6%, and low conformity of the kinetic curve with the experimental results.

As a result, it cannot be stated that in that trial it was possible to obtain for FOE Sulfonic acid a reliable kinetic curve and hence assess adequately the persistence of that compound in the trial **Breitenfelde, 30159/0**.

RMS performed also the fitting using the two other kinetic models for the parent compound (Flufenacet) – FOMC and DFOP. The kinetic fits for the parent compound were very similar to those for the parent fitted alone and no improvement of the fit was observed for the degradation product – FOE Sulfonic acid. Therefore it may be stated that the change of the kinetic model for parent compound will not result in better fitting. RMS decided to not present the results of those kinetic examinations in order to not overburden the Assessment Report.

Evaluation of the fitting exercise:

The presented above results of the kinetic examination of the data obtained in the trial **Breitenfelde, 30159/0**, demonstrated that reliable fit and reliable kinetic endpoints representing persistence in soil under realistic – field conditions, were obtained only for the parent compound – Flufenacet. The kinetic model identified as returning the best fit was SFO.

For the degradation product subjected to the kinetic examination – FOE Sulfonic acid, it was not possible to obtain reliable kinetic fit and hence reliable kinetic endpoints representing the persistence of that compound on the trial site.

As a result, it can be stated that the reliable persistence kinetic endpoints for that trial may be determined for the parent compound – Flufenacet, when fitted alone. These values will be presented in the List of End Points.

2) Results of the kinetic examination of the data obtained for the trial *Kirchlauter, 30162/0, Germany* (Study No. 107724, [Sommer; 1995]):

The analysis for this data-set was a single step analysis. That was due to the fact that from that data base only the values for Flufenacet could be derived. The results of the kinetic analysis are presented below, in graphical form on figure B.8.1.1.2.2.1._CA-59 and in numerical form in the table B.8.1.1.2.2.1._CA-76. Additionally the table B.8.1.1.2.2.1._CA-77 provides the kinetic endpoints obtained with each of the kinetic models tested.

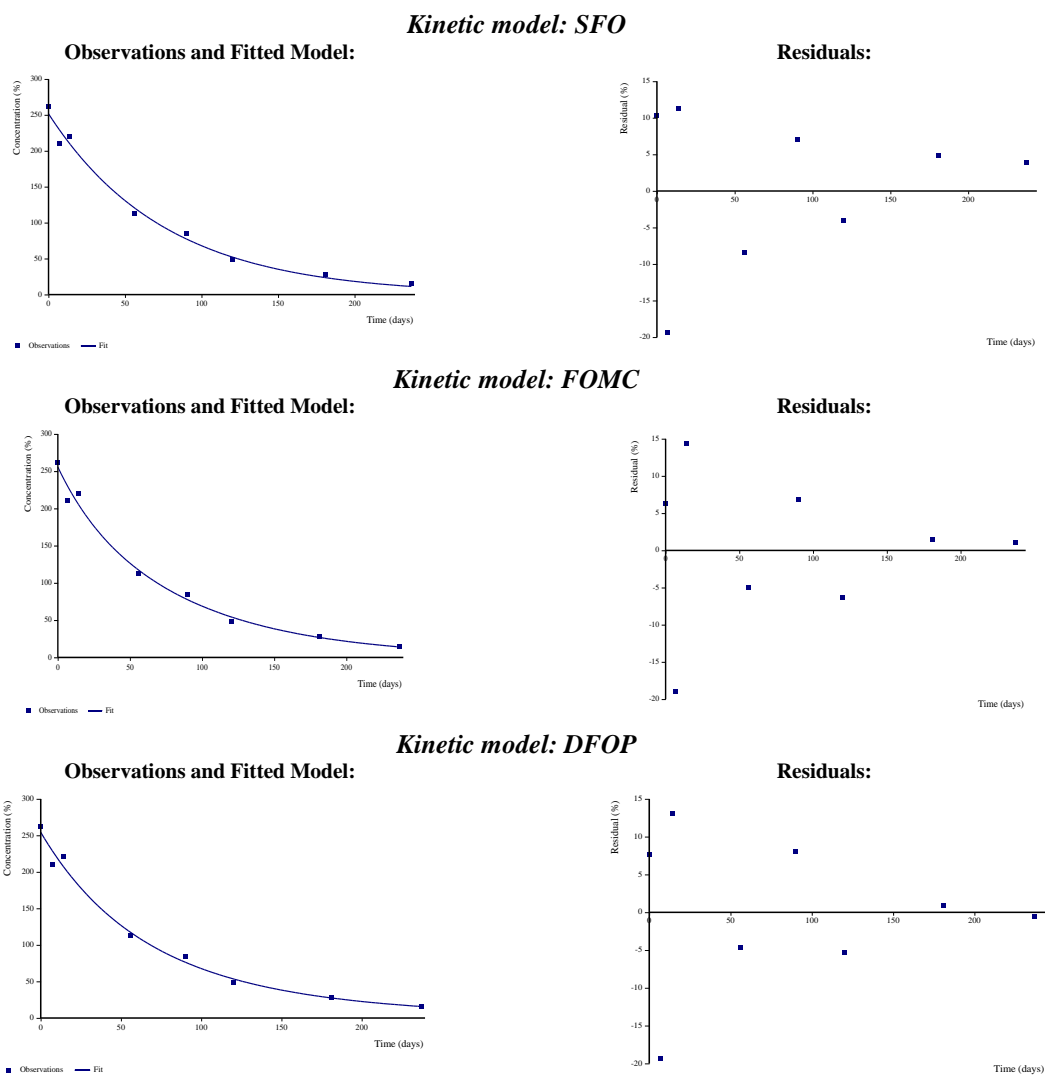


Figure B.8.1.1.2.2.1._CA-59: The graphical results of the kinetic analysis.

Table B.8.1.1.2.2.1._CA-76: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment
				Lower	Upper			
SFO	M_0	251.7	7.743	236.6	266.7	-----	6.43	0.988; Good fit
	k	0.0131	0.001011	0.01113	0.01506	6.53 E-6		
FOMC	M_0	254.4	9.347	235.6	273.2	-----	6.58	0.9888; Good fit
	α	6.373	10.0	-13.78	26.53	-----		
	β	433.2	760	-1098	1960	-----		
DFOP	M_0	255.7	15.27	223.2	288.3	-----	7.1	0.9888; Good fit
	k_1	0.03994	0.209	-0.4057	0.4855	0.4289		
	k_2	0.01148	0.008237	-0.006076	0.02904	0.1179		
	g	0.1607	0.9886	-1.947	2.268	not given		

Table B.8.1.1.2.2.1._CA-77: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested		
		SFO	FOMC	DFOP
Flufenacet	DT ₅₀ [days]	52.9	49.8	49.1
	DT ₉₀ [days]	176.0	189.0	185.0

The examination of the results showed that all three kinetic models returned visually and statistically good fits, very similar one to another. However, neither the FOMC fit nor that obtained using DFOP model may be considered acceptable because of the lack of reliability of the kinetic parameters – in case of FOMC fit for both α and β the CI passed through zero, while for DFOP for both k_1 and k_2 the $prob > t$ was higher than 0.1.

Only SFO returned visually and statistically acceptable fit with fully reliable kinetic parameters, hence it should be considered as the best-fit model for the parent compound – Flufenacet.

Evaluation of the fitting exercise:

The presented above results of the kinetic examination of the data obtained in the trial **Kirchlauter 30162/0**, demonstrated that kinetic model that returned reliable fit and reliable kinetic endpoints representing persistence in soil under realistic – field, conditions for the parent compound – Flufenacet, was SFO. Therefore the values obtained using that model will be presented in the List of End Points. The kinetic analysis for the degradation products – FOE Alcohol, FOE Oxalate and FOE Sulfonic acid, was not performed because of the lack of the appropriate data base for any of them.

3) Results of the kinetic examination of the data obtained for the trial *Monheim, 30163/9, Germany* (Study [Sommer; 1995]):

The analysis for this data-set was a single step analysis. That was due to the fact that from that data base only the values for Flufenacet could be derived. The results of the kinetic analysis are presented below, in graphical form on figure B.8.1.1.2.2.1._CA-60 and in numerical form in the table B.8.1.1.2.2.1._CA-78. Additionally the table B.8.1.1.2.2.1._CA-79 provides the kinetic endpoints obtained with each of the kinetic models tested.

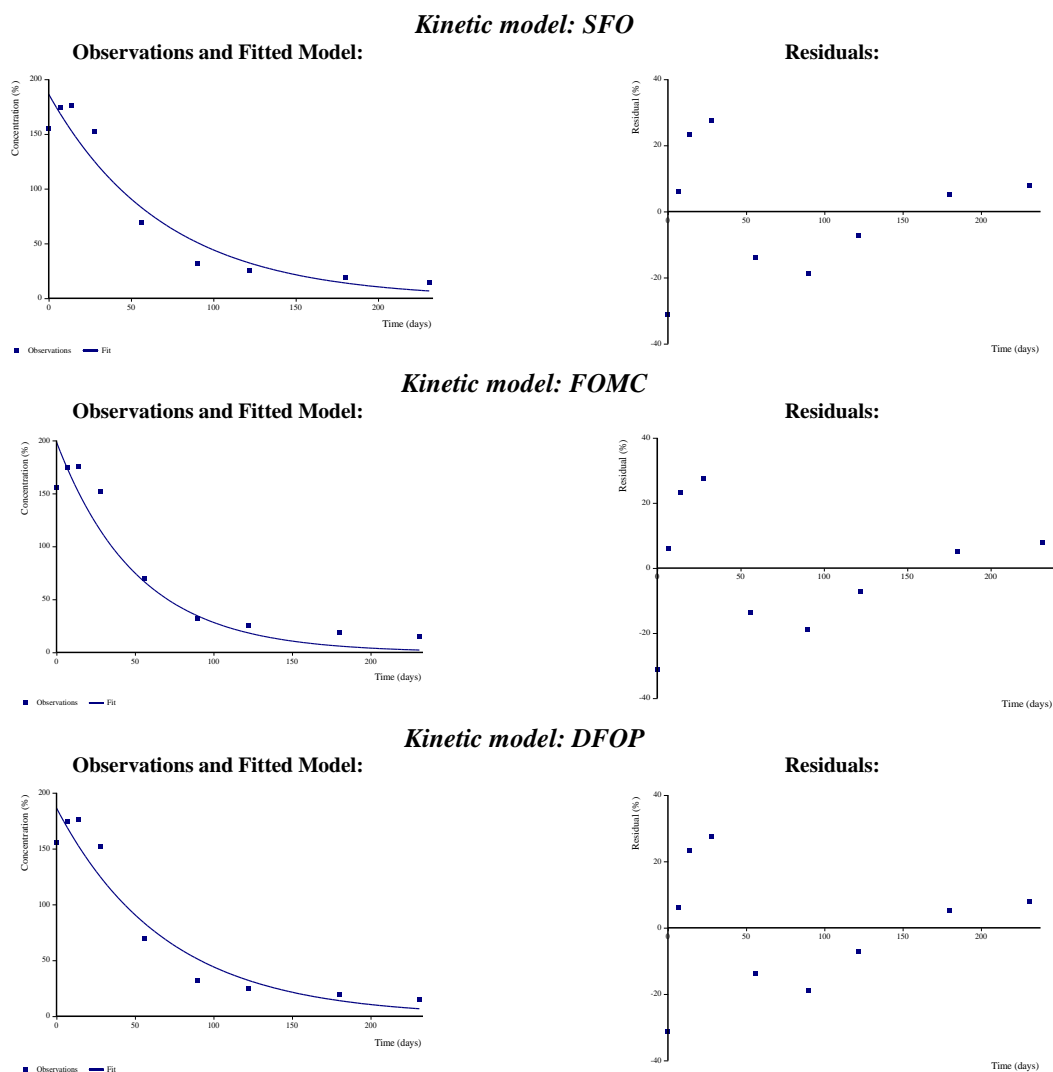


Figure B.8.1.1.2.2.1._CA-60: The graphical results of the kinetic analysis.

Table B.8.1.1.2.2.1._CA-78: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment
				Lower	Upper			
SFO	M_0	186.4	13.93	160.0	212.8	-----	16.1	0.9275; Acceptable fit
	k	0.0144	0.00272	0.009241	0.01955	5.67 E-4		
FOMC	M_0	198.6	17.66	164.3	232.9	-----	17.0	0.9648; Acceptable fit
	α	440.9	120.0	207.7	674.2	-----		
	β	22600	6450	10000	35100	-----		
DFOP	M_0	186.4	15.79	154.6	218.2	-----	18.1	0.9275; Acceptable fit
	k_1	0.01439	0.01655	-0.01896	0.04775	0.2121		
	k_2	0.0144	0.001542	0.01129	0.0175	1.19 E-4		
	g	0.08148	Not determined	Not determined	Not determined	not given		

Table B.8.1.1.2.2.1._CA-79: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested		
		SFO	FOMC	DFOP
Flufenacet	DT ₅₀ [days]	48.2	35.5	48.2
	DT ₉₀ [days]	160.0	118.0	160.0

The examination of the results showed that all three kinetic models returned visually acceptable fits, very similar one to another. The visual fit for all three models may be classified only as acceptable. That is due to the fact that although the correlation coefficient r was above 0.9, what indicated good conformity of the experimental points with the estimated kinetic curve, the visual inspection showed that it was not. Additionally the residuals were high, for some time points above the level $\pm 20\%$. On the other hand for all fits the residuals were randomly distributed.

As for their statistical acceptability, for all three kinetic models the χ^2 error was slightly above the threshold value of 15%, not surpassing however 20%. The lowest value was obtained for SFO model, the highest for DFOP kinetic fit, the sole of the three that cannot be considered acceptable because of the lack of reliability of the determined kinetic parameters. For that fit the $prob > t$ – for k_2 was higher than 0.1 and, because the covariance matrix could not have been created, it was not possible to calculate the error and CI values for parameter g . RMS also noticed that kinetic parameters k_1 and k_2 in DFOP fit were identical and the same as the kinetic parameter k determined using SFO kinetic model.

The fit obtained with FOMC model was visually almost identical to that obtained with SFO, but statistically worse - χ^2 error was higher than that for SFO (17.0% v/s 16.1% respectively). RMS also noticed that the kinetic parameters determined using FOMC model - α and β , although statistically reliable seem to be unrealistically high. Finally, it was noticed that DT₉₀ determined for FOMC fit was shorter than that determined using SFO model. That may suggest, taking into account the conceptual definition of FOMC model, that this model is not appropriate to characterise the kinetic behaviour of Flufenacet in the trial **Monheim, 30163/9**.

As a result it shall be stated that only SFO returned reliable fit and hence it should be considered as the best-fit model for the parent compound – Flufenacet.

Evaluation of the fitting exercise:

The presented above results of the kinetic examination of the data obtained in the trial **Monheim, 30163/9**, demonstrated that for that trial SFO shall be considered as the best-fit model for Flufenacet. The results of the fitting – the determined kinetic endpoints, will be presented in the List of End Points.

The kinetic analysis for the degradation products – FOE Alcohol, FOE Oxalate and FOE Sulfonic acid, was not performed for that trial due to the lack of the suitable data base for any of them.

4) Results of the kinetic examination of the data obtained for the trial *Burscheid, 30164/7, Germany* (Study No. 107724, [Sommer; 1995]):

The analysis for this data-set was a single step analysis. That was due to the fact that from that data base only the values for Flufenacet could be derived. The results of the kinetic analysis are presented below, in graphical form on figure B.8.1.1.2.2.1_CA-61 and in numerical form in the table B.8.1.1.2.2.1_CA-80. Additionally the table B.8.1.1.2.2.1_CA-81 provides the kinetic endpoints obtained with each of the kinetic models tested.

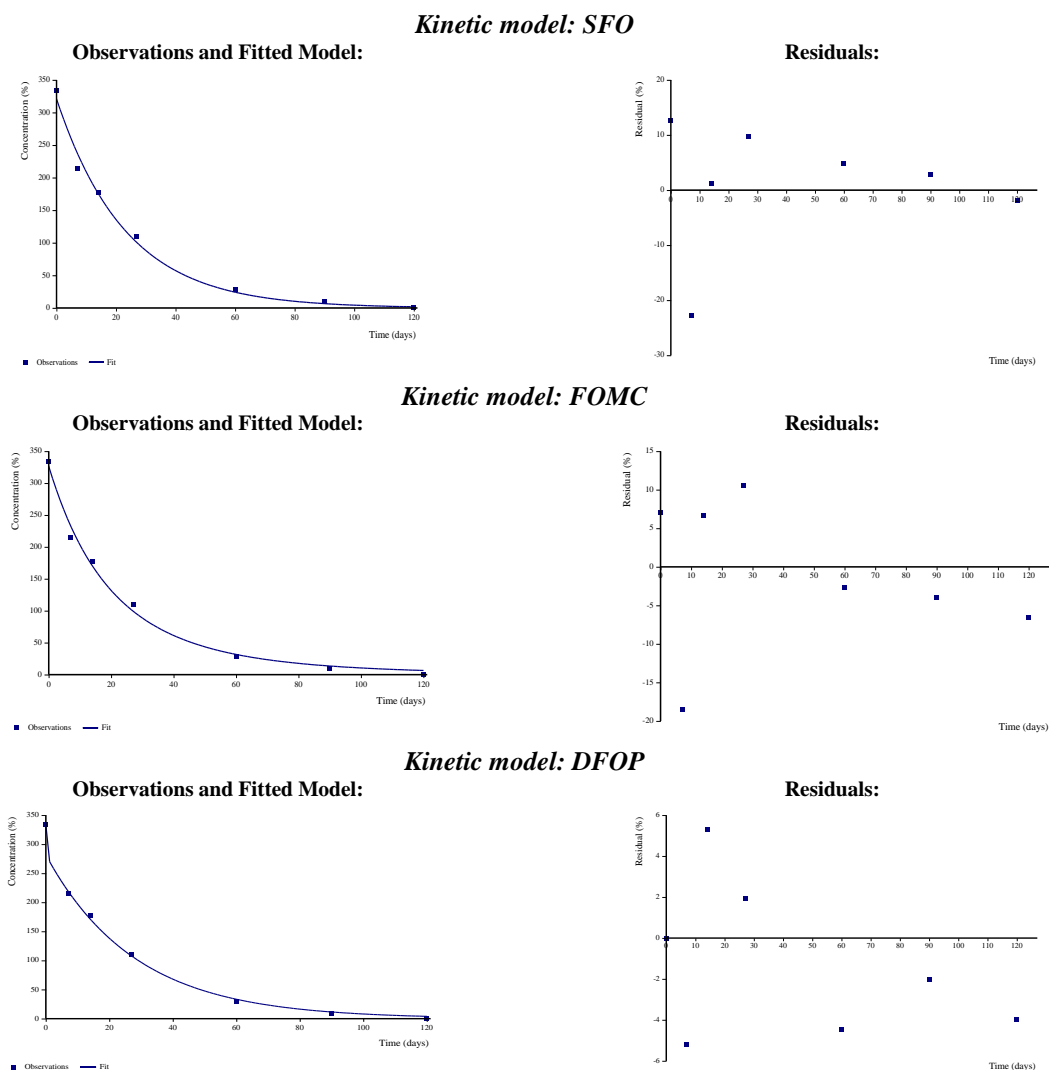


Figure B.8.1.1.2.2.1_CA-61: The graphical results of the kinetic analysis.

Table B.8.1.1.2.2.1._CA-80: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment
				Lower	Upper			
SFO	M_0	321.0	11.23	298.3	343.6	-----	6.83	0.9915; Good fit
	k	0.04309	0.003632	0.03577	0.05041	3.75 E-5		
FOMC	M_0	326.6	11.85	301.3	351.8	-----	6.43	0.9936; Good fit
	α	4.903	4.224	-4.144	13.95	-----		
	β	98.42	97.02	-108.4	305.2	-----		
DFOP	M_0	333.6	5.72	320.1	347.1	-----	2.85	0.9991; Good fit
	k_1	3.869	309.9	-725.3	733.1	0.4954		
	k_2	0.03551	0.002005	0.03079	0.040023	1.96 E-4		
	g	0.1569	0.3041	0.08531	0.2284	not given		

Table B.8.1.1.2.2.1._CA-81: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested		
		SFO	FOMC	DFOP
Flufenacet	DT ₅₀ [days]	16.1	14.9	14.7
	DT ₉₀ [days]	53.4	59.0	60.0

The examination of the results showed that all three kinetic models returned visually and statistically good fits, very similar one to another. The visual fits displayed good conformity with the experimental results and low level of residuals, randomly distributed. However, neither the FOMC fit nor that obtained using DFOP model may be considered acceptable because of the lack of reliability of the kinetic parameters – in case of FOMC fit for both α and β the CI passes through zero, while for DFOP for k_1 the $prob > t$ was significantly higher than 0.1.

Only SFO returned visually and statistically acceptable fit with fully reliable kinetic parameters, hence it should be considered as the best-fit model for the parent compound – Flufenacet in that trial.

Evaluation of the fitting exercise:

The presented above results of the kinetic examination of the data obtained in the trial **Burscheid, 30164/7**, demonstrated that for that trial SFO shall be considered as the best-fit model for Flufenacet. The results of the fitting – the determined kinetic endpoints, will be presented in the List of End Points.

The kinetic analysis for the degradation products – FOE Alcohol, FOE Oxalate and FOE Sulfonic acid, was not performed for this trial due to the lack of the suitable data base for any of them.

5) Results of the kinetic examination of the data obtained for the trial *Fresne-L'Archeveque, 30248/1, North France* (Study No. 107724, [Sommer; 1995]):

The analysis for this data-set was a two-step analysis. Its results are presented below, individually for each step.

a) Results obtained at **Step 1** – fitting of the data for the parent compound (Flufenacet) alone:

The results of the kinetic analysis are presented below, in graphical form on figure B.8.1.1.2.2.1._CA-62 and in numerical form in the table B.8.1.1.2.2.1._CA-82. Additionally, the table B.8.1.1.2.2.1._CA-83 provides the kinetic endpoints obtained with each of the kinetic models tested.

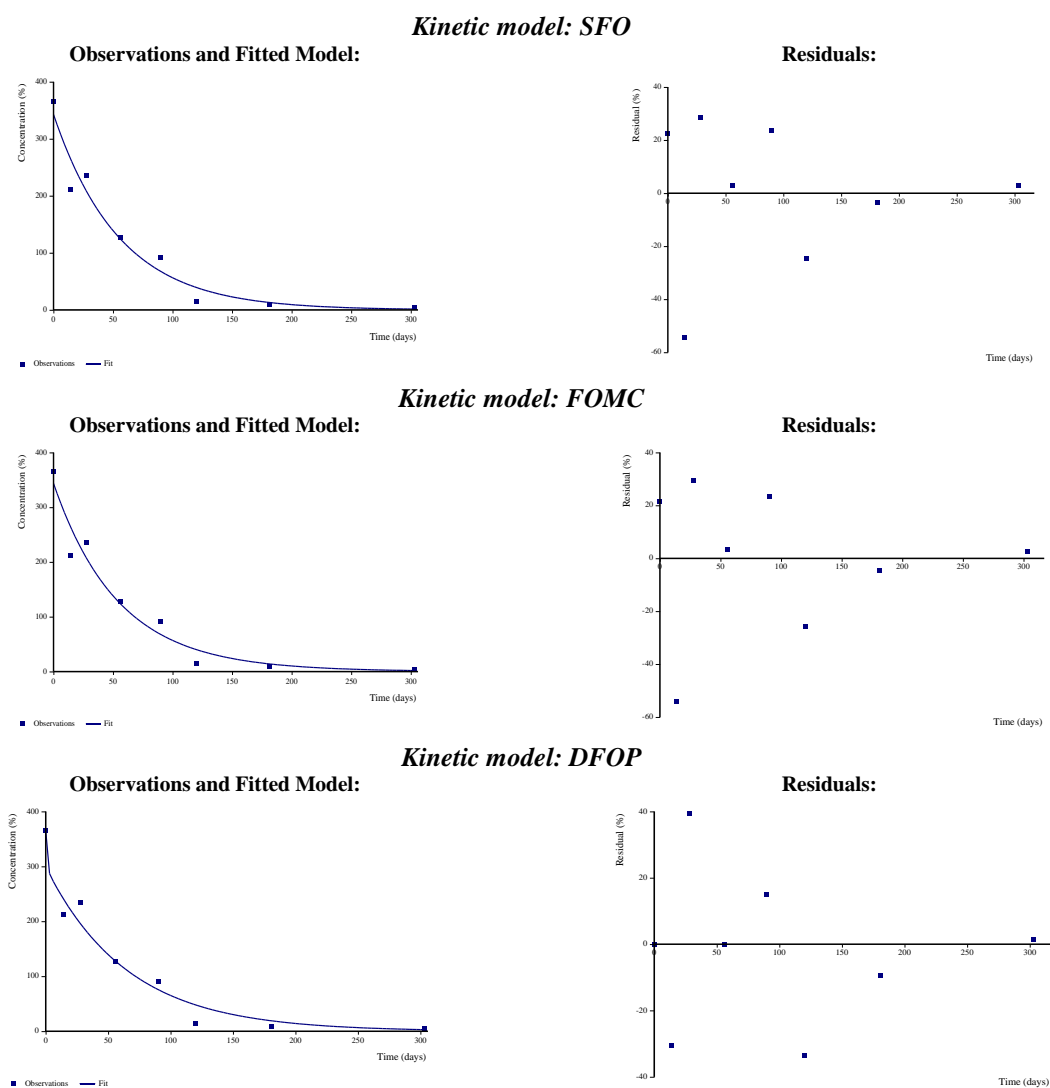


Figure B.8.1.1.2.2.1._CA-62: The graphical results of the kinetic analysis.

Table B.8.1.1.2.2.1._CA-82: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment
				Lower	Upper			
SFO	M_0	342.7	25.23	293.7	391.7	-----	15.8	0.9536; Acceptable fit
	k	0.01805	0.002917	0.01239	0.02372	4.10 E-4		
FOMC	M_0	343.6	30.6	282.0	405.3	-----	16.8	0.9537; Acceptable fit
	α	36.84	594.4	-1161.0	1240.0	-----		
	β	2000.0	32900	-62400	68200	-----		
DFOP	M_0	365.2	31.37	298.3	432.1	-----	15.4	0.9673; Acceptable fit
	k_1	1.243	174.8	-371.4	373.9	0.4973		
	k_2	0.01526	0.003287	0.008247	0.02226	0.004865		
	g	0.1811	0.1306	-0.09725	0.4595	not given		

Table B.8.1.1.2.2.1._CA-83: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested		
		SFO	FOMC	DFOP
Flufenacet	DT ₅₀ [days]	38.4	38.0	32.3
	DT ₉₀ [days]	128.0	129.0	138.0

The visual fit for all three models may be classified only as acceptable. That is due to the fact that although the correlation coefficient r was above 0.9, what indicated good conformity of the experimental points with the estimated kinetic curve, the visual inspection showed that it was not. Additionally the residuals were high, for some time points above the level $\pm 20\%$. On the other hand for all fits the residuals were randomly distributed.

As for their statistical acceptability, for all three kinetic models the χ^2 error was slightly above the threshold value of 15%, not surpassing however 17%. The lowest value was obtained for DFOP model, the highest for FOMC kinetic fit. At the same time it shall be noted that for all three kinetic fits the χ^2 error values were very close and in case of DFOP and SFO fits almost identical.

Additionally it was noticed that neither the FOMC fit nor that obtained using DFOP model may be considered acceptable because of the lack of reliability of the kinetic parameters – in case of FOMC fit for both α and β the CI passes through zero, while for DFOP for k_1 the $prob > t$ was significantly higher than 0.1.

Only SFO returned visually and statistically acceptable fit with fully reliable kinetic parameters, hence it should be considered as the best-fit model for the parent compound – Flufenacet and as such was used at the next stage of analysis.

- b) Results obtained at **Step 2** – fitting of the data for the parent compound (Flufenacet) and its degradation products:

The results of the kinetic analysis are presented below, in graphical form on figure B.8.1.1.2.2.1._CA-63 and in numerical form in the table B.8.1.1.2.2.1._CA-84. The fitting was performed for combination SFO-SFO.

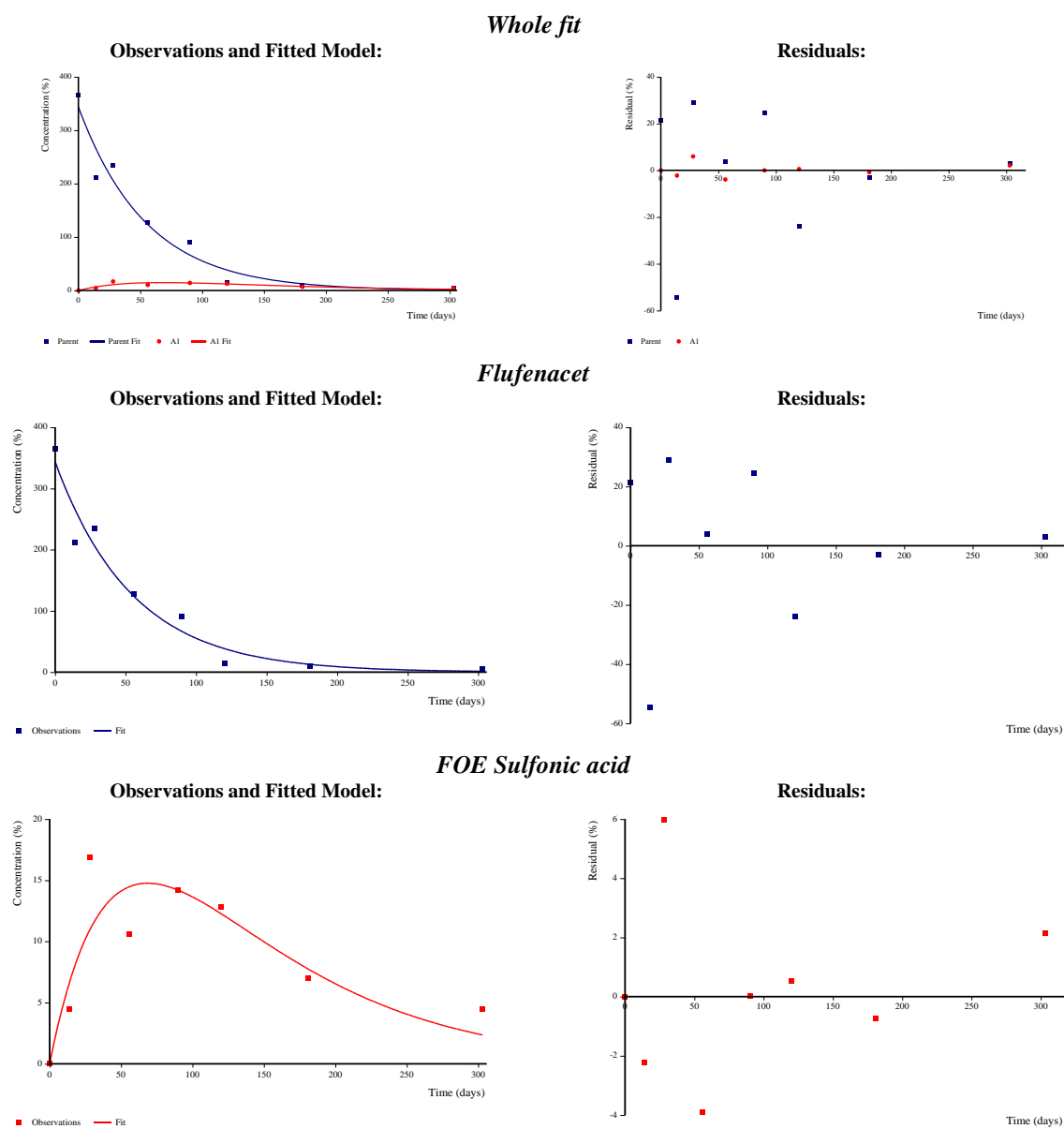


Figure B.8.1.1.2.2.1._CA-63: The graphical results of the kinetic examination of the data for Flufenacet and FOE Sulfonic acid obtained in the trial Fresne-L'Archeveque, 30248/1.

Table B.8.1.1.2.2.1._CA-84: The numerical results of the kinetic examination of the data for Flufenacet and FOE Sulfonic acid obtained in the trial Fresne-L'Archeveque, 30248/1.

Compound	Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
			Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment
					Lower	Upper			
Flufenacet	SFO	M ₀	343.7	26.39	296.3	391.1	-----	15.8	0.9536
		k	0.01827	0.003069	0.01275	0.02378	4.79 E-5		Acceptable fit
FOE Sulfonic acid	SFO	M ₀	0.0	-----	-----	-----	-----	23.3	0.7441;
		k	0.01144	0.004436	0.003473	0.01941	0.01282		Acceptable fit
		ff	0.09409	0.02776	0.04423	0.1439	-----		

The kinetic endpoints derived from the study are presented below in the table B.8.1.1.2.2.1._CA-85.

Table B.8.1.1.2.2.1._CA-85: The kinetic endpoints determined in the experiment.

Determined parameter	Compound	
	Flufenacet	FOE Sulfonic acid
DT ₅₀ [days]	38.0	60.6
DT ₉₀ [days]	126.0	201
Kinetic formation fraction ff	Not applicable – parent compound	0.0941 ± 0.028
Precursor	Not applicable – parent compound	Flufenacet
Kinetic model	SFO	SFO

The kinetic fit obtained for Flufenacet may be classified as statistically and visually acceptable. Also the calculated kinetic parameters and derived from them kinetic endpoints are reliable.

The kinetic fit obtained for FOE Sulfonic acid can also be considered acceptable, despite the χ^2 error > 15% (23.3%). That is due to the fact that the conformity of the kinetic curve with the experimental results may be classified as good, the residuals are low and randomly distributed.

As a result, it can be stated that in that trial it was possible to obtain reliable fits for Flufenacet and FOE Sulfonic acid using a combination SFO-SFO.

RMS performed also the fitting using the two other kinetic models for the parent compound (Flufenacet) – FOMC and DFOP. The kinetic fits for the parent compound were very similar to those for the parent fitted alone and no improvement of the fit was observed for the degradation product – FOE Sulfonic acid. Therefore it may be stated that the change of the kinetic model for parent compound would not result in better fitting. RMS decided to not present the results of those kinetic examinations in order to not overburden the Assessment Report.

Evaluation of the fitting exercise:

The presented above results of the kinetic examination of the data obtained in the trial **Fresne-L'Archeveque, 30248/1**, demonstrated that reliable fit, and hence reliable kinetic endpoints representing persistence in soil under realistic – field conditions, was obtained for both parent compound – Flufenacet and its degradation product – FOE Sulfonic acid when the combination of the kinetic models SFO-SFO was used. The kinetic endpoints resulting from this kinetic assessment will be presented in the List of End Points as persistence kinetic endpoints for Flufenacet and FOE Sulfonic acid in the trial **Fresne-L'Archeveque, 30248/1**.

6) Results of the kinetic examination of the data obtained for the trial *Fresne-L'Archeveque 1, 30250/3, North France* (Study No. 107724, [Sommer; 1995]):

The analysis for this data-set was a two-step analysis. Its results are presented below, individually for each step.

a) Results obtained at **Step 1** – fitting of the data for the parent compound (Flufenacet) alone:

The results of the kinetic analysis are presented below, in graphical form on figure B.8.1.1.2.2.1._CA-64 and in numerical form in the table B.8.1.1.2.2.1._CA-86. Additionally the table B.8.1.1.2.2.1._CA-87 provides the kinetic endpoints obtained with each of the kinetic models tested.

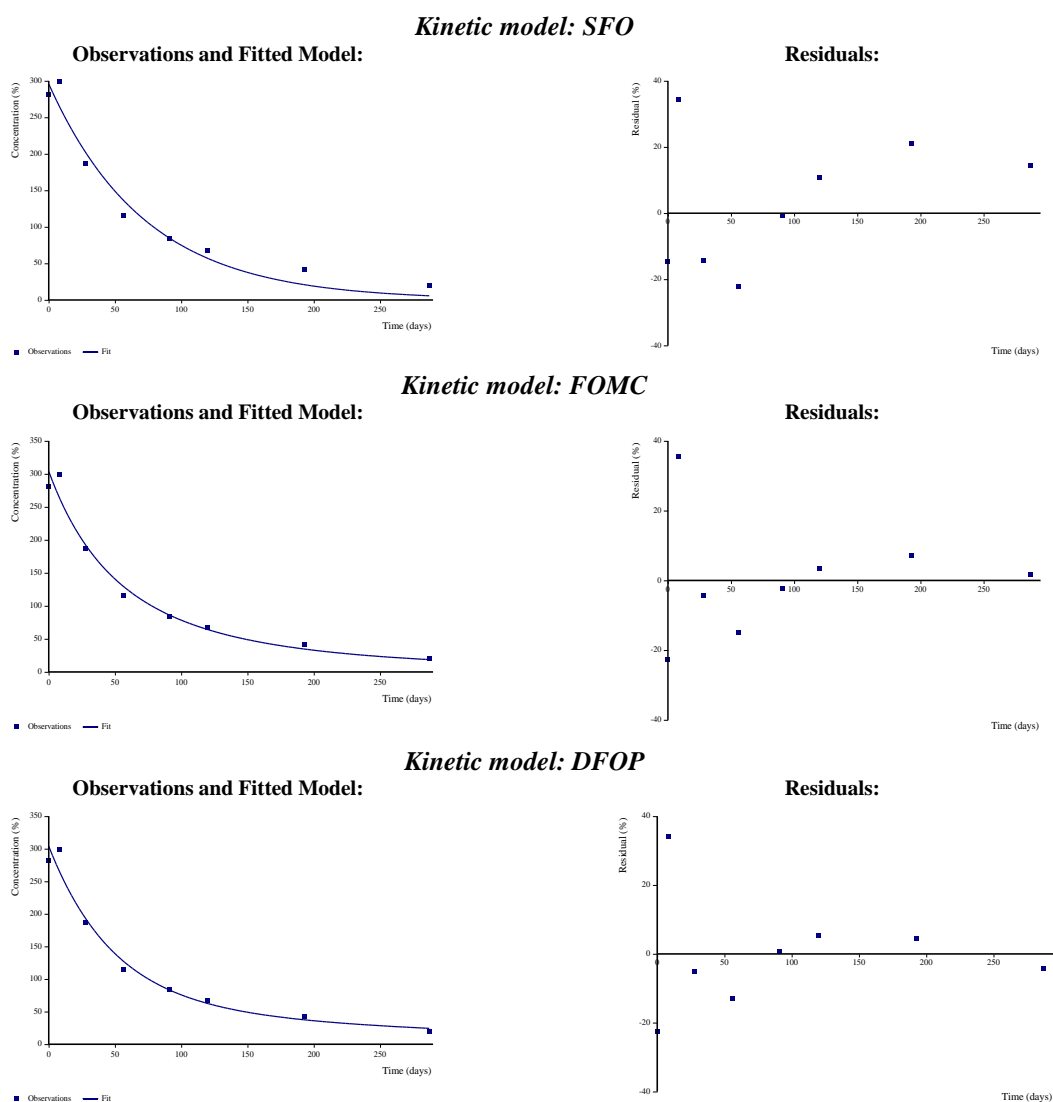


Figure B.8.1.1.2.2.1._CA-64: The graphical results of the kinetic analysis.

Table B.8.1.1.2.2.1._CA-86: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment
				Lower	Upper			
SFO	M_0	296.0	16.16	264.6	327.4	-----	11.0	0.9681; Acceptable fit
	k	0.01374	0.001757	0.01032	0.01715	1.15 E-4		
FOMC	M_0	304.0	17.55	268.7	339.4	-----	10.0	0.9741; Acceptable fit
	α	2.448	2.117	-1.819	6.714	-----		
	β	135.2	152.0	-171.1	441.4	-----		
DFOP	M_0	304.0	18.76	264.0	344.0	-----	10.4	0.9761; Acceptable fit
	k_1	0.02088	0.01564	-0.01247	0.05423	0.1264		
	k_2	0.003541	0.01107	-0.02005	0.02713	0.3825		
	g	0.7834	0.5767	-0.4461	2.013	not given		

Table B.8.1.1.2.2.1._CA-87: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested		
		SFO	FOMC	DFOP
Flufenacet	DT ₅₀ [days]	50.5	44.2	43.7
	DT ₉₀ [days]	168.0	211.0	235.0

The examination of the results showed that all three kinetic models returned visually acceptable and statistically reliable – for all three models the χ^2 error was < 15%. The fits were similar one to another. In case of the SFO model the visual fit was classified as acceptable, despite the fact that correlation coefficient $r > 0.9$, what suggested a good conformity of the estimated kinetic curve and experimental points. In reality the kinetic curve did not represent well the distribution of the experimental points. Additionally some of the residuals were high and their distribution, especially for later time points, not random.

For FOMC and DFOP fits the conformity of the estimated kinetic curve and experimental points was better, what was also reflected in lower χ^2 error and higher correlation coefficient r . However, the residuals for these two fits were very similar to those determined for the SFO fit, both in terms of their values and their spatial distribution.

At the same time it shall be stated that neither FOMC nor DFOP may be considered acceptable, due to the lack of reliability of the kinetic parameters – in case of FOMC fit for both α and β the CI passes through zero, while for DFOP for both k_1 and k_2 the $prob > t$ was higher than 0.1.

Only SFO returned visually and statistically acceptable fit with fully reliable kinetic parameters, hence it should be considered as the best-fit model for the parent compound – Flufenacet, and as such was used at the next stage of analysis.

- b) Results obtained at **Step 2** – fitting of the data for the parent compound (Flufenacet) and its degradation products:

The results of the kinetic analysis are presented below, in graphical form on figure B.8.1.1.2.2.1._CA-65 and in numerical form in the table B.8.1.1.2.2.1._CA-88. The fitting was performed for combination SFO-SFO-SFO. In the modelling tool A1 was used to denominate FOE Oxalate and B1 – FOE Sulfonic acid.

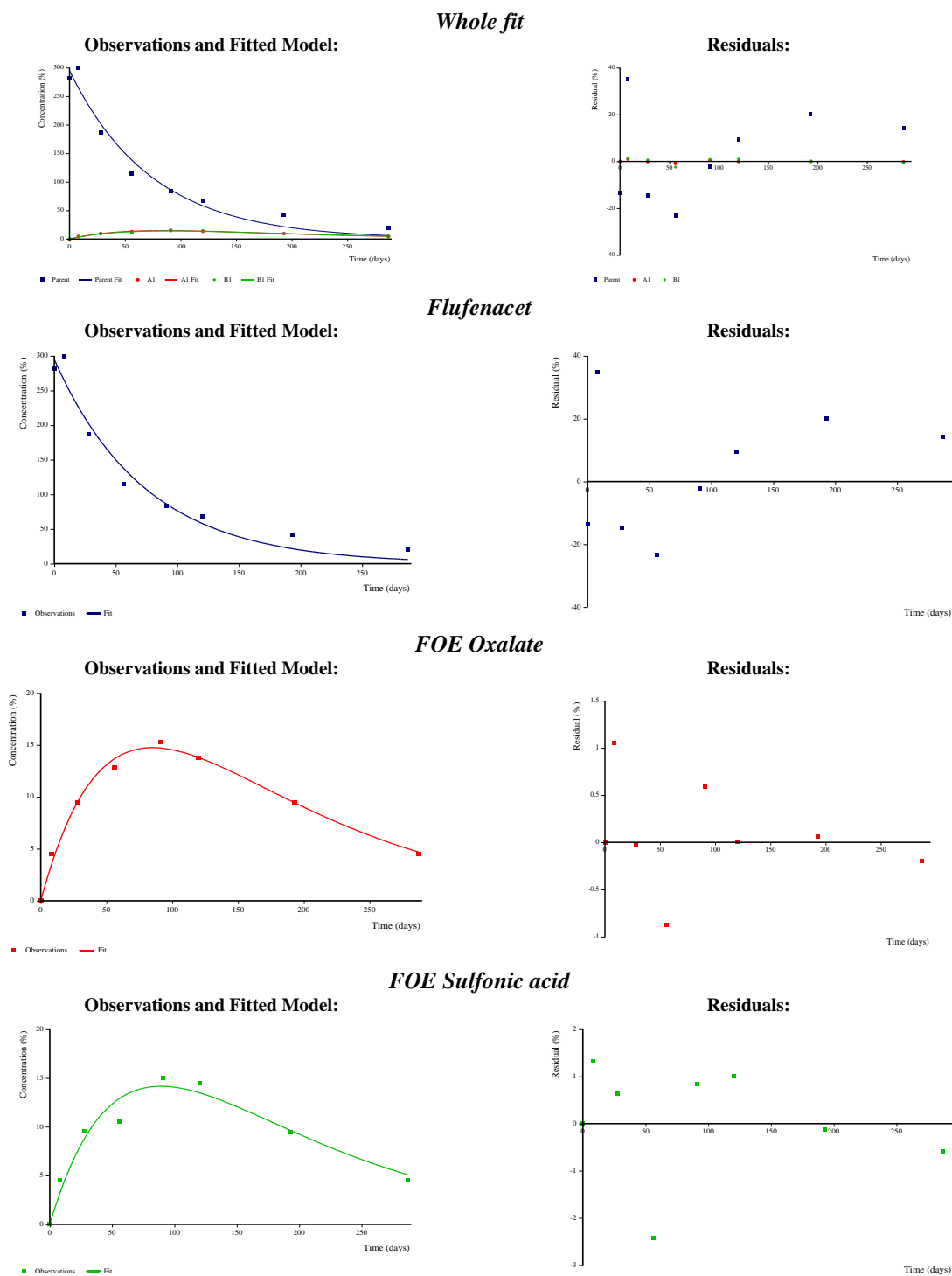


Figure B.8.1.1.2.2.1._CA-65: The graphical results of the kinetic examination of the data for Flufenacet and FOE Sulfonic acid obtained in the trial Fresne-L'Archeveque 1, 30250/3.

Table B.8.1.1.2.2.1._CA-88: The numerical results of the kinetic examination of the data for Flufenacet, FOE Oxalate and FOE Sulfonic acid obtained in the trial Fresne-L'Archeveque 1, 30250/3.

Compound	Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
			Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment
					Lower	Upper			
Flufenacet	SFO	M ₀	294.9	17.0	265.2	324.6	-----	11.0	0.9672; Acceptable fit
		k	0.01352	0.001798	0.01038	0.01666	6.14 E-7		
FOE Oxalate	SFO	M ₀	0.0	----	----	----	----	4.53	0.9895; Good fit
		k	0.01091	0.001515	0.007544	0.01284	2.44 E-6		
		ff	0.1188	0.01973	0.08434	0.1532	----		
FOE Sulfonic acid	SFO	M ₀	0.0	----	----	----	----	9.83	0.9477; Good fit
		k	0.00921	0.001872	0.005942	0.01248	7.69 E-5		
		ff	0.1091	0.01994	0.07424	0.1439	----		

The kinetic endpoints derived from the study are presented below in the table B.8.1.1.2.2.1._CA-89.

Table B.8.1.1.2.2.1._CA-89: The kinetic endpoints determined in the experiment.

Determined parameter	Compound		
	Flufenacet	FOE Sulfonic acid	FOE Oxalate
DT ₅₀ [days]	51.3	75.3	68.0
DT ₉₀ [days]	170.0	250.0	226.0
Kinetic formation fraction ff	Not applicable	0.109 ± 0.020	0.119 ± 0.020
Precursor	Not applicable	Flufenacet	Flufenacet
Kinetic model	SFO	SFO	SFO

The kinetic fit obtained for Flufenacet may be classified as statistically and visually acceptable. Also the calculated kinetic parameters and derived from them kinetic endpoints are reliable.

The kinetic fits obtained for both FOE Oxalate and FOE Sulfonic acid can also be considered acceptable. They display very good conformity of the estimated kinetic curve with the experimental points and low, randomly distributed residuals. They are also statistically reliable – the χ^2 error for them both is well below 15%, not surpassing the level of 10%. Finally, for all three compounds the determined kinetic parameters, and hence kinetic endpoints, are fully reliable.

As a result, it can be stated that in this trial it was possible to obtain reliable fits for Flufenacet, FOE Oxalate and FOE Sulfonic acid using a combination SFO-SFO-SFO.

RMS performed also the fitting using the two other kinetic models for the parent compound (Flufenacet) – FOMC and DFOP. The kinetic fits for the parent compound were similar to those for the parent compound fitted alone and no improvement of the fit was observed for the degradation products – FOE Oxalate and FOE Sulfonic acid. Therefore it may be stated that the change of the kinetic model for parent compound will not result in better fitting. RMS decided to not present the results of those kinetic examinations in order to not overburden the Assessment Report.

Evaluation of the fitting exercise:

The presented above results of the kinetic examination of the data obtained in the trial **Fresne-L'Archeveque 1, 30250/3**, demonstrated that reliable fit, and hence reliable kinetic endpoints representing persistence in soil under realistic – field conditions, was obtained for all compounds for which assessment was carried out – Flufenacet (parent compound), FOE Oxalate (primary degradation product of Flufenacet) and FOE Sulfonic acid (primary degradation product of Flufenacet), when the combination of the kinetic models SFO-SFO-SFO was used. The kinetic endpoints resulting from this kinetic assessment will be presented in the List of End Points as persistence kinetic endpoints for Flufenacet, FOE Oxalate and FOE Sulfonic acid in the trial **Fresne-L'Archeveque 1, 30250/3**.

7) Results of the kinetic examination of the data obtained for the trial *Laudun, 30251/1, South France* (Study No. 107724, [Sommer; 1995]):

The analysis for this data-set was a two-step analysis. Its results are presented below, individually for each step.

a) Results obtained at **Step 1** – fitting of the data for the parent compound (Flufenacet) alone:

The results of the kinetic analysis are presented below, in graphical form on figure B.8.1.1.2.2.1._CA-66 and in numerical form in the table B.8.1.1.2.2.1._CA-90. Additionally the table B.8.1.1.2.2.1._CA-91 provides the kinetic endpoints obtained with each of the kinetic models tested.

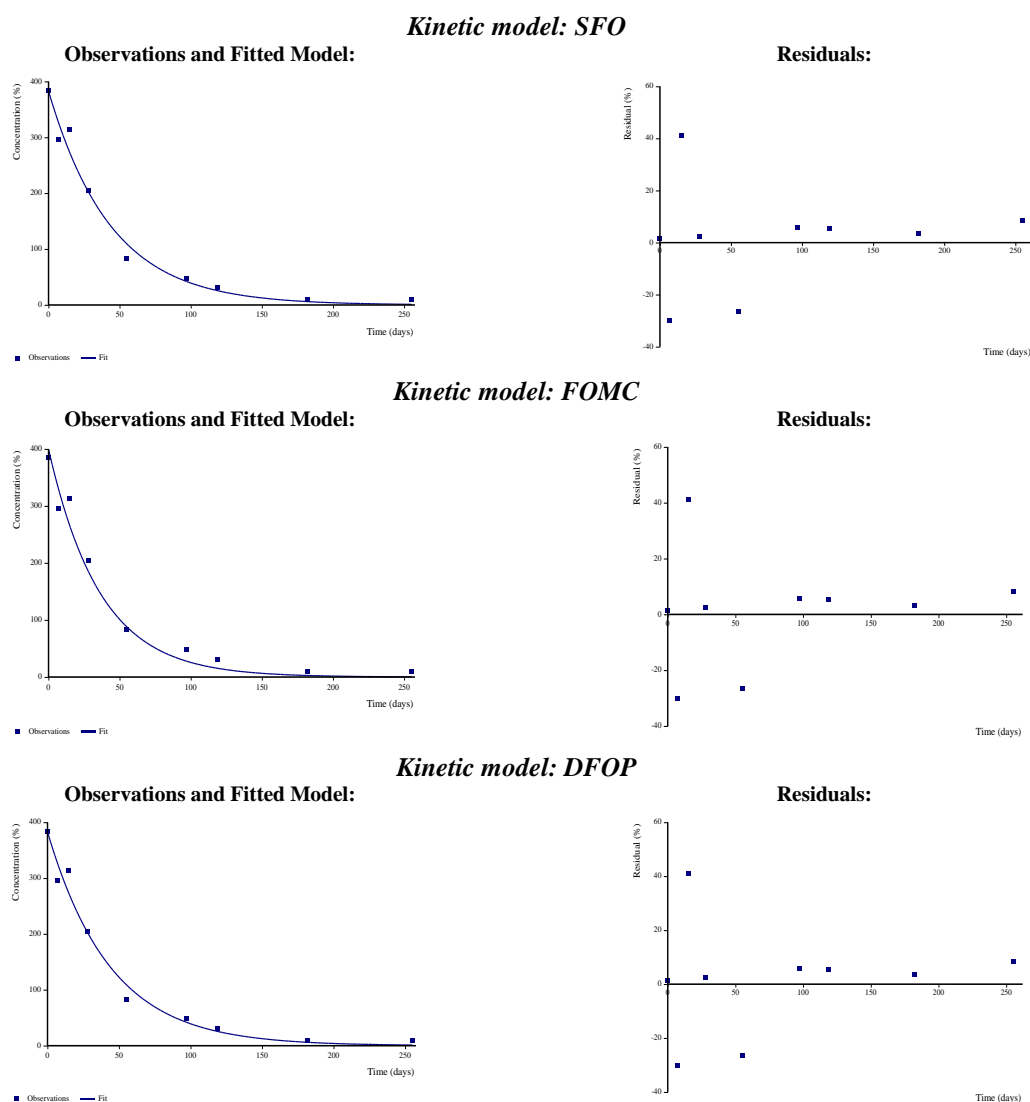


Figure B.8.1.1.2.2.1._CA-66: The graphical results of the kinetic analysis.

Table B.8.1.1.2.2.1._CA-90: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment
				Lower	Upper			
SFO	M_0	382.9	16.96	350.8	415.0	-----	10.2	0.9804; Acceptable fit
	k	0.02278	0.00253	0.01799	0.02757	2.13 E-5		
FOMC	M_0	400.0	21.82	357.6	442.4	-----	10.8	0.9804; Acceptable fit
	α	683.7	161.2	370.5	996.8	-----		
	β	24800	6110	12900	36700	-----		
DFOP	M_0	382.9	26.19	330.1	435.7	-----	11.5	0.9804; Acceptable fit
	k_1	0.02278	364.1	-733.6	733.7	0.5000		
	k_2	0.02278	187.8	-378.4	378.4	0.5000		
	g	0.3402	154000	-310000	311000	not given		

Table B.8.1.1.2.2.1._CA-91: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested		
		SFO	FOMC	DFOP
Flufenacet	DT ₅₀ [days]	30.4	25.2	30.4
	DT ₉₀ [days]	101.0	83.7	101.0

The examination of the results showed that all three kinetic models returned visually acceptable and statistically reliable – for all three models the χ^2 error was < 15%. It was stated that of the three SFO returned superior fit, although the differences between the fits were minimal.

DFOP cannot be considered acceptable, because it returned not reliable kinetic parameters. It was noted that for that kinetic model the rate constants k_1 and k_2 were equal and. Moreover, they were equal to the rate constant k determined using SFO model.

FOMC returned fit visually almost identical to that obtained with SFO and statistically slightly worse. The determined kinetic parameters – α and β , were reliable, but very high. RMS noted that the DT₉₀ determined for FOMC model was shorter than that for SFO, what puts a question mark over the problem whether the FOMC model adequately describes the kinetic behaviour of Flufenacet in the evaluated trial.

As a result SFO was identified as kinetic model returning the best fit for this trial and hence adequate to be used at the next stage of the assessment.

- b) Results obtained at **Step 2** – fitting of the data for the parent compound (Flufenacet) and its degradation products:

The results of the kinetic analysis are presented below, in graphical form on figure B.8.1.1.2.2.1._CA-67 and in numerical form in the table B.8.1.1.2.2.1._CA-92. The fitting was performed for combination SFO-SFO-SFO. In the modelling tool A1 was used to denominate FOE Oxalate and B1 – FOE Sulfonic acid.

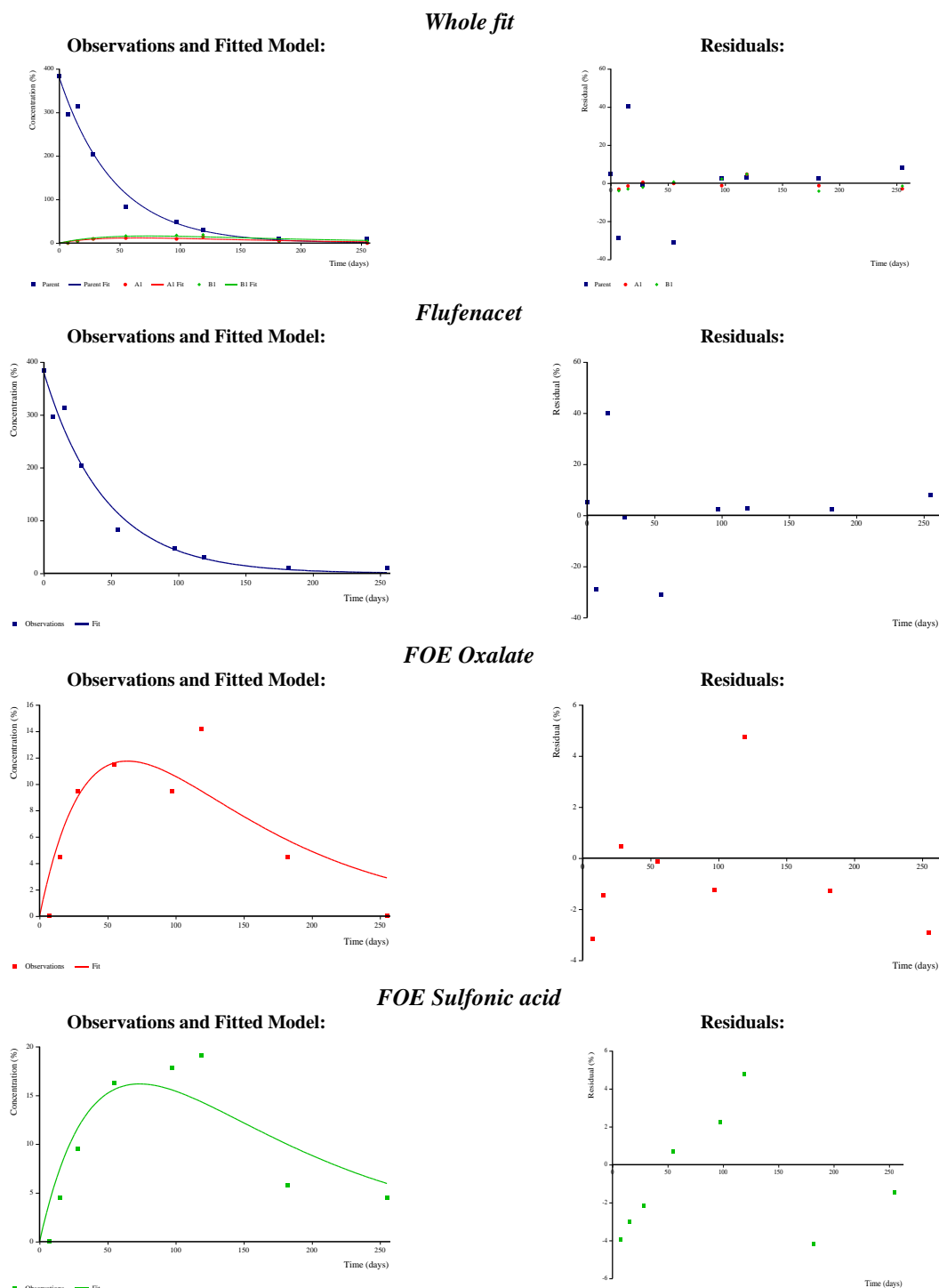


Figure B.8.1.1.2.2.1._CA-67: The graphical results of the kinetic examination of the data for Flufenacet and FOE Sulfonic acid obtained in the trial Laudun, 30251/1.

Table B.8.1.1.2.2.1._CA-92: The numerical results of the kinetic examination of the data for Flufenacet, FOE Oxalate and FOE Sulfonic acid obtained in the trial Laudun, 30251/1.

Compound	Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
			Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment
					Lower	Upper			
Flufenacet	SFO	M ₀	379.3	17.08	349.8	408.9	-----	10.3	0.9798; Acceptable fit
		k	0.02189	0.002458	0.01764	0.02614	1.65 E-8		
FOE Oxalate	SFO	M ₀	0.0	----	----	----	----	28.6	0.8631; Acceptable fit
		k	0.01047	0.003737	0.004007	0.01693	0.005696		
		ff	0.0609	0.01469	0.03549	0.08631	----		
FOE Sulfonic acid	SFO	M ₀	0.0	----	----	----	----	25.6	0.9141; Acceptable fit
		k	0.007746	0.002802	0.002901	0.01259	0.006172		
		ff	0.07534	0.01657	0.04669	0.104	----		

The kinetic endpoints derived from the study are presented below in the table B.8.1.1.2.2.1._CA-93.

Table B.8.1.1.2.2.1._CA-93: The kinetic endpoints determined in the experiment.

Determined parameter	Compound		
	Flufenacet	FOE Sulfonic acid	FOE Oxalate
DT ₅₀ [days]	31.7	89.5	66.2
DT ₉₀ [days]	105.0	297.0	220.0
Kinetic formation fraction ff	Not applicable	0.075 ± 0.003	0.061 ± 0.015
Precursor	Not applicable	Flufenacet	Flufenacet
Kinetic model	SFO	SFO	SFO

The kinetic fit obtained for Flufenacet may be classified as statistically and visually acceptable. Also the calculated kinetic parameters and derived from them kinetic endpoints are reliable.

The kinetic fits obtained for both FOE Oxalate and FOE Sulfonic acid cannot be considered acceptable. They display only intermediate conformity of the estimated kinetic curve with the experimental points and the residuals are not randomly distributed. In addition they are not fully statistically reliable – the χ^2 error for them both is well above 15%, reaching 28.6% for the fit FOE Oxalate and 25.6% for that for FOE Sulfonic acid.

As a result, it can be stated that in this trial it was possible to obtain reliable fit only for Flufenacet.

RMS performed also the fitting using the two other kinetic models for the parent compound (Flufenacet) – FOMC and DFOP. The kinetic fits for the parent compound were similar to those for the parent fitted alone and no improvement of the fit was observed for the degradation products – FOE Oxalate and FOE Sulfonic acid. Therefore it may be stated that the change of the kinetic model for parent compound will not result in better fitting. RMS decided to not present the results of those kinetic examinations in order to not overburden the Assessment Report.

Evaluation of the fitting exercise:

The presented above results of the kinetic examination of the data obtained in the trial **Laudun, 30251/1**, demonstrated that reliable fit and reliable kinetic endpoints representing persistence in soil under realistic – field conditions was obtained only for the parent compound – Flufenacet. The kinetic model identified as returning the best fit was SFO.

For the degradation products subjected to the kinetic examination – FOE Oxalate and FOE Sulfonic acid, it was not possible to obtain reliable kinetic fit and hence reliable kinetic endpoints representing the persistence of that compound on the trial site.

As a result, it can be stated that the reliable persistence kinetic endpoints for that trial may be determined for the parent compound – Flufenacet, when fitted alone. These values will be presented in the List of End Points.

8) Results of the kinetic examination of the data obtained for the trial *St. Etienne du Gres, 30253/8, South France* (Study No. 107724, [Sommer; 1995]):

The analysis for this data-set was a two-step analysis. Its results are presented below, individually for each step.

a) Results obtained at **Step 1** – fitting of the data for the parent compound (Flufenacet) alone:

The results of the kinetic analysis are presented below, in graphical form on figure B.8.1.1.2.2.1_CA-68 and in numerical form in the table B.8.1.1.2.2.1_CA-94. Additionally the table B.8.1.1.2.2.1_CA-95 provides the kinetic endpoints obtained with each of the kinetic models tested.

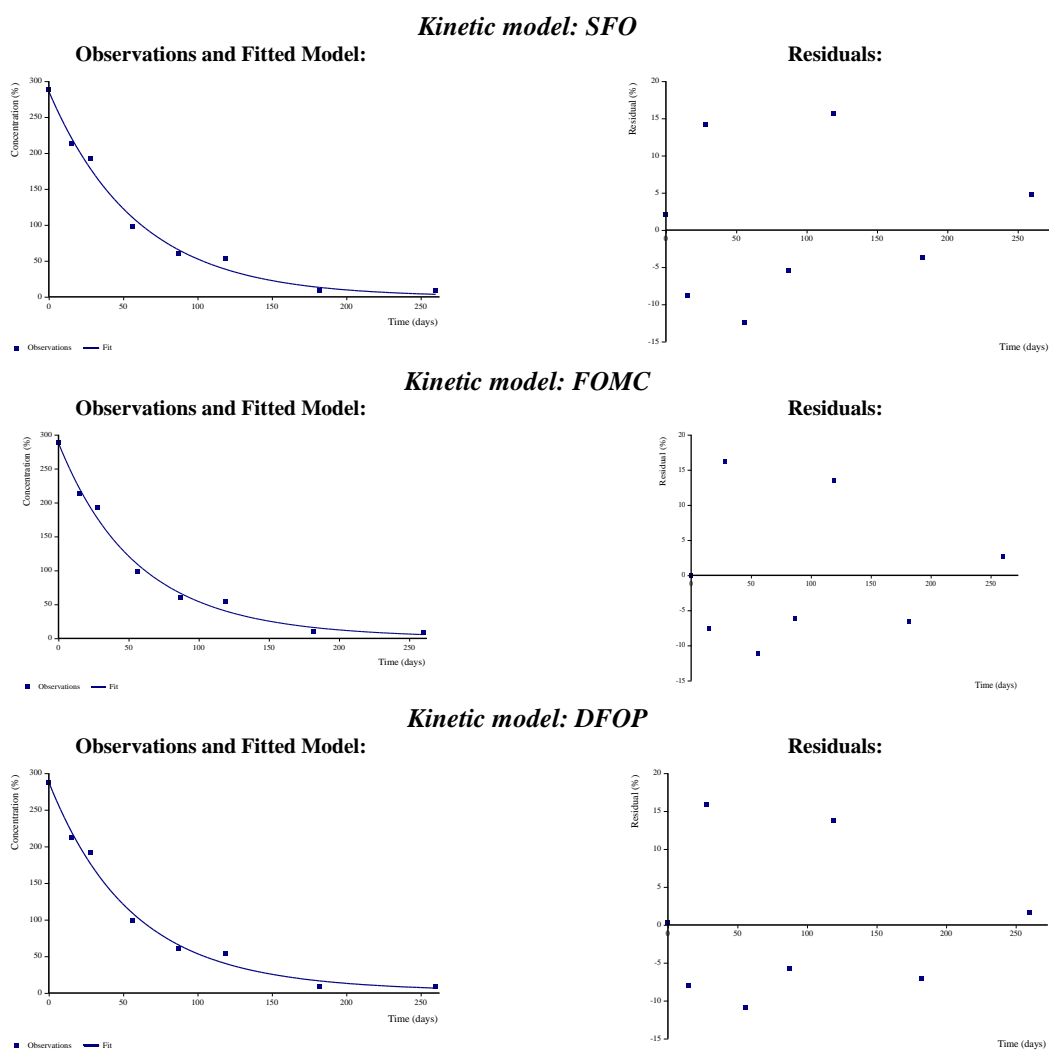


Figure B.8.1.1.2.2.1_CA-68: The graphical results of the kinetic analysis.

Table B.8.1.1.2.2.1._CA-94: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment
				Lower	Upper			
SFO	M_0	285.9	9.279	267.9	303.9	-----	6.68	0.9902; Good fit
	k	0.01691	0.001191	0.0146	0.01923	3.81 E-6		
FOMC	M_0	288.0	11.1	265.6	310.3	-----	6.97	0.9904; Good fit
	α	11.85	26.16	-40.86	64.56	-----		
	β	660.	1550.0	-2455.0	3780.0	-----		
DFOP	M_0	287.7	12.59	160.9	314.6	-----	7.51	0.9905; Good fit
	k_1	0.01901	0.01755	-0.0184	0.05642	0.1698		
	k_2	0.007222	0.052887	-0.1055	0.1200	0.4490		
	g	0.8899	1.563	-2.443	4.222	not given		

Table B.8.1.1.2.2.1._CA-95: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested		
		SFO	FOMC	DFOP
Flufenacet	DT ₅₀ [days]	41.0	39.8	39.8
	DT ₉₀ [days]	136.0	142.0	142.0

All three models returned visually and statistically good fits. Of the three SFO fit was superior, although they were all very similar.

However, neither FOMC nor DFOP fits may be considered acceptable because of the lack of reliability of the kinetic parameters they returned. In case of FOMC for both α and β the CI passes through zero. In case of DFOP fit for k_1 and k_2 the $prob > t$ was significantly higher than 0.1.

Only SFO returned visually and statistically acceptable fit with fully reliable kinetic parameters, hence it should be considered as the best-fit model for the parent compound – Flufenacet and as such was used at the next stage of analysis.

- b) Results obtained at **Step 2** – fitting of the data for the parent compound (Flufenacet) and its degradation products:

The results of the kinetic analysis are presented below, in graphical form on figure B.8.1.1.2.2.1._CA-69 and in numerical form in the table B.8.1.1.2.2.1._CA-96. The fitting was performed for combination SFO-SFO.

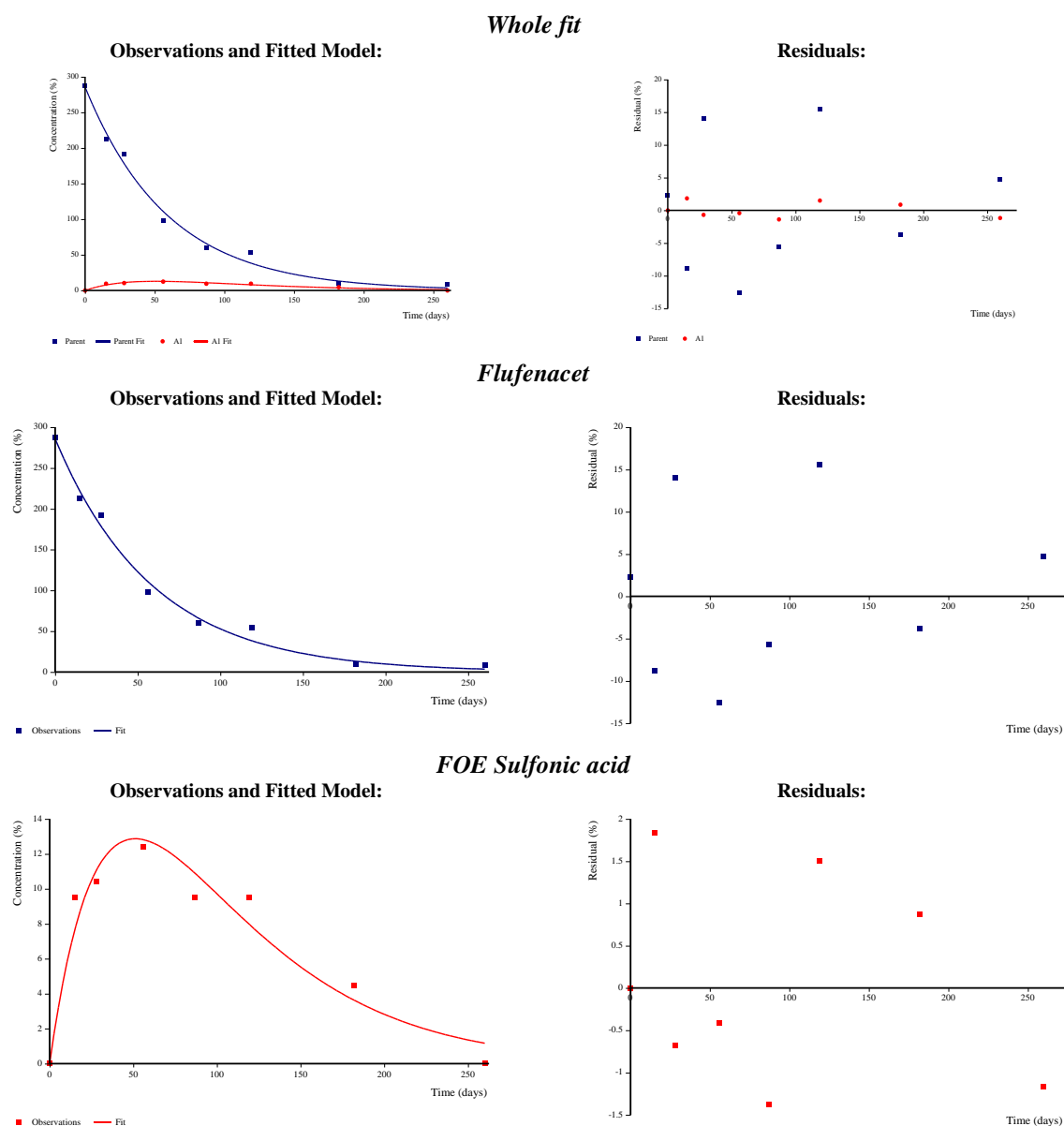


Figure B.8.1.1.2.2.1._CA-69: The graphical results of the kinetic examination of the data for Flufenacet and FOE Sulfonic acid obtained in the trial St. Etienne du Gres, 30253/8.

Table B.8.1.1.2.2.1._CA-96: The numerical results of the kinetic examination of the data for Flufenacet and FOE Sulfonic acid obtained in the trial St. Etienne du Gres, 30253/8.

Compound	Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
			Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment
					Lower	Upper			
Flufenacet	SFO	M ₀	285.7	9.682	268.3	303.1	-----	6.68	0.9902; Good fit
		k	0.01687	0.001239	0.01465	0.01910	1.58 E-8		
FOE Sulfonic acid	SFO	M ₀	0.0	-----	-----	-----	-----	12.1	0.9379; Good fit
		k	0.02249	0.003981	0.01534	0.02964	7.46 E-5		
		ff	0.1423	0.02255	0.1018	0.1828	-----		

The kinetic endpoints derived from the study are presented below in the table B.8.1.1.2.2.1._CA-97.

Table B.8.1.1.2.2.1._CA-97: The kinetic endpoints determined in the experiment.

Determined parameter	Compound	
	Flufenacet	FOE Sulfonic acid
DT ₅₀ [days]	41.1	30.8
DT ₉₀ [days]	137.0	102.0
Kinetic formation fraction ff	Not applicable – parent compound	0.1423 ± 0.023
Precursor	Not applicable – parent compound	Flufenacet
Kinetic model	SFO	SFO

The kinetic fit obtained for Flufenacet may be classified as statistically and visually acceptable. Also the calculated kinetic parameters and derived from them kinetic endpoints are reliable.

The kinetic fit obtained for FOE Sulfonic acid can also be considered acceptable. It displays good conformity of the estimated kinetic curve with the experimental points and low, randomly distributed residuals. It is also statistically reliable – the χ^2 error for it is below 15% (12.1%). Finally, for both compounds the determined kinetic parameters, and hence kinetic endpoints, are fully reliable.

As a result, it can be stated that in that trial it was possible to obtain reliable fits for Flufenacet and FOE Sulfonic acid using a combination SFO-SFO.

RMS performed also the fitting using the two other kinetic models for the parent compound (Flufenacet) – FOMC and DFOP. The kinetic fits for the parent compound were very similar to those for the parent fitted alone and no improvement of the fit was observed for the degradation product – FOE Sulfonic acid. Therefore it may be stated that the change of the kinetic model for parent compound will not result in better fitting. RMS decided to not present the results of those kinetic examinations in order to not overburden the Assessment Report.

Evaluation of the fitting exercise:

The presented above results of the kinetic examination of the data obtained in the trial **St. Etienne du Gres, 30253/8**, demonstrated that reliable fit, and hence reliable kinetic endpoints representing persistence in soil under realistic – field conditions, was obtained for both parent compound – Flufenacet, and its degradation product – FOE Sulfonic acid, when the combination of the kinetic models SFO-SFO was used. The kinetic endpoints resulting from this kinetic assessment will be presented in the List of End Points as persistence kinetic endpoints for Flufenacet and FOE Sulfonic acid in the trial **St. Etienne du Gres, 30253/8**.

9) Results of the kinetic examination of the data obtained for the trial *Burscheid, 30499/9, Germany* (Study No 107722, [Sommer; 1995a]):

The analysis for this data-set was a single step analysis. That was due to the fact that from that data base only the values for Flufenacet could be derived. The results of the kinetic analysis are presented below, in graphical form on figure B.8.1.1.2.2.1_CA-70 and in numerical form in the table B.8.1.1.2.2.1_CA-98. Additionally the table B.8.1.1.2.2.1_CA-99 provides the kinetic endpoints obtained with each of the kinetic models tested.

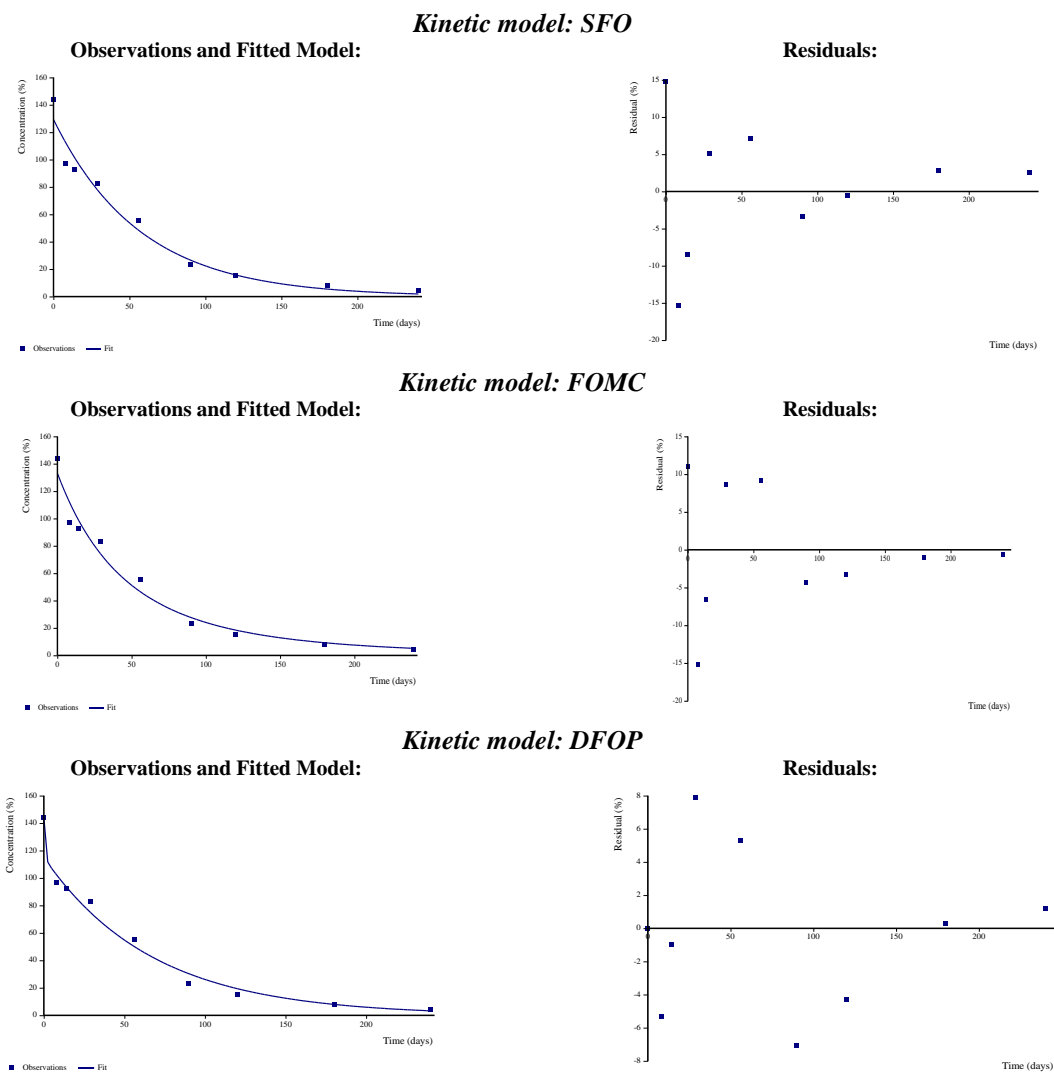


Figure B.8.1.1.2.2.1_CA-70: The graphical results of the kinetic analysis.

Table B.8.1.1.2.2.1._CA-98: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment
				Lower	Upper			
SFO	M_0	129.4	6.807	116.5	142.3	-----	11.5	0.9674; Acceptable fit
	k	0.01755	0.002294	0.0132	0.02189	6.06 E-5		
FOMC	M_0	133.1	8.538	116.5	149.7	-----	11.7	0.9695; Acceptable fit
	α	3.64	4.452	-5.011	12.29	-----		
	β	166.7	246.9	-313.1	646.7	-----		
DFOP	M_0	144.2	6.141	131.8	156.6	-----	7.11	0.9902; Good fit
	k_1	1.501	0.5315	0.4301	2.572	0.01846		
	k_2	0.01481	0.001467	0.011861	0.01777	8.15 E-5		
	g	0.2025	0.05184	0.09802	0.3069	not given		

Table B.8.1.1.2.2.1._CA-99: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested		
		SFO	FOMC	DFOP
Flufenacet	DT ₅₀ [days]	39.5	35.0	31.5
	DT ₉₀ [days]	131.0	147.0	140.0

The examination of the results showed that all three kinetic models returned visually and statistically acceptable fits, very similar one to another. Of them the best fit was obtained using DFOP model, which additionally returned fully reliable kinetic parameters. SFO and FOMC were statistically worse, both having χ^2 error slightly above 11%. Also for these two models the residuals were higher than those for DFOP fit, although their distribution was very similar for all three models tested.

Finally it shall be noted that while for SFO and DFOP the determined kinetic parameters were reliable, these were not for FOMC model – for both α and β the CI passes through zero, rendering them not reliable.

As a result it shall be stated that for that trial DFOP kinetic model returned the best kinetic fit for Flufenacet.

Evaluation of the fitting exercise:

The presented above results of the kinetic examination of the data obtained in the trial **Burscheid, 30499/9**, demonstrated that for that trial DFOP shall be considered as the best-fit model for Flufenacet. The results of the fitting – the determined kinetic endpoints, will be presented in the List of End Points.

The kinetic analysis for the degradation products – FOE Alcohol, FOE Oxalate and FOE Sulfonic acid, was not performed for this trial due to the lack of the suitable data base for any of them.

10) Results of the kinetic examination of the data obtained for the trial *Monheim, 30500/6, Germany* (Study No. 107722, [Sommer; 1995a]):

The analysis for this data-set was a single step analysis. That was due to the fact that from that data base only the values for Flufenacet could be derived. The results of the kinetic analysis are presented below, in graphical form on figure B.8.1.1.2.2.1._CA-71 and in numerical form in the table B.8.1.1.2.2.1._CA-100. Additionally the table B.8.1.1.2.2.1._CA-101 provides the kinetic endpoints obtained with each of the kinetic models tested.

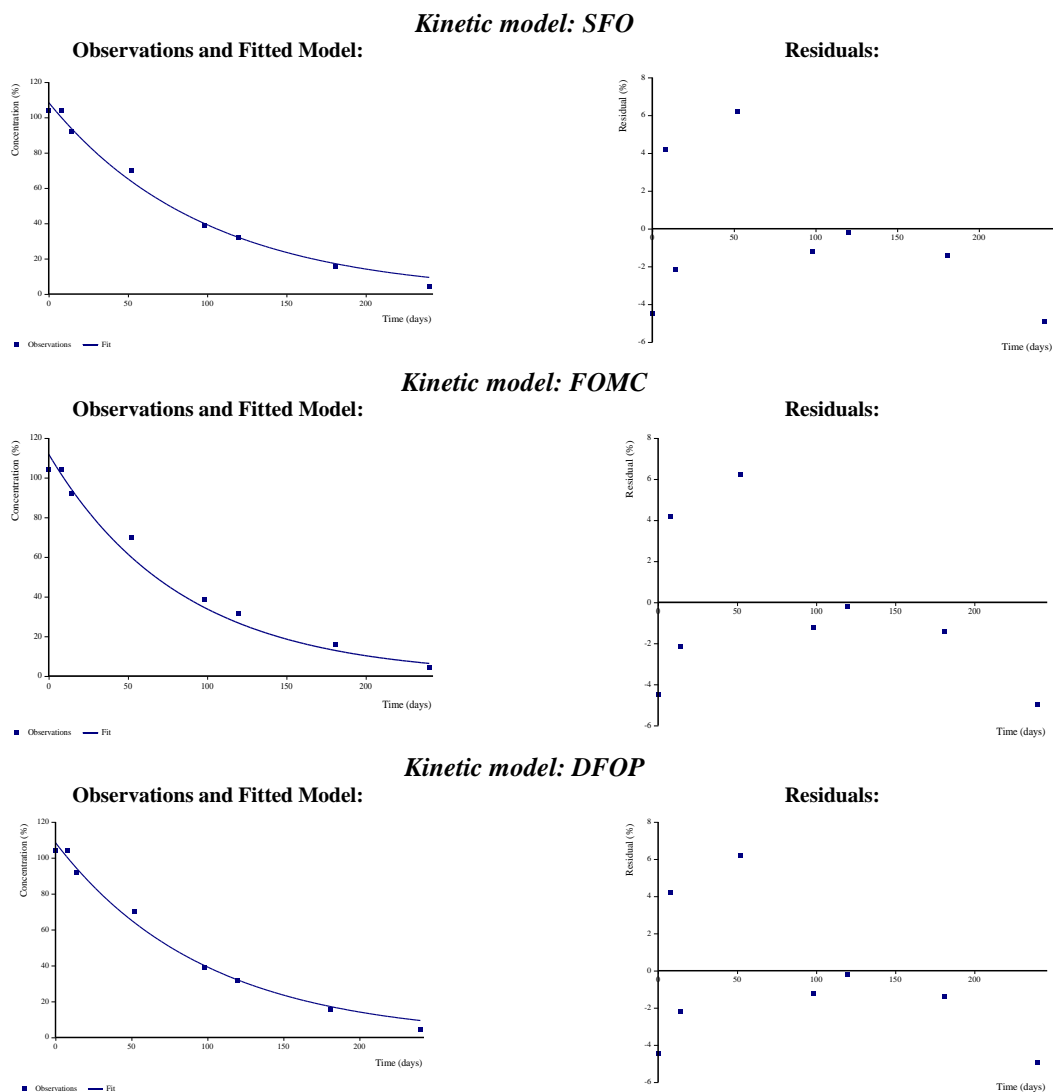


Figure B.8.1.1.2.2.1._CA-71: The graphical results of the kinetic analysis.

Table B.8.1.1.2.2.1._CA-100: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment
				Lower	Upper			
SFO	M_0	108.5	2.782	103.1	113.9	-----	5.1	0.991; Good fit
	k	0.01017	6.52 E-4	0.008908	0.01144	2.19 E-6		
FOMC	M_0	111.8	4.501	102.8	120.9	-----	5.46	0.9909; Acceptable fit
	α	310.9	612.6	-923.4	1550	-----		
	β	26000	59300	-93500	146000	-----		
DFOP	M_0	108.5	4.847	98.14	118.8	-----	5.87	0.991; Good fit
	k_1	0.01017	1480	-3144	3140	0.5		
	k_2	0.01017	32.06	-68.33	68.35	0.4999		
	g	0.0332	2.551	-5.107	5.174	not given		

Table B.8.1.1.2.2.1._CA-101: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested		
		SFO	FOMC	DFOP
Flufenacet	DT ₅₀ [days]	68.1	57.9	68.1
	DT ₉₀ [days]	226.0	193.0	226.0

The examination of the results showed that all three kinetic models returned visually acceptable and statistically reliable – for all three models the χ^2 error was well <15%. It was stated that of the three SFO returned superior fit, although the differences between the fits were minimal.

DFOP cannot be considered acceptable, because it returned not reliable kinetic parameters. It was noted that for that kinetic model the rate constants k_1 and k_2 were equal. Moreover, they were equal to the rate constant k determined using SFO model.

Also FOMC did not return reliable kinetic parameters – for both α and β the CI contained zero. RMS noted that the DT₉₀ determined for FOMC model was shorter than that for SFO or DFOP, what additionally puts into doubt the problem of whether the FOMC model adequately describes the kinetic behaviour of Flufenacet in the evaluated trial.

As a result SFO was identified as kinetic model returning the best fit for this trial.

Evaluation of the fitting exercise:

The presented above results of the kinetic examination of the data obtained in the trial **Monheim, 30500/6**, demonstrated that for that trial SFO shall be considered as the best-fit model for Flufenacet. The results of the fitting – the determined kinetic endpoints, will be presented in the List of End Points.

The kinetic analysis for the degradation products – FOE Alcohol, FOE Oxalate and FOE Sulfonic acid, was not performed for this trial due to the lack of the suitable data base for any of them.

11) Results of the kinetic examination of the data obtained for the trial *Saussay-la-Campagne, 30254/6, South France* (Study No. 107723, [Sommer; 1995b]):

The analysis for this data-set was a single step analysis. That was due to the fact that from that data base only the values for Flufenacet could be derived. The results of the kinetic analysis are presented below, in graphical form on figure B.8.1.1.2.2.1._CA-72 and in numerical form in the table B.8.1.1.2.2.1._CA-102. Additionally the table B.8.1.1.2.2.1._CA-103 provides the kinetic endpoints obtained with each of the kinetic models tested.

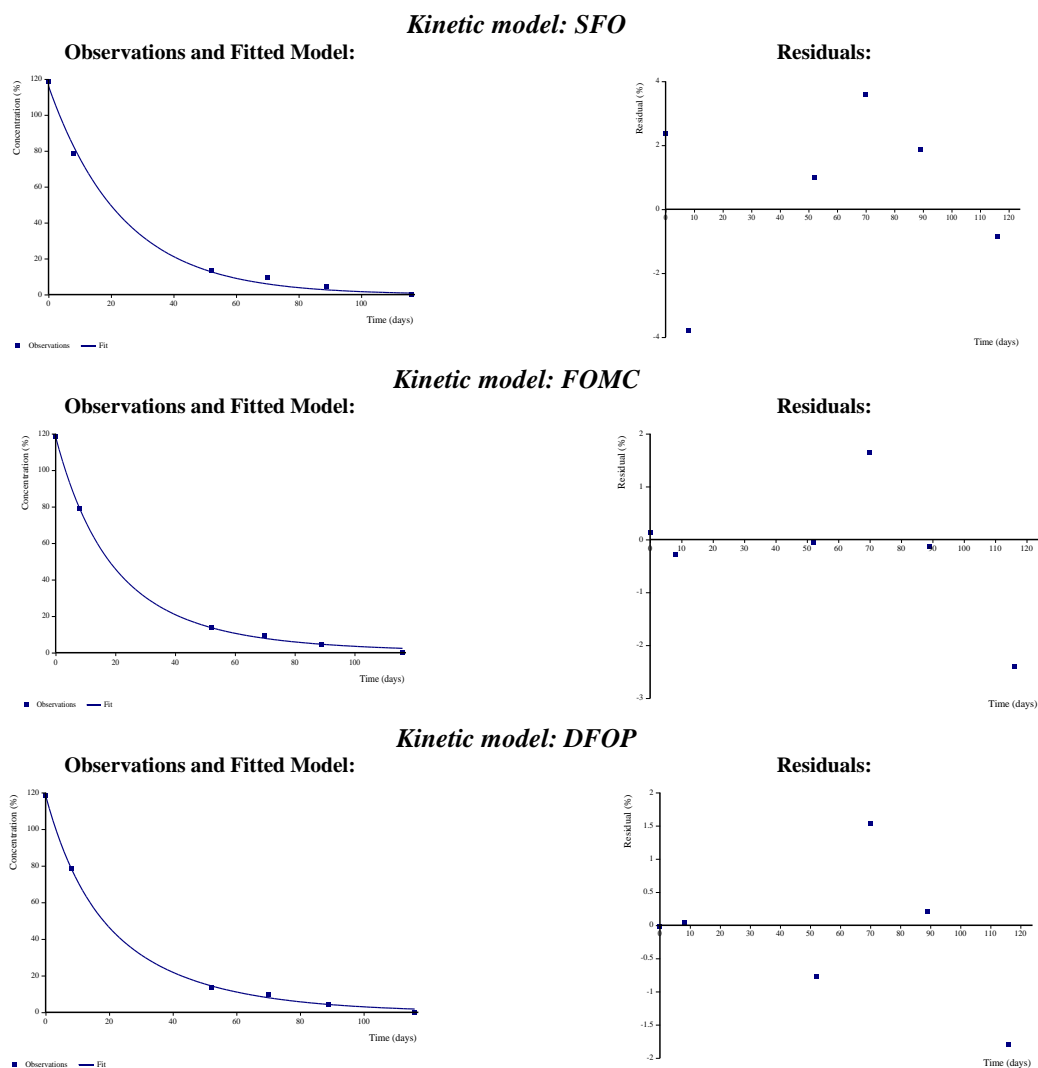


Figure B.8.1.1.2.2.1._CA-72: The graphical results of the kinetic analysis.

Table B.8.1.1.2.2.1._CA-102: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment
				Lower	Upper			
SFO	M_0	116.0	2.775	110.1	122.0	-----	5.33	0.9973; Good fit
	k	0.04253	0.00325	0.0356	0.04946	9.85 E-5		
FOMC	M_0	118.3	1.68	114.3	122.2	-----	2.79	0.9648; Good fit
	α	4.673	1.459	1.238	8.108	-----		
	β	88.96	33.43	10.28	167.6	-----		
DFOP	M_0	118.4	1.76	113.3	123.6	-----	2.71	0.9995; Good fit
	k_1	0.0933	0.07921	-0.138	0.3246	0.180		
	k_2	0.03229	0.0112	-0.00042	0.06501	0.05111		
	g	0.3595	0.4998	-1.100	1.819	not given		

Table B.8.1.1.2.2.1._CA-103: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested		
		SFO	FOMC	DFOP
Flufenacet	DT ₅₀ [days]	16.3	14.2	14.2
	DT ₉₀ [days]	54.1	56.7	58.0

The examination of the results showed that all three kinetic models returned visually and statistically good fits, very similar one to another. Of the three kinetic models used the best fit was obtained for FOMC model. In addition, SFO and FOMC returned fully reliable kinetic parameters, while in case of DFOP fit the *prob* > *t* value was above 0.05 for both k_1 and k_2 , in case k_2 , surpassing that level very slightly, but in case of k_1 being higher than 0.1. For that reason the DFOP fit cannot be considered acceptable.

As a result, RMS decided to indicate the FOMC model as returning the best fit for Flufenacet in this trial. At the same time it shall be pointed out that the quality of the SFO fit, comparable to FOMC fit, enables to indicate that fit as providing an accurate estimation of persistence of Flufenacet in the trial **Saussay-la-Campagne, 30254/6**, thus avoiding the would-be overparametrisation in case of the selection of the endpoints from that trial in the exposure assessment.

Evaluation of the fitting exercise:

The presented above results of the kinetic examination of the data obtained in the trial **Saussay-la-Campagne, 30254/6**, demonstrated that reliable fit and reliable kinetic endpoints representing persistence in soil under realistic – field, conditions for flufenacet was obtained with FOMC kinetic model. These values will be presented in the List of End Points.

At the same time it shall be indicated that the fit obtained using SFO model was of the comparable quality, therefore it may be also considered as an adequate representation of the persistence of Flufenacet in that trial.

The kinetic analysis for the degradation products – FOE Alcohol, FOE Oxalate and FOE Sulfonic acid, was not performed for this trial due to the lack of the suitable data base for any of them.

12) Results of the kinetic examination of the data obtained for the trial *Fresne-L'Archeveque, 30455/7, North France* (Study No. 107723, [Sommer; 1995b]):

The analysis for this data-set was a single step analysis. That was due to the fact that from that data base only the values for Flufenacet could be derived. The results of the kinetic analysis are presented below, in graphical form on figure B.8.1.1.2.2.1._CA-73 and in numerical form in the table B.8.1.1.2.2.1._CA-104. Additionally the table B.8.1.1.2.2.1._CA-105 provides the kinetic endpoints obtained with each of the kinetic models tested.

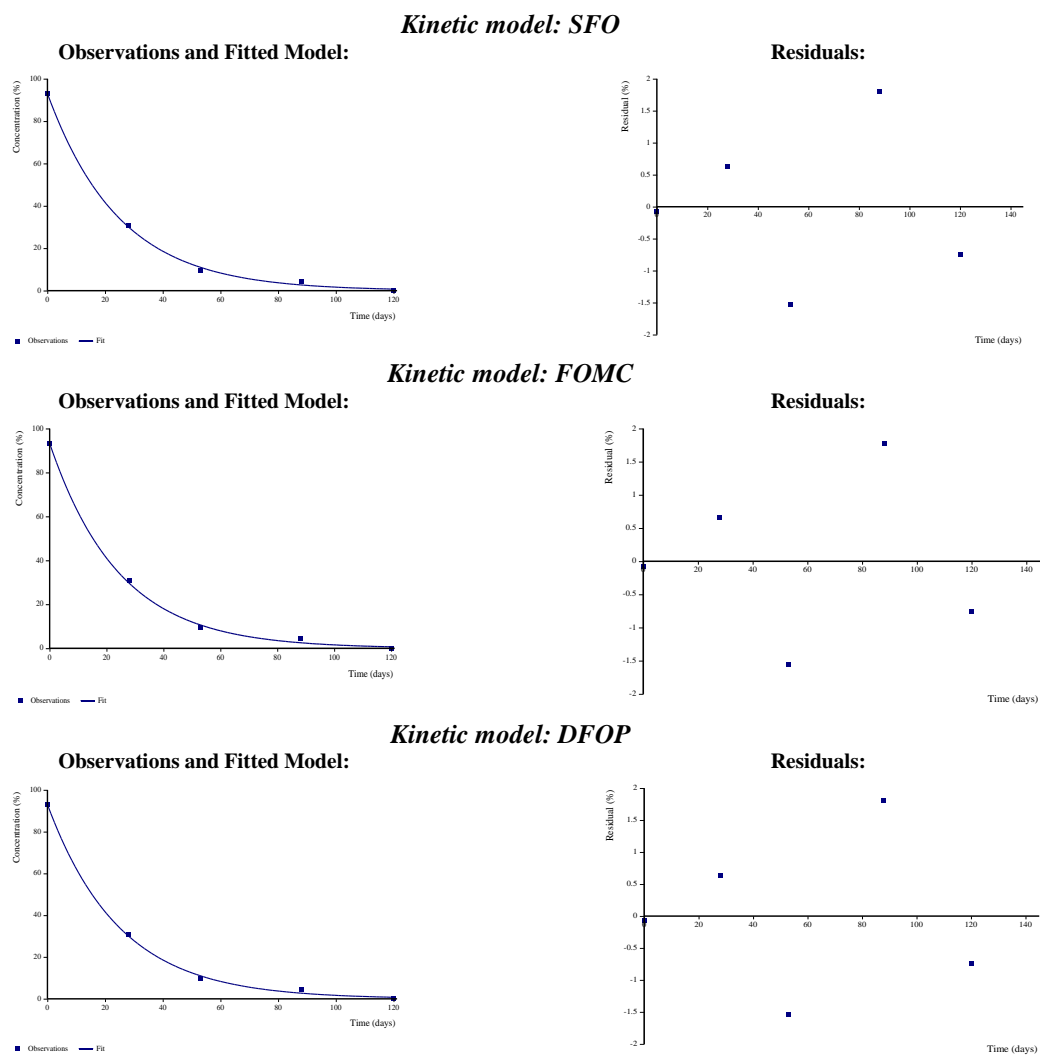


Figure B.8.1.1.2.2.1._CA-73: The graphical results of the kinetic analysis.

Table B.8.1.1.2.2.1._CA-104: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment
				Lower	Upper			
SFO	M_0	93.07	1.471	89.61	96.53	-----	3.32	0.9989; Good fit
	k	0.04024	0.001471	0.03677	0.0437	5.36 E-5		
FOMC	M_0	93.32	1.892	87.8	98.84	-----	3.8	0.9989; Good fit
	α	64.32	Not determined	Not determined	Not determined	-----		
	β	3040	Not determined	Not determined	Not determined	-----		
DFOP	M_0	93.07	2.547	76.99	109.2	-----	4.74	0.9989; Good fit
	k_1	0.04024	0.002465	0.02467	0.0558	0.01947		
	k_2	0.04024	0.002619	0.0237	0.05677	0.02069		
	g	0.5086	Not determined	Not determined	Not determined	Not determined		

Table B.8.1.1.2.2.1._CA-105: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested		
		SFO	FOMC	DFOP
Flufenacet	DT ₅₀ [days]	17.2	16.9	17.2
	DT ₉₀ [days]	57.2	56.2	57.2

The examination of the results showed that all three kinetic models returned visually and statistically good fits, all three practically identical. RMS noted that the statistical evaluation of the kinetic parameters was provided for SFO and DFOP fits, while in case of FOMC fit the modelling tool did not return the values. That was due to the fact that, according to the comment provided in the report generated by the tool, it was not possible to create the covariance matrix.

In case of DFOP fit the k_1 and k_2 values were identical and they were the same as the rate constant k determined for SFO model. The $prob > t$ values calculated for them indicated that they were reliable (in both cases they were lower than the threshold value of 0.05). In case of the g value its statistical evaluation was not provided by the model, for the same reason as given above for the kinetic parameters determined in FOMC fit. It shall be also indicated that the value was very close to 0.5, indicating that the would-be amounts of the compound degrading in the compartment at rate k_1 and in that at rate k_2 are almost even.

That in turn indicated that for that trial site the SFO is the only kinetic model adequately describing the persistence of Flufenacet.

Evaluation of the fitting exercise:

The presented above results of the kinetic examination of the data obtained in the trial **Fresne-L'Archeveque, 30455/7**, demonstrated that for that trial SFO shall be considered as the best-fit model for Flufenacet. The results of the fitting – the determined kinetic endpoints, will be presented in the List of End Points.

The kinetic analysis for the degradation products – FOE Alcohol, FOE Oxalate and FOE Sulfonic acid, was not performed for this trial due to the lack of the suitable data base for any of them.

13) Results of the kinetic examination of the data obtained for the trial *Laudun, 40163/3, South France* (Study No. 107721, [Sommer; 1995c]):

The analysis for this data-set was a two-step analysis. Its results are presented below, individually for each step.

a) Results obtained at **Step 1** – fitting of the data for the parent compound (Flufenacet) alone:

The results of the kinetic analysis are presented below, in graphical form on figure B.8.1.1.2.2.1._CA-74 and in numerical form in the table B.8.1.1.2.2.1._CA-106. Additionally the table B.8.1.1.2.2.1._CA-107 provides the kinetic endpoints obtained with each of the kinetic models tested.

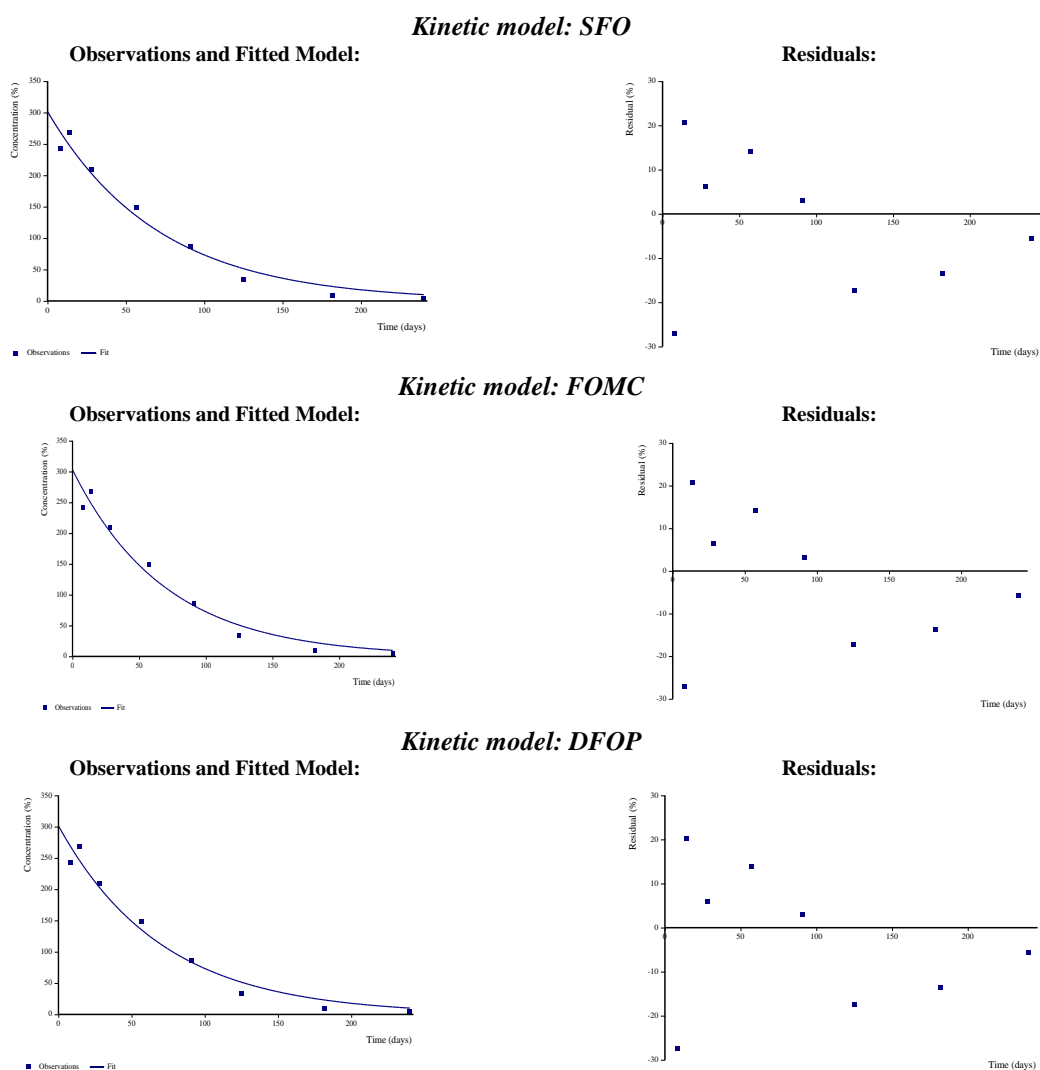


Figure B.8.1.1.2.2.1._CA-74: The graphical results of the kinetic analysis.

Table B.8.1.1.2.2.1._CA-106: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment
				Lower	Upper			
SFO	M_0	301.6	16.51	269.5	333.7	-----	9.86	0.9774; Acceptable fit
	k	0.01451	0.001628	0.01099	0.01731	6.40 E-5		
FOMC	M_0	302.9	17.63	267.4	338.4	-----	10.6	0.9773; Acceptable fit
	α	257.4	53.15	150.3	364.5	-----		
	β	17900	3110	11700	24200	-----		
DFOP	M_0	301.6	19.51	260.0	343.2	-----	11.3	0.9774; Acceptable fit
	k_1	0.1081	Not determined	Not determined	Not determined	Not determined		
	k_2	0.01451	0.001834	0.01024	0.01806	7.59 E-4		
	g	4.47 E-9	1.10 E-4	-0.000235	0.000235	not given		

Table B.8.1.1.2.2.1._CA-107: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested		
		SFO	FOMC	DFOP
Flufenacet	DT ₅₀ [days]	49.0	48.4	49.0
	DT ₉₀ [days]	163.0	161.0	163.0

The examination of the results showed that all three kinetic models returned visually acceptable and statistically reliable fits – for all three models the χ^2 error was < 15%. It was stated that of the three SFO returned superior fit, although the differences between the fits were minimal.

DFOP cannot be considered acceptable, because it returned not reliable kinetic parameters. It was noted that for that kinetic model the rate constant k_1 was not statistically evaluated, what was due to the fact that it was not possible to create the covariance matrix. As for k_2 , it was equal to the rate constant k determined by the SFO model. Finally, the extremely low value of g – 4.47 E-9, indicated that the compound degraded in a single compartment. That indicated that SFO is a kinetic model most accurately describing the kinetic behaviour of Flufenacet in the evaluated trial.

FOMC returned fit visually almost identical to that obtained with SFO and statistically slightly worse. The determined kinetic parameters – α and β , were reliable, but very high. RMS noted that the DT₉₀ determined for FOMC model was shorter than that for SFO. That also indicates that FOMC is not appropriate kinetic model to characterise the kinetic behaviour of Flufenacet in the examined trial.

As a result SFO was identified as kinetic model returning the best fit for this trial and hence adequate to be used at the next stage of the assessment.

- b) Results obtained at **Step 2** – fitting of the data for the parent compound (Flufenacet) and its degradation products:

The results of the kinetic analysis are presented below, in graphical form on figure B.8.1.1.2.2.1._CA-75 and in numerical form in the table B.8.1.1.2.2.1._CA-108. The fitting was performed for combination SFO-SFO-SFO. In the modelling tool A1 was used to denominate FOE Oxalate and B1 – FOE Sulfonic acid.

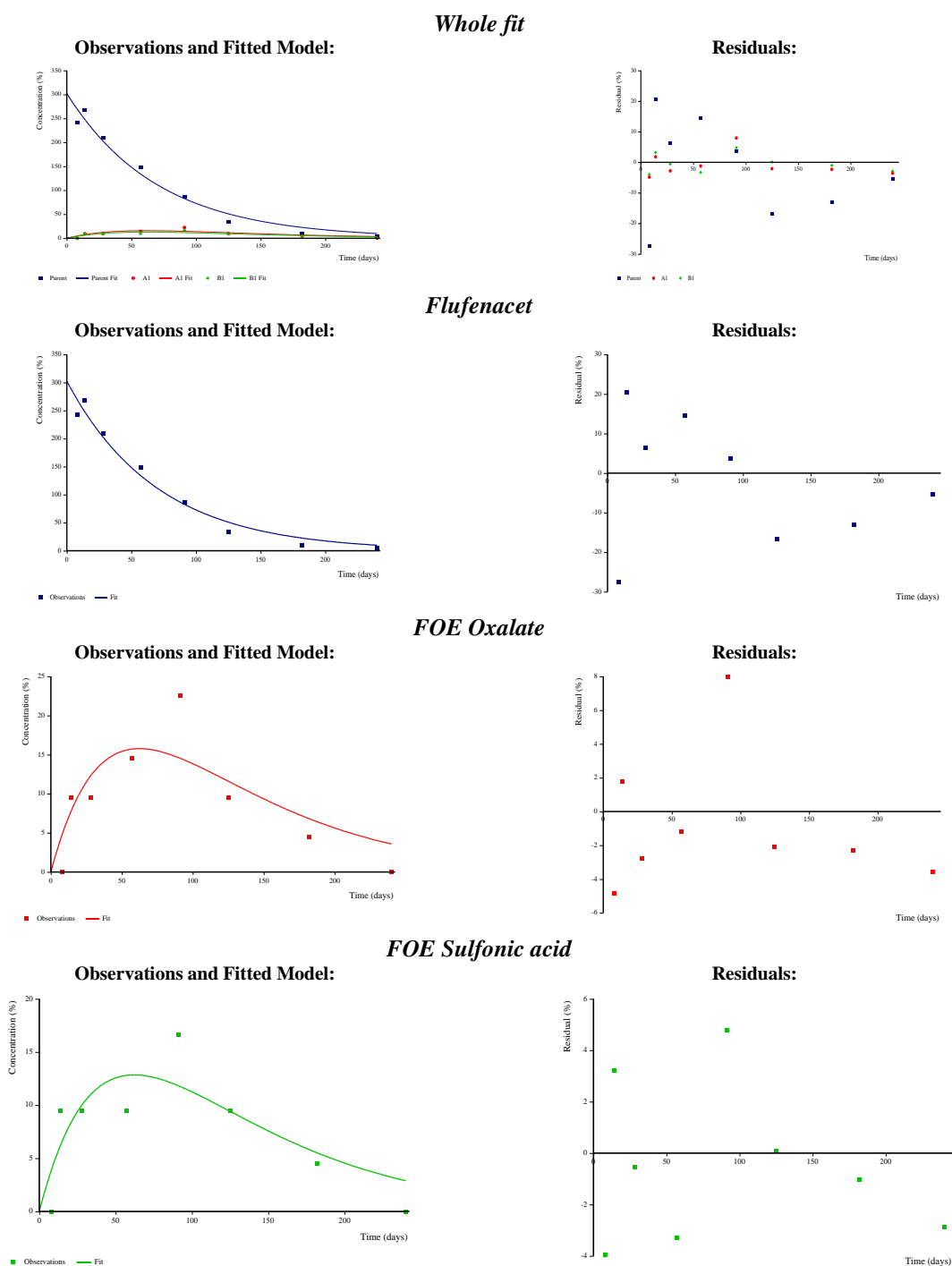


Figure B.8.1.1.2.2.1._CA-75: The graphical results of the kinetic examination of the data for Flufenacet, FOE Oxalate and FOE Sulfonic acid obtained in the trial Laudun, 40163/3.

Table B.8.1.1.2.2.1._CA-108: The numerical results of the kinetic examination of the data for Flufenacet, FOE Oxalate and FOE Sulfonic acid obtained in the trial Laudun, 40163/3.

Compound	Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
			Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment
					Lower	Upper			
Flufenacet	SFO	M ₀	302.3	16.56	273.5	331.0	-----	9.86	0.9772; Acceptable fit
		k	0.01424	0.001638	0.0114	0.01708	3.67 E-8		
FOE Oxalate	SFO	M ₀	0.0	----	----	----	----	35.6	0.7892; Acceptable fit
		k	0.01799	0.007525	0.004938	0.03104	0.01399		
		ff	0.1601	0.05435	0.06583	0.2543	----		
FOE Sulfonic acid	SFO	M ₀	0.0	----	----	----	----	31.8	0.732; Acceptable fit
		k	0.0181	0.007052	0.005867	0.03033	0.009719		
		ff	0.1309	0.04198	0.05808	0.2037	----		

The kinetic endpoints derived from the study are presented below in the table B.8.1.1.2.2.1._CA-109.

Table B.8.1.1.2.2.1._CA-109: The kinetic endpoints determined in the experiment.

Determined parameter	Compound		
	Flufenacet	FOE Sulfonic acid	FOE Oxalate
DT ₅₀ [days]	48.7	38.5	38.3
DT ₉₀ [days]	162.0	128.0	127.0
Kinetic formation fraction ff	Not applicable	0.160 ± 0.054	0.131 ± 0.042
Precursor	Not applicable	Flufenacet	Flufenacet
Kinetic model	SFO	SFO	SFO

The kinetic fit obtained for Flufenacet may be classified as statistically and visually acceptable. Also the calculated kinetic parameters and derived from them kinetic endpoints are reliable.

The kinetic fits obtained for both FOE Oxalate and FOE Sulfonic acid cannot be considered acceptable. They display only intermediate conformity of the estimated kinetic curve with the experimental points and the residuals are not randomly distributed. In addition they are not fully statistically reliable – the χ^2 error for them both is well above 15%, reaching 35.6% for the fit FOE Oxalate and 31.8% for that for FOE Sulfonic acid.

As a result, it can be stated that in this trial it was possible to obtain reliable fits only for Flufenacet.

RMS performed also the fitting using the two other kinetic models for the parent compound (Flufenacet) – FOMC and DFOP. The kinetic fits for the parent compound were similar to those for the parent fitted alone and no improvement of the fit was observed for the degradation products – FOE Oxalate and FOE Sulfonic acid. Therefore it may be stated that the change of the kinetic model for parent compound will not result in better fitting. RMS decided to not present the results of those kinetic examinations in order to not overburden the Assessment Report.

Evaluation of the fitting exercise:

The presented above results of the kinetic examination of the data obtained in the trial **Laudun, 40163/3**, demonstrated that reliable fit and reliable kinetic endpoints representing persistence in soil under realistic – field conditions was obtained only for the parent compound – Flufenacet. The kinetic model identified as returning the best fit was SFO.

For the degradation products subjected to the kinetic examination – FOE Oxalate and FOE Sulfonic acid, it was not possible to obtain reliable kinetic fit and hence reliable kinetic endpoints representing the persistence of that compound on the trial site.

As a result, it can be stated that the reliable persistence kinetic endpoints for that trial may be determined for the parent compound – Flufenacet, when fitted alone. These values will be presented in the List of End Points.

14) Results of the kinetic examination of the data obtained for the trial *St. Etienne du Gres, 40164/1, South France* (Study No. 107721, [Sommer; 1995c]):

The analysis for this data-set was a two-step analysis. Its results are presented below, individually for each step.

a) Results obtained at **Step 1** – fitting of the data for the parent compound (Flufenacet) alone:

The preliminary analysis of the data set used in the kinetic analysis resulted in the identification of the two possible outliers – DAT 14 and DAT 28. Due to the distribution of the preceding and following data points it was not possible to identify, on the basis of the simple assessment, which data point is an outlier. Therefore RMS decided to carry out the fitting exercise firstly using the whole data set, then repeating it for the data set with either DAT 14 or DAT 28 time point removed, compare the results and on that basis decide which of the data points is an outlier. The results are presented below. The fitting in each case was performed using all three models, in order not to bias the results by eliminating the models not providing the acceptable fit at the initial stage – when the kinetic examination was performed for the whole data set.

Results for the whole data set

The results of the kinetic analysis are presented below, in graphical form on figure B.8.1.1.2.2.1._CA-76 and in numerical form in the table B.8.1.1.2.2.1._CA-110. Additionally the table B.8.1.1.2.2.1._CA-111 provides the kinetic endpoints obtained with each of the kinetic models tested.

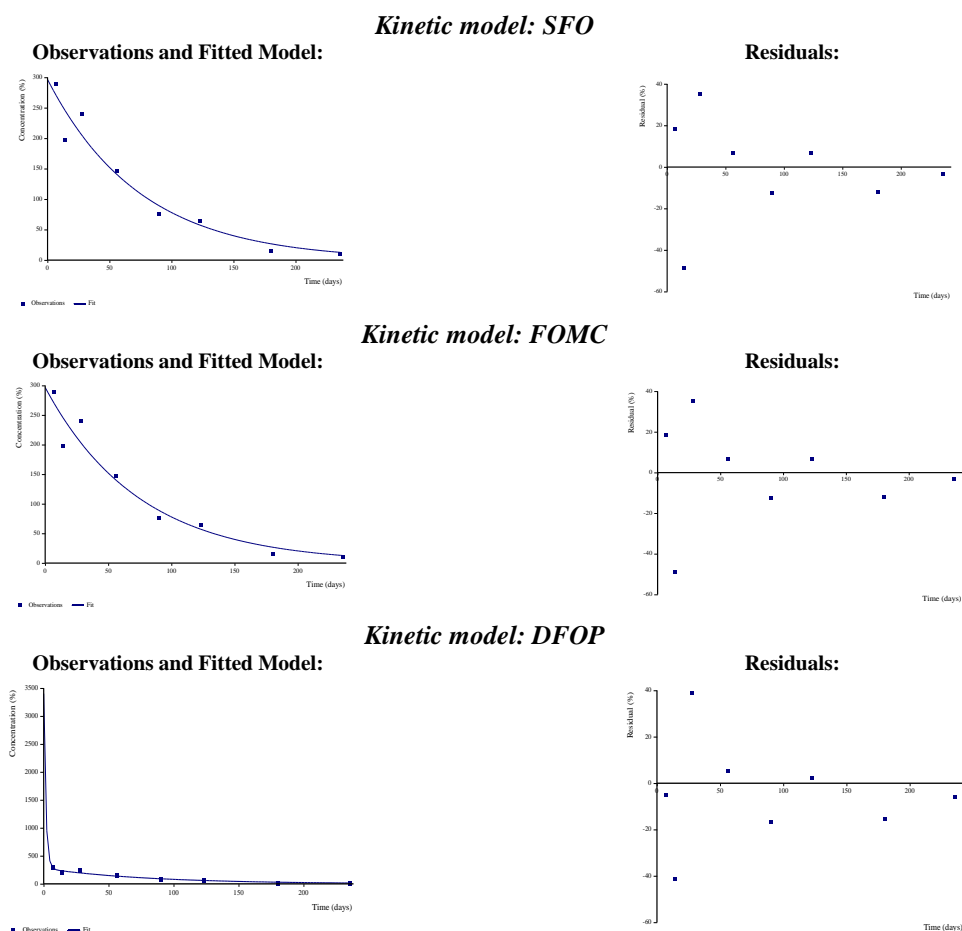


Figure B.8.1.1.2.2.1._CA-76: The graphical results of the kinetic analysis.

Table B.8.1.1.2.2.1._CA-110: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment
SFO	M_0	296.6	23.82	250.3	342.9	-----	14.4	0.9437; Acceptable fit
	k	0.01336	0.002282	0.008922	0.01779	5.49 E-4		
FOMC	M_0	296.8	25.73	245.0	348.7	-----	15.3	0.9436; Acceptable fit
	α	350.4	Not determined	Not determined	Not determined	-----		
	β	26100	Not determined	Not determined	Not determined	-----		
DFOP	M_0	3400	1510	191.2	6620	-----	15.5	0.9524; Poor fit
	k_1	0.6458	0.1827	0.2562	1.035	0.01207		
	k_2	0.01236	0.002589	0.006842	0.01788	0.004406		
	g	0.9188	0.03745	0.8389	0.9986	not given		

Table B.8.1.1.2.2.1._CA-111: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested		
		SFO	FOMC	DFOP
Flufenacet	DT ₅₀ [days]	51.9	51.8	1.21
	DT ₉₀ [days]	172.0	172.0	5.63

Only SFO model returned fit that can be classified as visually and statistically acceptable. In case of FOMC fit the shape of kinetic curve, its conformity to the experimental data and the distribution of the residuals are similar to the corresponding features of the SFO fit. However the fit cannot be considered acceptable due to the lack of any statistical evaluation of the kinetic parameters α and β . Additionally the χ^2 error is, slightly, higher than the threshold value – 15%. Finally, RMS noticed that the kinetic endpoints – DT₅₀ and DT₉₀ values, returned by the SFO and FOMC fits are the same.

In case of DFOP fit it was stated that it cannot be considered acceptable, because the visual fit is poor, despite the fact that the correlation coefficient $r = 0.9524$. The main reason for classifying it as such is abnormally high M_0 calculated by the modelling tool – 3400 [µg/kg soil], several times higher than the theoretical application rate. That not only significantly altered the shape of the kinetic curve in its initial stage, but also artificially caused its better conformity with the experimental data after the break point. The problems with fitting were reflected also in the calculated kinetic endpoints, which were very short and not represented the kinetic behaviour of the test compound.

As a result it can be stated that:

- the fitting showed already at that stage that neither FOMC nor DFOP are the kinetic models adequately describing the persistence of Flufenacet in this trial;
- the distribution of the data points in relation to the determined kinetic curve for SFO model, in combination with the residuals, seem to indicate that the DAT-14 point should be considered an outlier and removed from the data base.

Both hypotheses will be verified further down the report.

Results for the data set without DAT 14 time point

The results of the kinetic analysis are presented below, in graphical form on figure B.8.1.1.2.2.1._CA-77 and in numerical form in the table B.8.1.1.2.2.1._CA-112. Additionally the table B.8.1.1.2.2.1._CA-113 provides the kinetic endpoints obtained with each of the kinetic models tested.

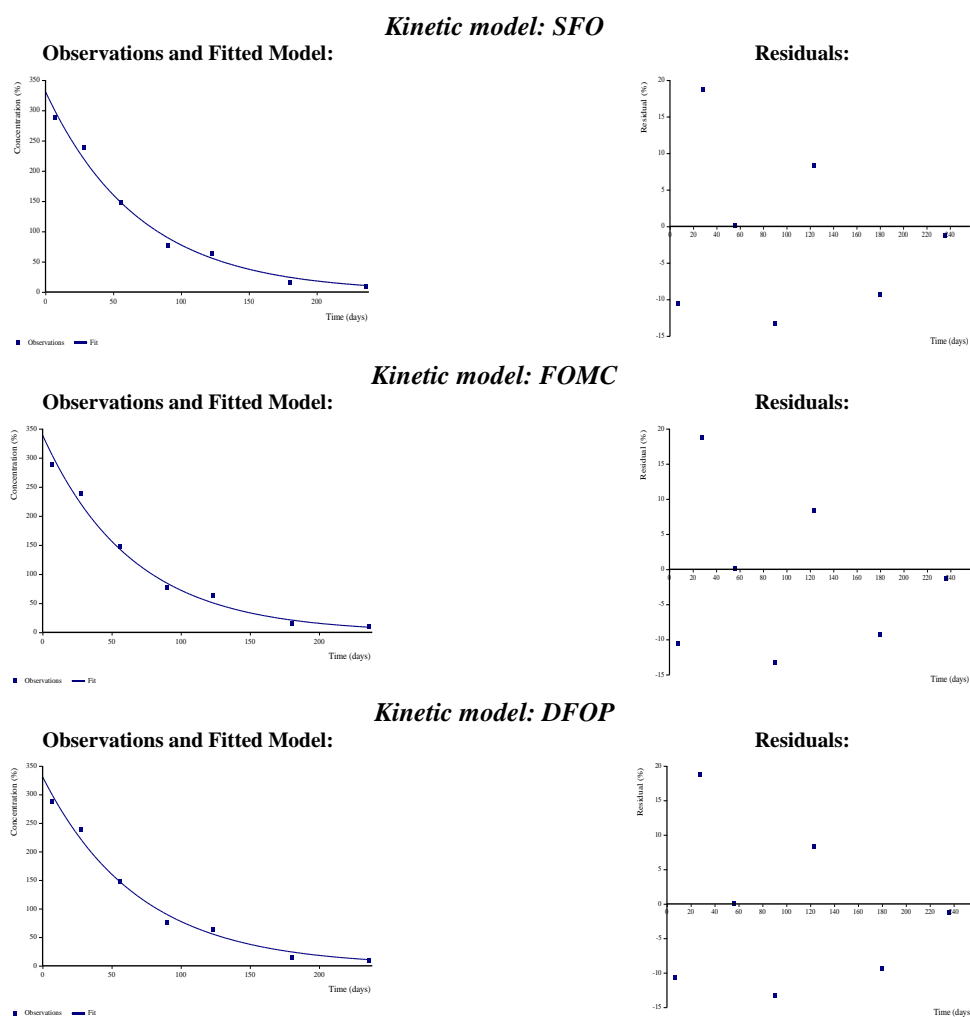


Figure B.8.1.1.2.2.1._CA-77: The graphical results of the kinetic analysis.

Table B.8.1.1.2.2.1._CA-112: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment
SFO	M_0	331.1	13.77	303.3	358.8	-----	7.08	0.9891; Good fit
	k	0.0145	0.001094	0.0123	0.01671	2.91 E-5		
FOMC	M_0	339.0	12.1	313.2	364.8	-----	7.64	0.9891; Good fit
	α	413.5	Not determined	Not determined	Not determined	-----		
	β	26700	Not determined	Not determined	Not determined	-----		
DFOP	M_0	331.1	23.27	276.3	385.8	-----	8.42	0.9905; Good fit
	k_1	0.0145	1900	-4468.0	4470.0	0.5000		
	k_2	0.0145	472.5	-1112.0	1110.0	0.5000		
	g	0.1992	31500	-74090	74100	not given		

Table B.8.1.1.2.2.1._CA-113: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested		
		SFO	FOMC	DFOP
Flufenacet	DT ₅₀ [days]	47.8	44.9	47.8
	DT ₉₀ [days]	159.0	149.0	159.0

The removal of DAT-14 time point resulted in general improvement of all three fits, which became visually good and statistically reliable.

However, as it was in case of the whole data set, neither FOMC nor DFOP fits may be considered acceptable because of the lack of reliability of the kinetic parameters they returned. In case of FOMC the statistical evaluation of α and β was not provided, while for DFOP fit for k_1 and k_2 the $prob > t$ was significantly higher than 0.1. It was also noted that the values k_1 and k_2 were the same and that they were identical to the rate constant k determined using SFO kinetic model.

As a result it was stated that:

- the removal of DAT-14 time point substantially improved the fitting results for all three models, what may conform that this data point is an outlier not to be take into consideration in the kinetic analysis;
- both FOMC and DFOP fits cannot be considered acceptable because of the lack of reliability of the kinetic parameters determined for them, so SFO shall be, as previously considered a sole kinetic model adequately characterising the persistence of Flufenacet in soil of the trial site.

Results for the data set without DAT 28 time point:

The results of the kinetic analysis are presented below, in graphical form on figure B.8.1.1.2.2.1._CA-78 and in numerical form in the table B.8.1.1.2.2.1._CA-114. Additionally the table B.8.1.1.2.2.1._CA-115 provides the kinetic endpoints obtained with each of the kinetic models tested.

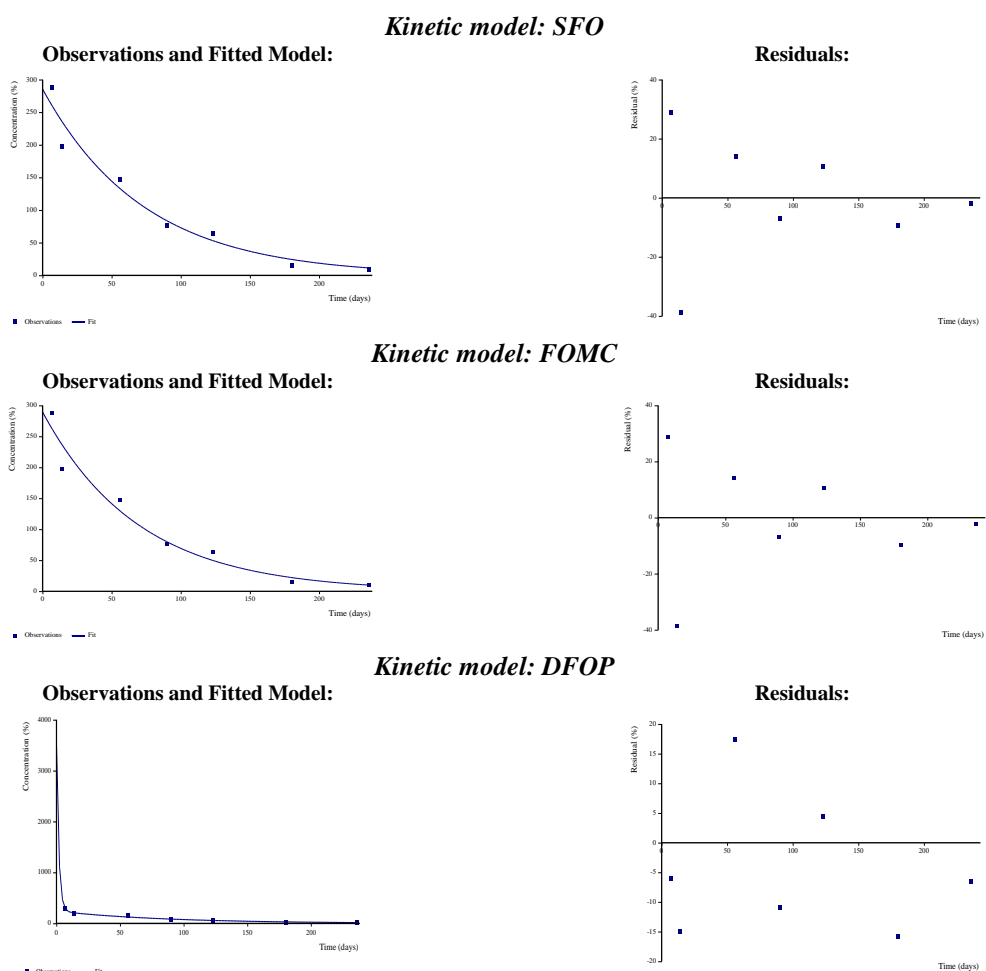


Figure B.8.1.1.2.2.1._CA-78: The graphical results of the kinetic analysis.

Table B.8.1.1.2.2.1._CA-114: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment
				Lower	Upper			
SFO	M_0	285.5	22.05	241.1	330.0	-----	13.9	0.9558; Acceptable fit
	k	0.01365	0.002146	0.009323	0.01797	7.10 E-4		
FOMC	M_0	289.4	24.87	236.4	342.4	-----	15.1	0.9558; Acceptable fit
	α	192.5	Not determined	Not determined	Not determined	-----		
	β	13400	Not determined	Not determined	Not determined	-----		
DFOP	M_0	3540	Not determined	Not determined	Not determined	-----	9.92	0.9866; Poor fit
	k_1	0.5588	Not determined	Not determined	Not determined	Not determined		
	k_2	0.01159	0.00161	0.007797	0.01538	0.002765		
	g	0.8899	Not determined	Not determined	Not determined	not given		

Table B.8.1.1.2.2.1._CA-115: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested		
		SFO	FOMC	DFOP
Flufenacet	DT ₅₀ [days]	50.8	48.4	1.37
	DT ₉₀ [days]	169.0	161.0	5.81

The elimination of the DAT-28 data point only slightly improved the results of the fitting in comparison to what was achieved for the whole data base. They were however worse than the results obtained when the DAT-14 time point was removed from the set. Additionally, the kinetic curve for DFOP fit took a shape very similar to that obtained for the whole data base with that kinetic model used. All that conforms the hypothesis about the DAT-14 data point being an outlier, which had to be removed from the data base.

Additionally it was determined that neither FOMC nor DFOP returned fully acceptable and reliable kinetic fits, the fact consistently stated for all three fitting exercises.

As a result, it can be stated that solely SFO shall be considered as a kinetic model adequately characterising the kinetic behaviour and persistence of Flufenacet in soil on St. Etienne du Gres, 40164/1 trial site.

Evaluation of the fitting:

The presented above results of the kinetic examination of the data obtained in the trial **St. Etienne du Gres, 40164/1**, demonstrated that reliable fit, and hence reliable kinetic endpoints representing persistence in soil under realistic – field conditions, was obtained for Flufenacet using SFO when the DAT-14 time point was removed from the set. Therefore such combination will be further used to examine the kinetic behaviour of Flufenacet and its degradation product – FOE Sulfonic acid in this trial.

- b) Results obtained at **Step 2** – fitting of the data for the parent compound (Flufenacet) and its degradation products:

The results of the kinetic analysis are presented below, in graphical form on figure B.8.1.1.2.2.1_CA-79 and in numerical form in the table B.8.1.1.2.2.1_CA-116. The fitting was performed for combination SFO-SFO.

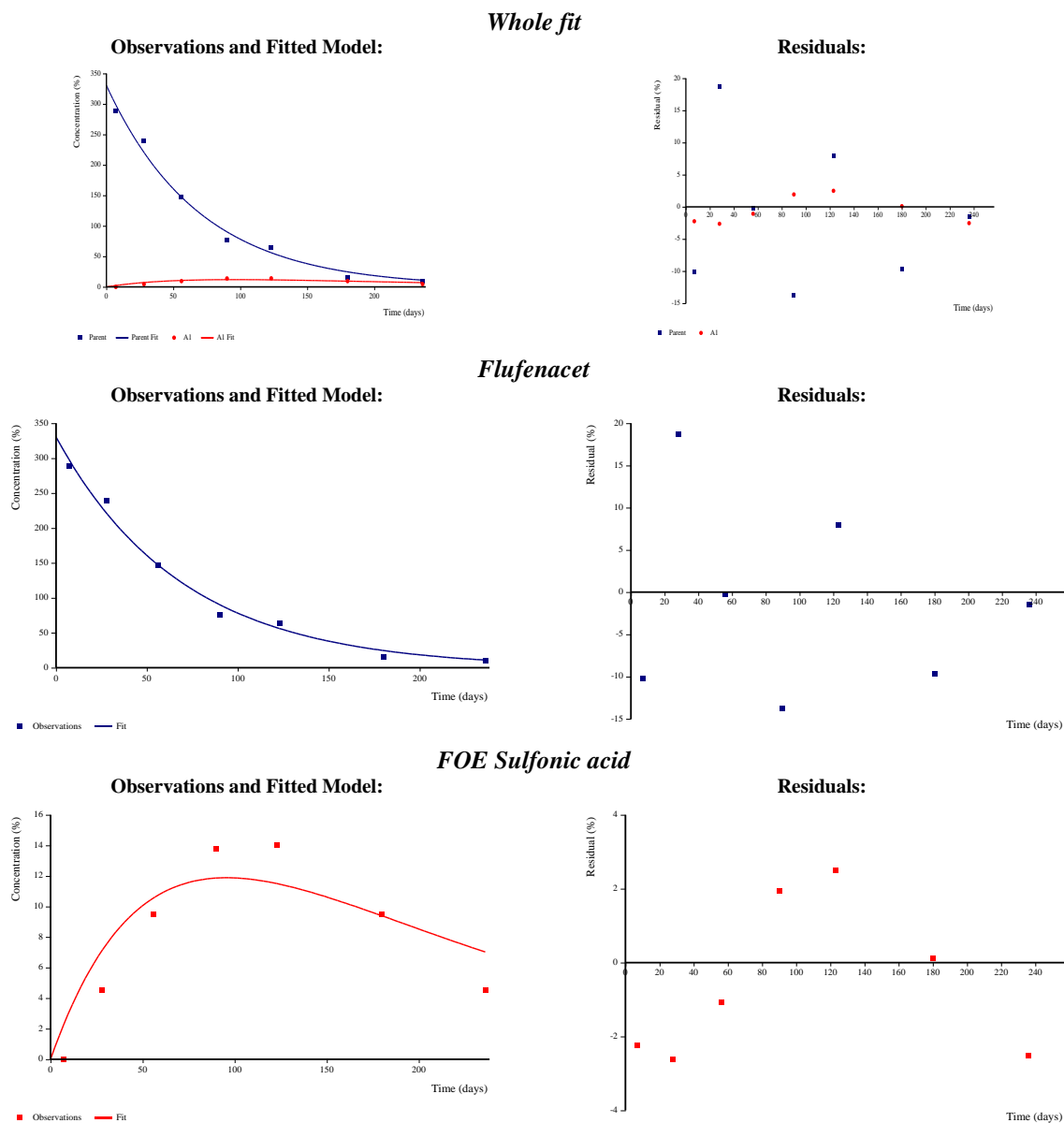


Figure B.8.1.1.2.2.1_CA-79: The graphical results of the kinetic examination of the data for Flufenacet and FOE Sulfonic acid obtained in the trial St. Etienne du Gres, 40164/1.

Table B.8.1.1.2.2.1. CA-116: The numerical results of the kinetic examination of the data for Flufenacet and FOE Sulfonic acid obtained in the trial St. Etienne du Gres, 40164/1.

Compound	Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
			Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment
					Lower	Upper			
Flufenacet	SFO	M ₀	330.4	13.75	305.5	355.3	-----	7.08	0.9892; Acceptable fit
		k	0.01442	0.001089	0.01245	0.0164	5.75 E-8		
FOE Sulfonic acid	SFO	M ₀	0.0	-----	-----	-----	-----	20.5	0.9319; Acceptable fit
		k	0.007303	0.002706	0.002399	0.01221	0.01117		
		ff	0.0723	0.01594	0.0434	0.1021	-----		

The kinetic endpoints derived from the study are presented below in the table B.8.1.1.2.2.1._CA-117.

Table B.8.1.1.2.2.1. CA-117: The kinetic endpoints determined in the experiment.

Determined parameter	Compound	
	Flufenacet	FOE Sulfonic acid
DT ₅₀ [days]	48.1	94.9
DT ₉₀ [days]	160.0	315.0
Kinetic formation fraction ff	Not applicable – parent compound	0.0723 ± 0.003
Precursor	Not applicable – parent compound	Flufenacet
Kinetic model	SFO	SFO

The kinetic fit obtained for Flufenacet may be classified as statistically and visually acceptable. Also the calculated kinetic parameters and derived from them kinetic endpoints are reliable.

The kinetic fit obtained for FOE Sulfonic acid can also be considered acceptable, although it displays only intermediate conformity of the estimated kinetic curve with the experimental points and the χ^2 error > 15% (20.5%). However, the residuals are low and randomly distributed. Finally, for both compounds the determined kinetic parameters, and hence kinetic endpoints, are fully reliable.

As a result, it can be stated that in that trial it was possible to obtain reliable fits for Flufenacet and FOE Sulfonic acid using a combination SFO-SFO.

RMS performed also the fitting for other combinations – for this data set (without DAT-14 data point) using the two remaining kinetic models for the parent – FOMC and DFOP, as well as the whole data set and for the data set without DAT-28 time point using all three kinetic models for the parent compound – SFO, FOMC and DFOP. The kinetic fits for the parent compound were very similar to those for the parent fitted alone and no improvement of the fit, if not its worsening, was observed for the degradation product – FOE Sulfonic acid. Therefore it may be stated that the change of the kinetic model for parent compound will not result in better fitting. RMS decided to not present the results of those kinetic examinations in order to not overburden the Assessment Report.

Final evaluation of the fitting exercise:

The presented above results of the kinetic examination of the data obtained in the trial **St. Etienne du Gres, 40164/1**, demonstrated that reliable fit, and hence reliable kinetic endpoints representing persistence in soil under realistic – field conditions, was obtained for both parent compound – Flufenacet and its degradation product – FOE Sulfonic acid when the combination of the kinetic models SFO-SFO was used and when the DAT-14 time point was removed from the data set as an outlier. The kinetic endpoints resulting from this kinetic assessment will be presented in the List of End Points as persistence kinetic endpoints for Flufenacet and FOE Sulfonic acid in the trial **St. Etienne du Gres, 40164/1**.

15) Results of the kinetic examination of the data obtained for the trial *Ravenna, 40494/2, Italy* (Study No. 107721, [Sommer; 1995c]):

The analysis for this data-set was a two-step analysis. Its results are presented below, individually for each step.

a) Results obtained at **Step 1** – fitting of the data for the parent compound (Flufenacet) alone:

The results of the kinetic analysis are presented below, in graphical form on figure B.8.1.1.2.2.1._CA-80 and in numerical form in the table B.8.1.1.2.2.1._CA-118. Additionally the table B.8.1.1.2.2.1._CA-119 provides the kinetic endpoints obtained with each of the kinetic models tested.

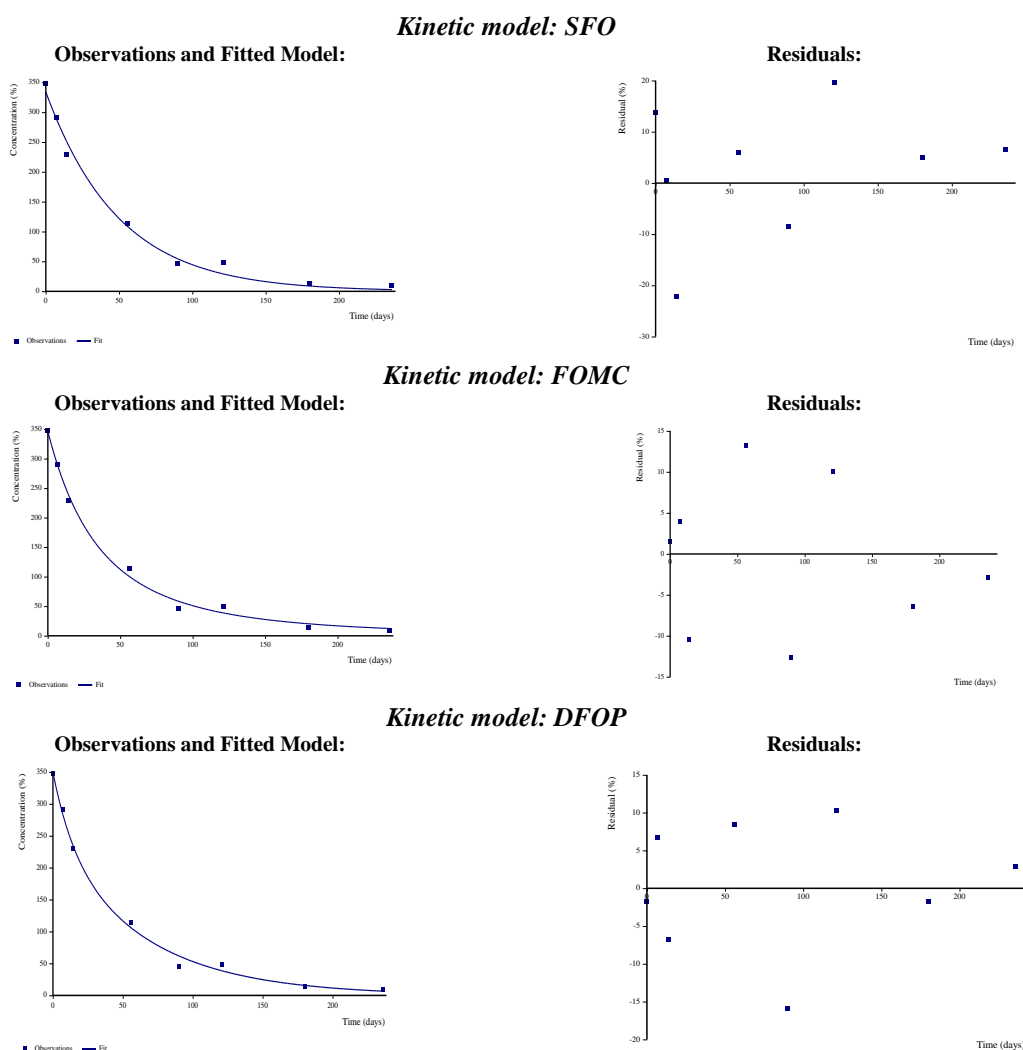


Figure B.8.1.1.2.2.1._CA-80: The graphical results of the kinetic analysis.

Table B.8.1.1.2.2.1._CA-118: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment
				Lower	Upper			
SFO	M_0	334.1	10.59	313.6	354.7	-----	7.23	0.991; Good fit
	k	0.02016	0.001727	0.0168	0.02352	1.19 E-5		
FOMC	M_0	346.3	10.08	326.0	366.6	-----	5.42	0.9951; Good fit
	α	2.684	1.129	0.4048	4.960	-----		
	β	95.94	53.62	-12.12	204.0	-----		
DFOP	M_0	349.6	11.3	325.5	373.7	-----	5.46	0.9957; Good fit
	k_1	0.06935	0.05467	-0.0472	0.1859	0.1367		
	k_2	0.01523	0.004248	0.006175	0.02429	0.01153		
	g	0.3055	0.2639	-0.2571	0.8681	not given		

Table B.8.1.1.2.2.1._CA-119: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested		
		SFO	FOMC	DFOP
Flufenacet	DT ₅₀ [days]	34.4	28.3	27.7
	DT ₉₀ [days]	114.0	130.0	127.0

All three models returned visually and statistically good fits. Of the three FOMC was superior and DFOP was the second best, although they were all very similar.

However, neither FOMC nor DFOP fits may be considered acceptable because of the lack of reliability of the kinetic parameters they returned. In case of FOMC for β the CI passes through zero. In case of DFOP fit for k_1 the $prob > t$ was higher than 0.1.

Only SFO returned visually and statistically acceptable fit with fully reliable kinetic parameters, hence it should be considered as the best-fit model for the parent compound – Flufenacet and as such was used at the next stage of analysis.

- b) Results obtained at **Step 2** – fitting of the data for the parent compound (Flufenacet) and its degradation products:

The results of the kinetic analysis are presented below, in graphical form on figure B.8.1.1.2.2.1_CA-81 and in numerical form in the table B.8.1.1.2.2.1_CA-120. The fitting was performed for combination SFO-SFO.

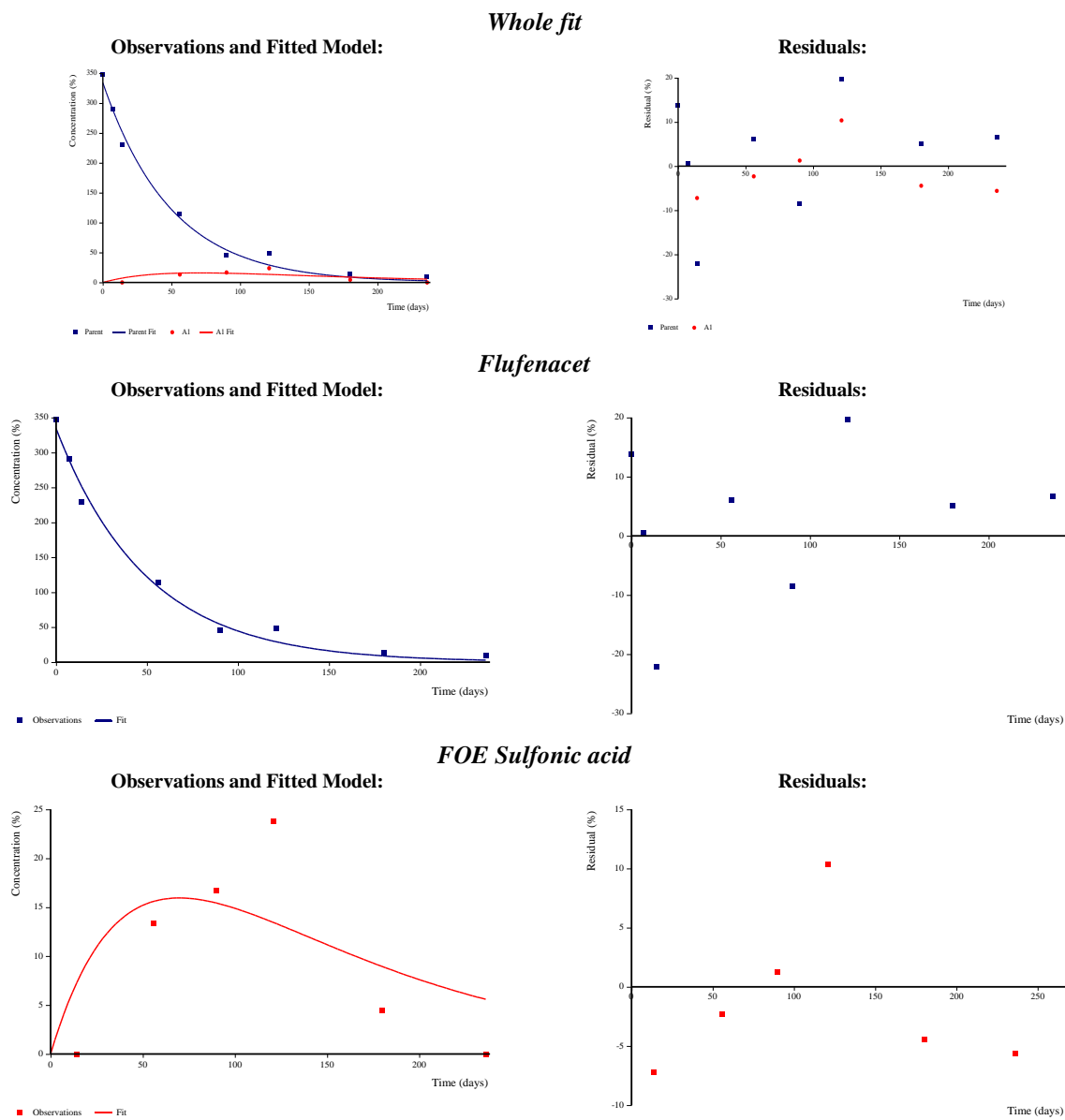


Figure B.8.1.1.2.2.1_CA-81: The graphical results of the kinetic examination of the data for Flufenacet and FOE Sulfonic acid obtained in the trial Ravenna, 40494/1.

Table B.8.1.1.2.2.1._CA-120: The numerical results of the kinetic examination of the data for Flufenacet and FOE Sulfonic acid obtained in the trial Ravenna, 40494/1.

Compound	Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
			Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment
					Lower	Upper			
Flufenacet	SFO	M ₀	333.9	10.84	314.2	353.5	-----	7.23	0.9909; Acceptable fit
		k	0.02007	0.001759	0.01688	0.02325	2.35 E-7		
FOE Sulfonic acid	SFO	M ₀	0.0	-----	-----	-----	-----	49.2	0.7348; Poor fit
		k	0.009774	0.007263	-0.00339	0.02294	0.1041		
		ff	0.0946	0.04661	0.01012	0.1791	-----		

The kinetic endpoints derived from the study are presented below in the table B.8.1.1.2.2.1._CA-121.

Table B.8.1.1.2.2.1._CA-121: The kinetic endpoints determined in the experiment.

Determined parameter	Compound	
	Flufenacet	FOE Sulfonic acid
DT ₅₀ [days]	34.5	70.9
DT ₉₀ [days]	115.0	236.0
Kinetic formation fraction ff	Not applicable – parent compound	0.0946 ± 0.047
Precursor	Not applicable – parent compound	Flufenacet
Kinetic model	SFO	SFO

The kinetic fit obtained for Flufenacet may be classified as statistically and visually acceptable. Also the calculated kinetic parameters and derived from them kinetic endpoints are reliable.

The kinetic fits obtained for FOE Sulfonic acid cannot be considered acceptable. It displays no conformity of the estimated kinetic curve with the experimental points and the residuals are high and not randomly distributed. In addition the fit is not fully statistically reliable – the χ^2 error for it is well above 15%, reaching 49.2%. Finally, it shall be noted that also the determined kinetic parameter – the rate constant *k* is not statistically reliable.

As a result, it can be stated that in this trial it was possible to obtain reliable fits only for Flufenacet.

RMS performed also the fitting using the two other kinetic models for the parent compound (Flufenacet) – FOMC and DFOP. The kinetic fits for the parent compound were very similar to those for the parent fitted alone and no improvement of the fit was observed for the degradation product – FOE Sulfonic acid. Therefore it may be stated that the change of the kinetic model for parent compound will not result in better fitting. RMS decided to not present the results of those kinetic examinations in order to not overburden the Assessment Report.

Evaluation of the fitting exercise:

The presented above results of the kinetic examination of the data obtained in the trial **Ravenna, 40494/1** demonstrated that reliable fit and reliable kinetic endpoints representing persistence in soil under realistic – field conditions was obtained only for the parent compound – Flufenacet. The kinetic model identified as returning the best fit was SFO.

For its degradation product, subjected to the kinetic examination, – FOE Sulfonic acid, it was not possible to obtain reliable kinetic fit and hence reliable kinetic endpoints representing the persistence of that compound on the trial site.

As a result, it can be stated that the reliable persistence kinetic endpoints for that trial may be determined for the parent compound – Flufenacet, when fitted alone. These values will be presented in the List of End Points.

16) Results of the kinetic examination of the data obtained for the trial *S. Romualdo, 40495/0, Italy* (Study No. 107721, [Sommer; 1995c]):

The analysis for this data-set was a single step analysis. That was due to the fact that for that data base only the values for Flufenacet could be derived. The initial inspection of the data set showed that it contained two possible outliers – the DAT-14 and DAT-28 time points. As it was not possible to state which of them is a real outlier using simple method, the RMS decided to perform the fitting for three options – the whole data base, data base without DAT-14 time point and the data base without DAT-28 time point. The method of the identification of outlier data point was identical to that used earlier for the data set obtained in *St. Etienne du Gres, 40164/1* trial. The results are presented below, individually for each option.

The results of the fitting for the whole data set:

The results of the kinetic analysis are presented below, in graphical form on figure B.8.1.1.2.2.1._CA-82 and in numerical form in the table B.8.1.1.2.2.1._CA-122. Additionally the table B.8.1.1.2.2.1._CA-123 provides the kinetic endpoints obtained with each of the kinetic models tested.

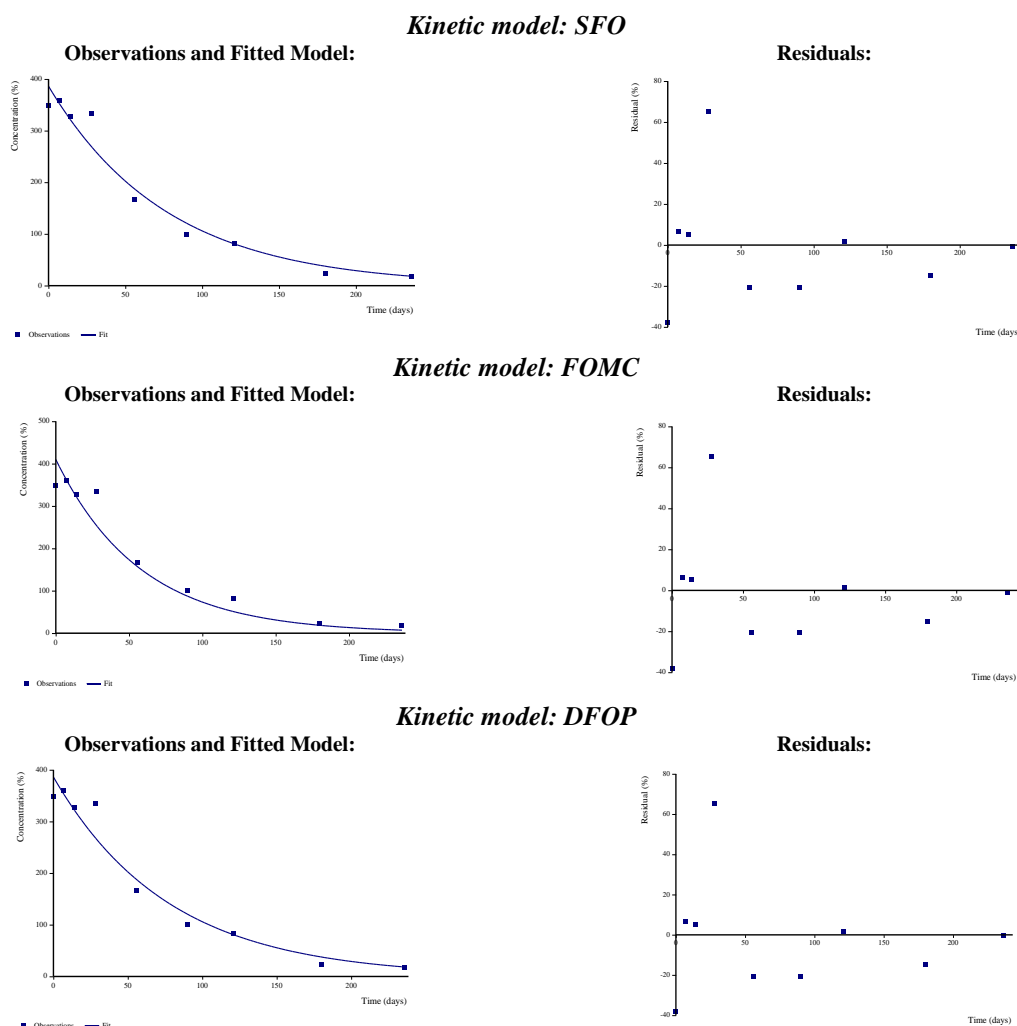


Figure B.8.1.1.2.2.1._CA-82: The graphical results of the kinetic analysis.

Table B.8.1.1.2.2.1._CA-122: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment
				Lower	Upper			
SFO	M_0	386.2	20.55	347.3	425.1	-----	11.3	0.9605; Acceptable fit
	k	0.01293	0.001747	0.009624	0.01625	7.46 E-5		
FOMC	M_0	410.0	28.71	354.2	465.8	-----	12.0	0.9604; Acceptable fit
	α	64.32	Not determined	Not determined	Not determined	-----		
	β	3040	Not determined	Not determined	Not determined	-----		
DFOP	M_0	386.2	35.54	314.6	457.8	-----	12.7	0.9605; Acceptable fit
	k_1	0.01293	1940.0	-3917.0	3920.0	0.5000		
	k_2	0.01293	542.4	-1093.0	1090.0	0.5000		
	g	0.2182	52200.0	-105200	105000	not given		

Table B.8.1.1.2.2.1._CA-123: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested		
		SFO	FOMC	DFOP
Flufenacet	DT ₅₀ [days]	53.6	40.2	53.6
	DT ₉₀ [days]	178.0	134.0	178.0

The examination of the results showed that all three kinetic models returned visually and statistically acceptable fits, very similar one to another. However, neither the FOMC fit nor that obtained using DFOP model may be considered acceptable because of the lack of reliability of the kinetic parameters. In case of FOMC fit the results of the statistical analysis – error and CI values, for both α and β , was not provided by the modelling tool. The reason for that was that the model was not able to create the covariance matrix.

In case of DFOP fit for both k_1 and k_2 the $prob > t$ was significantly higher than 0.1, reaching the level of 0.5. RMS also noticed that the k_1 and k_2 values were identical, and also the same as the rate constant k determined for SFO model, what in turn indicates that the partition of the compound between the “fast-degrading” and “slow degrading” compartments is artificial.

On that basis it was stated that only SFO returned visually and statistically acceptable fit with fully reliable kinetic parameters, hence it should be considered as the best-fit model for the parent compound – Flufenacet in this trial.

Finally, RMS analysed the conformity of the estimated kinetic curve with experimental data points. The results indicate that the DAT-28 time point may be considered an outlier. In order to conform that an additional fitting using all three kinetic models was carried out.

The results of the fitting for the data set without DAT-14 data point:

As a next step DAT-14 time point was removed from the data set and kinetic fitting repeated. The results of the kinetic analysis are presented below, in graphical form on figure B.8.1.1.2.2.1._CA-83 and in numerical form in the table B.8.1.1.2.2.1._CA-124. Additionally the table B.8.1.1.2.2.1._CA-125 provides the kinetic endpoints obtained with each of the kinetic models tested.

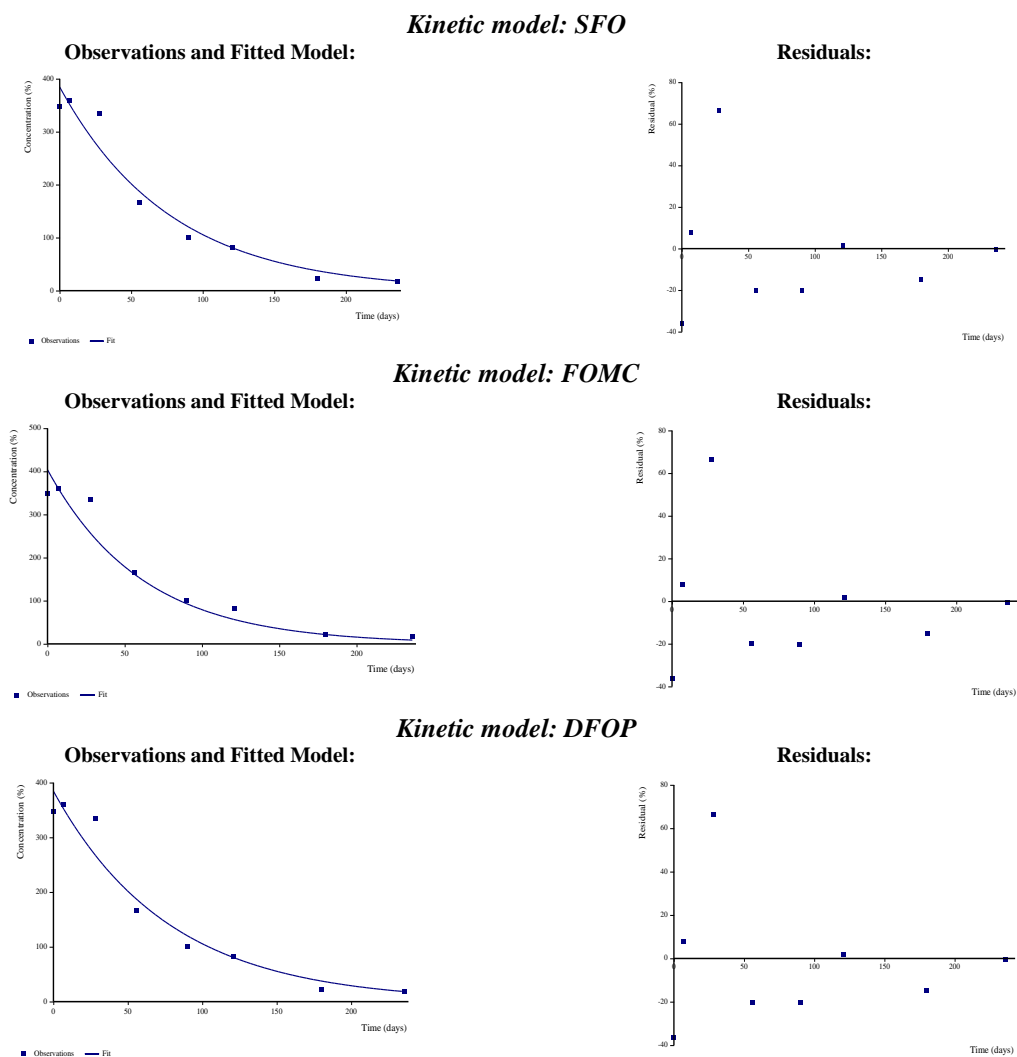


Figure B.8.1.1.2.2.1._CA-83: The graphical results of the kinetic analysis.

Table B.8.1.1.2.2.1._CA-124: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment
				Lower	Upper			
SFO	M_0	384.5	24.33	337.2	431.8	-----	13.0	0.9556; Acceptable fit
	k	0.01292	0.001892	0.009239	0.01659	2.43 E-4		
FOMC	M_0	404.0	31.93	339.7	468.3	-----	13.9	0.9555; Acceptable fit
	α	274.7	Not determined	Not determined	Not determined	-----		
	β	16800.0	Not determined	Not determined	Not determined	-----		
DFOP	M_0	384.5	28.46	323.9	445.2	-----	15.0	0.9556; Acceptable fit
	k_1	0.01292	0.01639	-0.02202	0.04786	0.2374		
	k_2	0.01292	0.001158	0.01045	0.01538	1.84 E-4		
	g	0.05023	Not determined	Not determined	Not determined	not given		

Table B.8.1.1.2.2.1._CA-125: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested		
		SFO	FOMC	DFOP
Flufenacet	DT ₅₀ [days]	53.7	42.5	53.7
	DT ₉₀ [days]	178.0	142.0	178.0

The examination of the results showed that all three kinetic models returned visually and statistically acceptable fits, very similar one to another. It was also noticed that statistically it worsened – the level of the χ^2 error increased, but was still below or equal to (for DFOP fit) 15%.

Nothing changed with regard to the acceptability of the fit – only SFO fit can be considered fully reliable and acceptable. In case of FOMC the modelling tool did not return, for the same reason as given for the fitting using the whole data set, statistical parameters of the determined kinetic parameters – error and CIs. In case of DFOP fit the removal of DAT-14 time point resulted only in that that the k_2 value became reliable, but k_1 lacked reliability. It was also noticed that, as previously, k_1 and k_2 were identical, and also the same as the rate constant k determined for SFO model. On that basis it may be stated that DFOP fit is artificial, as in fact there is no “fast degradation” and “slow degradation” compartments.

Therefore the conclusions from that fitting are following:

- SFO, also identified as such at previous stage of the analysis, is a model returning the best fit;
- the removal of DAT-14 time point from the data set did not let to the improvement of the fits, so that time point is conformed **not to be an outlier**.

The results of the fitting for the data set without DAT-28 data point:

The final stage was the verification whether DAT-28 data point was an outlier. To do that the data base was modified by removing that point and the fitting repeated. The results of the kinetic analysis are presented below, in graphical form on figure B.8.1.1.2.2.1._CA-84 and in numerical form in the table B.8.1.1.2.2.1._CA-126. Additionally the table B.8.1.1.2.2.1._CA-127 provides the kinetic endpoints obtained with each of the kinetic models tested.

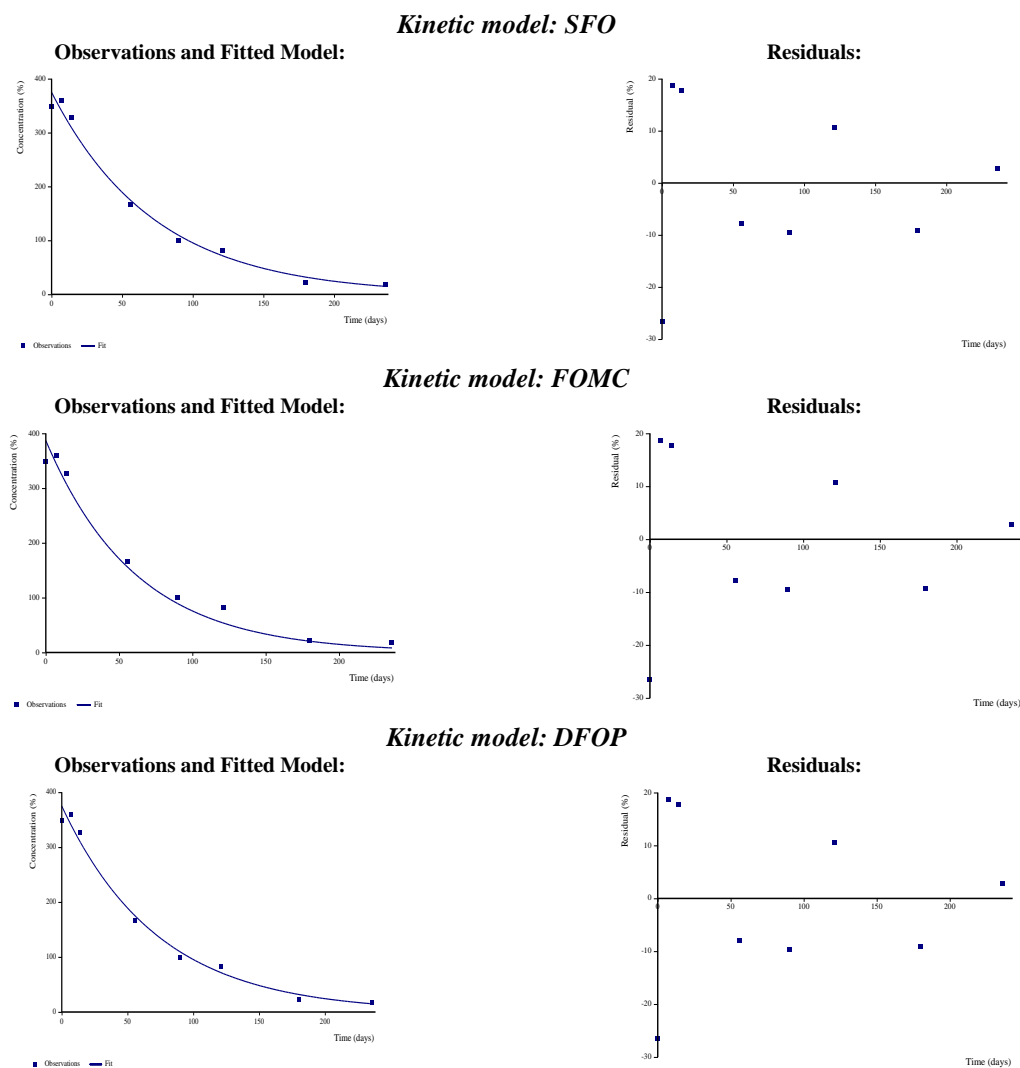


Figure B.8.1.1.2.2.1._CA-84: The graphical results of the kinetic analysis.

Table B.8.1.1.2.2.1._CA-126: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R^2 and visual assessment
				Lower	Upper			
SFO	M_0	374.9	11.58	352.3	397.4	-----	6.58	0.9884; Good fit
	k	0.01368	0.001066	0.01161	0.01575	6.87 E-6		
FOMC	M_0	387.0	17.27	352.2	421.8	-----	7.02	0.9884; Good fit
	α	942.6	99.42	742.3	1140.0	-----		
	β	57700.0	3000.0	51700.0	63800.0	-----		
DFOP	M_0	374.9	19.02	334.3	415.4	-----	7.58	0.9884; Good fit
	k_1	0.01368	4690.0	-9989.0	9990.0	0.5000		
	k_2	0.01368	1090.0	-2317.0	2320.0	0.5000		
	g	0.1883	48400.0	-103000.0	103000.0	not given		

Table B.8.1.1.2.2.1._CA-127: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested		
		SFO	FOMC	DFOP
Flufenacet	DT ₅₀ [days]	50.7	42.5	50.7
	DT ₉₀ [days]	168.0	141.0	168.0

The removal of DAT-28 time point from the data set led to significant improvement of the fits for all three models. The curves displayed good conformity with the experimental results, the levels of residuals were lower, although their distribution was not altered. That enabled to change the classification of the visual fits from “acceptable” to “good”. It was stated that all three kinetic models returned visually and statistically acceptable fits, very similar one to another.

In addition SFO and FOMC returned reliable kinetic parameters. That cannot be stated for DFOP fit, in case of which for both k_1 and k_2 the $prob > t$ was significantly higher than 0.1, reaching the level of 0.5. Additionally it was noticed that k_1 and k_2 were identical and moreover the same as the rate constant k determined for SFO fit. The results obtained for SFO and FOMC kinetic models did not differ significantly, although it was noticed that for SFO the χ^2 error was lower. Additionally SFO returned longer DT₉₀ than FOMC, what may indicate that for Flufenacet in that trial bi-phasic kinetic model does not provide an adequate description of its kinetic behaviour in soil.

The conclusions drawn from this fitting are following:

- the results indicate that DAT-28 time point should be considered as an outlier and removed from the data base subjected to the kinetic analysis;
- the best-fit model is SFO.

Evaluation of the fitting exercise:

The presented above results of the kinetic examination of the data obtained in the trial **S. Romualdo, 40495/0**, demonstrated that reliable fit and reliable kinetic endpoints representing persistence in soil under realistic – field conditions was obtained only for the parent compound – Flufenacet. The kinetic model identified as returning the best fit was SFO. The data base needs to be modified by the removal of DAT-28 time point identified as an outlier. The results of the fitting – the determined kinetic endpoints, will be presented in the List of End Points.

The kinetic analysis for the degradation products – FOE Alcohol, FOE Oxalate and FOE Sulfonic acid, was not performed for this trial due to the lack of the suitable data base for any of them.

Summary:

The kinetic examination of the data on the field dissipation of Flufenacet and its degradation products was performed for sixteen field trials. For eight of them the available data set enabled to carry out the fitting for Flufenacet only. In case of eight remaining trials it was possible to include also two of the three examined degradation products: FOE Oxalate in case of three trials and FOE Sulfonic acid for all eight trials. The final outcome of the fitting exercise – reliable key results for each evaluated compound, are presented below in tables B.8.1.1.2.2.1_CA-128 – B.8.1.1.2.2.1.CA-130.

Table B.8.1.2.2.1_CA-128: The results of the best-fit kinetic examination of the data for Flufenacet obtained in field dissipation trials.

Data on the trial		Soil properties (0-30 cm layer)			Identified best-fit model	Kinetic parameter		Evaluation of the fit		Kinetic endpoints	
Trial code	Location; type of trial	Soil type (USDA classif.)	pH ¹⁾	OC [%]		par.	value	Visual fit ²⁾ / r ³⁾	χ ² % error	DT ₅₀ [days]	DT ₉₀ [days]
30159/0	Breitenfelde, Germany; bare soil	Sandy loam	6.2	1.69	SFO	k	0.02092	A./0.9648	13.3	33.1	110.0
30162/0	Kirchlauter, Germany; bare soil	Heavy sandy loam ⁴⁾	7.1	0.61	SFO	k	0.0131	G./0.988	6.43	52.9	176.0
30163/9	Monheim, Germany; bare soil	Sandy loam	6.7	1.45	SFO	k	0.0144	A./0.9275	16.1	48.2	160.0
30164/7	Burscheid, Germany; bare soil	Silt loam	6.5	0.97	SFO	k	0.04309	G./0.9915	6.83	16.1	53.4
30248/1	Fresne-L'Archeveque; North France; cropped soil	Silt loam	6.0	1.11	SFO	k	0.01827	A./0.9536	15.8	38.0	126.0
30250/3	Fresne-L'Archeveque1, North France; cropped soil	Silt loam	5.2	1.86	SFO	k	0.01352	A./0.9672	11.0	51.3	170.0
30251/1	Laudun, South France; cropped soil	Loam	7.6	0.62	SFO	k	0.02278	A./0.9804	10.2	30.4	101.0
30253/8	St. Etienne du Gres, South France; cropped soil	Loam	7.7	0.80	SFO	k	0.01687	G./0.9902	6.68	41.1	137.0
30499/9	Burscheid, Germany; bare soil	Silt loam	6.5	0.97	DFOP	k ₁	1.501	A./0.9674	7.11	31.5	140.0
						k ₂	0.01481				
						g	0.2025				
30500/6	Monheim, Germany; bare soil	Sandy loam	6.7	1.45	SFO	k	0.01017	G./0.991	5.1	68.1	226.0
30254/6	Sausay-la-Campagne, South France; cropped soil	Silt loam	7.4	0.92	FOMC	α	4.673	G./0.9993	2.79	14.2	56.7
						β	88.960				
30455/7	Fresne-L'Archeveque; North France; cropped soil	Silt loam	6.6	1.00	SFO	k	0.04024	G./0.9989	3.32	17.2	57.2
40163/3	Laudun, South France; cropped soil	Clay loam	7.7	1.28	SFO	k	0.01451	A./0.9774	9.86	49.0	163.0
40164/1	St. Etienne du Gres, South France; cropped soil	Silt loam	7.7	0.96	SFO	k	0.01442	A./0.9892	7.08	48.1	160.0
40494/2	Ravenna, Italy; cropped soil	Silt loam	7.8	0.98	SFO	k	0.02016	G./0.991	7.23	34.4	114.0
40495/0	S. Romualdo, Italy; cropped soil	Silty loam	7.8	1.11	SFO	k	0.01368	G./0.9884	6.58	50.7	168.0

Footnotes to the table:

1) Determined in 0.01M CaCl₂;

2) Following abbreviations were used: P – Poor; A – Acceptable; G – Good;

3) r = correlation coefficient;

4) The DIN 19682 classification presented because the USDA classification not provided; in another report it was stated to be Sandy loam (USDA) containing 58.5% sand, 22.7% silt and 18.8% clay.

Table B.8.1.2.2.1_CA-129: The results of the best-fit kinetic examination of the data for FOE Oxalate obtained in field dissipation trials.

Data on the trial		Soil properties (0-30 cm layer)			Identified best-fit model	Kinetic parameter		Evaluation of the fit		Kinetic endpoints	
Trial code	Location; type of trial	Soil type (USDA classif.)	pH ¹⁾	OC [%]		par.	value	Visual fit ^{2)/ r³⁾}	χ ² % error	DT ₅₀ [days]	DT ₉₀ [days]
30250/3	Fresne-L'Archeveque1, North France; cropped soil	Silt loam	5.2	1.86	SFO	k	0.01091	G./0.9895	4.53	68.0	226.0

Footnotes to the table:

- 1) Determined in 0.01M CaCl₂;
 2) Following abbreviations were used: P – Poor; A – Acceptable; G – Good;
 3) *r* = correlation coefficient;

Table B.8.1.2.2.1_CA-130: The results of the best-fit kinetic examination of the data for FOE Sulfonic acid obtained in field dissipation trials.

Data on the trial		Soil properties (0-30 cm layer)			Identified best-fit model	Kinetic parameter		Evaluation of the fit		Kinetic endpoints	
Trial code	Location; type of trial	Soil type (USDA classif.)	pH ¹⁾	OC [%]		par.	value	Visual fit ^{2)/ r³⁾}	χ ² % error	DT ₅₀ [days]	DT ₉₀ [days]
30248/1	Fresne-L'Archeveque; North France; cropped soil	Silt loam	6.0	1.11	SFO	k	0.01144	A./0.7441	23.3	60.6	201.0
30250/3	Fresne-L'Archeveque1, North France; cropped soil	Silt loam	5.2	1.86	SFO	k	0.00921	G./0.9477	9.83	75.3	250.0
30253/8	St. Etienne du Gres, South France; cropped soil	Loam	7.7	0.80	SFO	k	0.02249	G./0.9379	12.1	30.8	102.0
40164/1	St. Etienne du Gres, South France; cropped soil	Silt loam	7.7	0.96	SFO	k	0.007303	A./0.9319	20.5	94.9	315.0

Footnotes to the table:

- 1) Determined in 0.01M CaCl₂;
 2) Following abbreviations were used: P – Poor; A – Acceptable; G – Good;
 3) *r* = correlation coefficient;

The results presented above will also be given in format recommended for their reporting in the List of Endpoints.

The Applicant performed the kinetic examination of the data obtained in the four soil dissipation studies summarized above as **Studies 1-4**. The aim of this evaluation was to obtain the kinetic endpoints for Flufenacet and FOE Sulfonic acid suitable for modelling. The Applicant performed the kinetic assessment of the data using the inverse modeling approach. Doing that the Applicant did not take into account the results of all studies for Flufenacet and FOE Sulfonic acid examining the persistence, sorption and mobility of these two compounds submitted for the current evaluation, as the assessment pre-dated several of them.

RMS evaluated the study taking into consideration, among the other factors, the findings of the kinetic examination of the data aimed on the identification of the best-fit kinetic model and determination of the persistence endpoints.

The study's summary together with the RMS's evaluation is presented below as **Study 7**.

Study 7:

Report: Hammel K., (2008): “Kinetic Evaluation of the Dissipation of Flufenacet and its Metabolite Flufenacet-sulfonic acid in soil based on Field Studies.”; Bayer CropScience AG, Institute for Metabolism and Environmental Fate, Alfred-Nobel-Strasse 50, 40789 Monheim, Germany; study Report No. MEF-08/266; 2008. 08. 25; study reference number: M-306683-01-1;

Guidelines: The study was declared to be performed following the guidance of the FOCUS Kinetics Work Group given in:

- FOCUS, 2005: “Guidance Document on Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration.”; Report of the FOCUS Work Group on Degradation Kinetics, EC Document Reference Sanco/10058/2005 version 1.0;

GLP: No, not required – this is a modelling study;

RMS comments: This is a newly submitted study, evaluated for the purpose of the current assessment. The Applicant stated that it was carried out to comply with the recommendations of the earliest version of the FOCUS Kinetics Guidance Document – version 1.0 issued in 2005. It shall be indicated that already at the date of issuing the report the updated version of that Guidance document – version 2.0 issued in June 2006, was available. Therefore RMS decided to evaluate that study using the updated version of FOCUS Kinetics Guidance document, and in particular:

- FOCUS, 2006: “Guidance Document on Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration.”; Report of the FOCUS Work Group on Degradation Kinetics, EC Document Reference Sanco/10058/2005 version 2.0, 434 pp.;
- FOCUS, 2011: “Generic Guidance for Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration.” Version 1.0, Nov. 23, 2011.

Additionally, to evaluate the study report in the area of the inverse modelling the following documents were consulted:

- European Commission (2014): “Assessing Potential for Movement of Active Substances and their Metabolites to Ground water in the EU.”; Report of FOCUS Ground Water Work Group, EC Document Reference Sanco/13144/2010 version 3, 613 pp. (Chapter 7 and Appendices 10 and 11);
- “The Application of Inverse Modelling Techniques to Pesticide Leaching Models.”; SSLRC support for PSD data evaluation and risk Assessment activities; MAFF project code PL0528, pp. 12- 23, available on-line on DEFRA webpage in the folder “Science and Research Projects”;
- Dubus I., Beulke S., Brown C. D., (2002): “Review: Calibration of pesticide leaching models: critical review and guidance for reporting.” *Pest Management Science* 2002, **58**, 745 – 758;

The summary of the study and its evaluation performed by the RMS is presented below.

Summary:

The aim of the study was to evaluate the degradation of Flufenacet and its major soil degradation product – FOE Sulfonic acid, and to determine the kinetic parameters suitable for modelling. Because of relatively high mobility of FOE Sulfonic acid in soil an inverse modelling approach was included into assessment to take account of the leaching of that compound.

The kinetic fitting of the data was performed using the PEST optimisation algorithm, while the losses due to leaching and other processes, such as plant uptake, were estimated using PEARL modelling tool in order to distinguish between degradation and dissipation.

Finally, the conservatism of the kinetic evaluation was assessed by comparison with independent data from two lysimeter studies.

The Applicant performed the kinetic analysis of the data obtained for Flufenacet and FOE sulfonic acid obtained in 16 field trials – 6 run in Germany, 8 in France and 2 in Italy, presented above in **Studies 1-4**.

The brief characterisation of these trials, as presented by the Applicant in the study report, is provided below in the table B.8.1.1.2.2.1._CA-131. Where necessary the data reported by the Applicant were corrected.

Table B.8.1.1.2.2.1._CA-131: The brief characteristic of field trials.

Study	Information on the trial site			Data on application		Data on crop cover		
	Trial number	Name of the trial site	Location - country	Application rate [g/ha]	Application date	Crop	Date of sowing	Sowing – days before application
[Sommer; 1995]	30159/0	Breitenfelde	Germany	480	15. 04. 1993	Bare soil	Not applicable	Not applicable
	30162/0	Kirchlauter	Germany	480	13. 04. 1993	Bare soil	Not applicable	Not applicable
	30163/9	Monheim	Germany	480	30. 04. 1993	Bare soil	Not applicable	Not applicable
	30164/7	Burscheid	Germany	480	22. 04. 1993	Bare soil	Not applicable	Not applicable
	30248/1	Fresne-L'Archeveque	France (North)	600	11. 05. 1993	Maize	04. 05. 1993	7
	30250/3	Fresne-L'Archeveque (1)	France (North)	600	27. 05. 1993	Maize	24. 05. 1993	3
	30251/1	Laudun	France (South)	600	18. 05. 1993	Sunflower	22. 04. 1993	26
	30253/8	St. Etienne du Gres	France (South)	600	17. 05. 1993	Sunflower	16. 05. 1993	1
[Sommer; 1995b]	30254/6	Saussay-la-Campagne	France (South)	240	11. 03. 1994	Winter wheat	14. 10. 1993	158
	30455/7	Fresne-L'Archeveque	France (North)	240	28. 04. 1994	Winter wheat	22. 10. 1993	169
[Sommer; 1995a]	30499/9	Burscheid	Germany	240	26. 10. 1993	Bare soil	Not applicable	Not applicable
	30500/6	Monheim	Germany	240	26. 10. 1993	Bare soil	Not applicable	Not applicable
[Sommer; 1995c]	40163/3	Laudun	France (South)	600	17. 05. 1994	Sunflower	04. 05. 1994	13
	40164/1	St. Etienne du Gres	France (South)	600	22. 04. 1994	Sunflower	16. 04. 1994	6
	40494/2	Ravenna	Italy	600	27. 04. 1994	Soybean	25. 04. 1994	2
	40495/0	S. Romualdo	Italy	600	27. 04. 1994	Soybean	26. 04. 1994	1

Characterising the trials the Applicant stated that seven of them were performed on bare soil while the remaining nine on soil cropped with maize, sunflower, winter wheat or soybean. It shall be indicated however that the trial 30248/1 – Fresne-L'Archeveque was incorrectly characterised as performed on the bare soil, while in fact it was performed on the cropped soil, on which maize was grown. The Applicant however subsequently corrected that mistake in the modelling assessment of the data set for that trial.

Next the residue data obtained for Flufenacet and its degradation product – FOE Sulfonic acid were pre-processed in order to obtain the data sets suitable for the kinetic evaluation.

Doing that the Applicant stated that the samples were taken as soil cores, in ten trials down to 30-cm – in the studies [Sommer; 1995] and [Sommer; 1995a], and in six remaining trials – in the studies by [Sommer; 1995b] and [Sommer; 1995c], down to 50 cm. These cores were next divided into 10-cm sections and analysed. It was stated that for the purpose of the evaluation only 0-30 cm layers were considered for two reasons:

- 1) no residues of either Flufenacet or FOE Sulfonic acid were detected below 30 cm in trials in which 50-cm soil cores were sampled;
- 2) potential leaching below the depth of 30 cm was accounted for by the inverse modelling procedure.

The trials lasted for 231 – 303 days after application of the test compound – Flufenacet. During that period samples were taken eight or nine times. Typically four replicates were analysed for 0-10 cm layer, two for 10-20 cm layer and one for 20-30 cm layer. The mean values for each layer were used in the evaluation. It was stated that in course of the trials the quantifiable (> LOQ) residues of Flufenacet and FOE Sulfonic acid were found almost uniquely in the topmost layer 0-10 cm.

The residue data were processed using the following analytical parameters: LOD = 3 µg/kg and LOQ = 10 µg/kg. These values were used in the data processing, following the recommendations given by FOCUS [2005]. That procedure was already presented in the paragraph summarising the kinetic evaluation of the data aimed on the identification of the best-fit model and determination of persistence endpoints and, for completeness, is outlined here:

- the residues < LOQ were set to 0.5 (LOD + LOQ) = 6.5 µg/kg – the mean of the interval between LOD and LOQ;
- values < LOD were set to 0.5 LOD = 1.5 µg/kg for their first appearance before or after the values > LOD, also in deeper layers, for samples between the values > LOQ.
- The kinetic curve was cut-off after the first non-detect (< LOD) unless later value > LOQ followed;
- On DAT 0 values < LOD in deeper layers were set to zero;
- To increase the conservatism of the assessment for FOE Sulfonic acid all depth were considered during the whole experimental period – starting from the second sampling for the layer 10-20 cm and from the third sampling for the layer 20-30 cm all values < LOD were set to 0.5 LOD irrespective of the values obtained in deeper layers.
- After averaging the residue concentrations in each layer were summed up to represent the concentration in the topmost 10-cm layer;
- Finally, the so determined concentrations were transformed, using the soil density determined for 0-30 cm soil layer of each trial site, to obtain the value expressed in g/ha, subsequently used in the kinetic evaluation of the data; in the study report it was explained that that was done because the amount expressed in units [mass/area down to a given soil depth] is a direct output of PEARL, what simplifies the inverse modelling.

The last step was not used by the RMS in the kinetic analysis of the data aimed on the identification of the best-fit model and determination of the persistence kinetic endpoints in each trial.

The resulting pre-processed data sets for each trial, with concentrations expressed in [µg/kg], are presented below in tables B.8.1.1.2.2.1._CA-132 and B.8.1.1.2.2.1._CA-132a.

Table B.8.1.1.2.2.1._CA-132: The pre-processed data used in the kinetic examination of the results of the study [Sommer; 1995]

Trial: 30159/0 Breitenfelde, Germany			Trial: 30162/0 Kirchlauter; Germany			Trial: 30163/9 Monheim, Germany			Trial: 30164/7 Burscheid, Germany		
Time point DAT [days]	Concentrations in [µg/kg] of:		Time point DAT [days]	Concentrations in [µg/kg] of:		Time point DAT [days]	Concentrations in [µg/kg] of:		Time point DAT [days]	Concentrations in [µg/kg] of:	
	Flufenacet	FOE Sulfonic acid		Flufenacet	FOE Sulfonic acid		Flufenacet	FOE Sulfonic acid		Flufenacet	FOE Sulfonic acid
0	244.0	0	0	261.8	0.0	0	152.0	0.0	0	331.0	0.0
7	257.5	1.5	7	210.0	0.0	7	173.5	1.5	7	213.5	1.5
14	164.0	4.3	14	221.0	3.0	14	174.5	3.0	14	175.5	3.0
28	145.0	9.5	28	285.0	5.8	28	150.5	9.5	27	109.5	8.3
56	89.6	17.5	56	111.5	9.5	56	68.2	9.5	60	27.5	14.5
90	33.8	15.8	90	83.0	11.3	90	30.8	7.0	90	8.0	4.5
120	13.0	4.5	120	46.7	9.5	122	23.6	7.6	120	8.0	4.5
180	8.0	4.5	181	26.9	12.0	180	17.6	4.5	180	1.5	4.5
240	8.0	4.5	237	13.7	4.5	231	13.2	4.5	239	0.0	4.5
Trial: 30248/1 Fresne-L'Archeveque, France			Trial: 30250/3 Fresne-L'Archeveque, France			Trial: 30251/1 Laudun, France			Trial: 30253/8 St. Etienne du Gres, France		
Time point DAT [days]	Concentrations in [µg/kg] of:		Time point DAT [days]	Concentrations in [µg/kg] of:		Time point DAT [days]	Concentrations in [µg/kg] of:		Time point DAT [days]	Concentrations in [µg/kg] of:	
	Flufenacet	FOE Sulfonic acid		Flufenacet	FOE Sulfonic acid		Flufenacet	FOE Sulfonic acid		Flufenacet	FOE Sulfonic acid
0	362.0	0.0	0	279.5	0.0	0	382.5	0.0	0	286.5	0.0
14	210.5	1.5	8	298.5	1.5	7	297.0	1.5	7	n. a. ¹⁾	1.5
28	233.5	15.4	28	190.0	8.0	15	311.5	3.0	15	213.0	8.0
56	125.5	10.4	56	113.5	10.5	28	203.5	9.5	28	197.0	10.4
90	94.3	14.3	91	82.5	15.0	55	81.3	16.3	56	97.0	12.4
120	58.0	12.9	120	66.2	14.5	87	50.4	17.8	87	58.7	9.5
181	31.7	7.0	193	40.4	9.5	119	29.4	19.1	119	52.4	9.5
303	25.2	4.5	287	18.8	4.5	182	8.0	5.75	182	8.0	4.5
						255	8.0	4.5	260	6.8	4.5

Footnotes to the table:

- 1) the time point not used in the evaluation as no measurable residues were found in soil sample;
- 2) not available – the values were below the LOD.

Table B.8.1.1.2.2.1_ CA-132a: The pre-processed data used in the kinetic examination of the results of the studies [Sommer; 1995a], [Sommer; 1995b] and [Sommer; 1995c].

Trial: 30254/6 Saussay-la-Campagne, France			Trial: 30455/7 Fresne-L'Archeveque, France			Trial: 30499/9 Bruscheid, Germany			Trial: 30500/6 Monheim, Germany		
Time point DAT [days]	Concentrations in [µg/kg] of:		Time point DAT [days]	Concentrations in [µg/kg] of:		Time point DAT [days]	Concentrations in [µg/kg] of:		Time point DAT [days]	Concentrations in [µg/kg] of:	
	Flufenacet	FOE Sulfonic acid		Flufenacet	FOE Sulfonic acid		Flufenacet	FOE Sulfonic acid		Flufenacet	FOE Sulfonic acid
0	115.0	n. a. ²⁾	0	93.0	n. a. ²⁾	0	141.0	0.0	0	101.0	n. a. ²⁾
7	77.3	n. a. ²⁾	28	29.3	n. a. ²⁾	8	95.6	5.3	8	102.5	n. a. ²⁾
52	12.2	n. a. ²⁾	53	8.0	n. a. ²⁾	14	92.6	8.0	14	91.9	n. a. ²⁾
70	8.0	n. a. ²⁾	88	8.0	n. a. ²⁾	29	82.9	9.5	28	112.0	n. a. ²⁾
89	8.0	n. a. ²⁾	120	1.5	n. a. ²⁾	56	54.1	7.0	52	68.6	n. a. ²⁾
116	1.5	n. a. ²⁾	178	0.0	n. a. ²⁾	90	21.8	4.5	98	37.3	n. a. ²⁾
180	0.0	n. a. ²⁾	240	0.0	n. a. ²⁾	120	13.7	4.5	120	29.1	n. a. ²⁾
242	0.0	n. a. ²⁾				180	8.0	4.5	181	14.3	n. a. ²⁾
						240	1.5	4.5	240	1.5	n. a. ²⁾
Trial: 40163/3 Laudun, France			Trial: 40164/1 St. Etienne du Gres, France			Trial: 40494/2 Ravenna, Italy			Trial: 40495/0 S. Romualdo, Italy		
Time point DAT [days]	Concentrations in [µg/kg] of:		Time point DAT [days]	Concentrations in [µg/kg] of:		Time point DAT [days]	Concentrations in [µg/kg] of:		Time point DAT [days]	Concentrations in [µg/kg] of:	
	Flufenacet	FOE Sulfonic acid		Flufenacet	FOE Sulfonic acid		Flufenacet	FOE Sulfonic acid		Flufenacet	FOE Sulfonic acid
0	202.0	0.0	0	227.0	0.0	0	345.0	0.0	0	345.0	0.0
8	241.5	6.5	8	286.5	1.5	7	289.5	1.5	7	357.5	1.5
14	226.5	8.0	14	195.5	3.0	14	228.5	3.0	14	325.5	3.0
28	207.5	9.5	28	237.5	9.5	28	278.5	4.5	28	332.5	9.5
57	146.0	9.5	56	145.5	13.8	56	112.5	13.3	56	164.5	9.5
91	84.8	16.6	90	75.0	14.0	90	44.5	16.7	90	98.4	9.5
125	32.7	9.5	123	62.5	9.5	121	47.3	23.8	121	80.8	9.5
182	8.0	4.5	180	13.5	4.5	180	12.4	4.5	180	21.2	4.5
240	1.5	4.5	236	8.0	4.5	236	8.0	4.5	236	16.2	4.5

Footnotes to the table:

- 1) the time point not used in the evaluation as no measurable residues were found in soil sample;
 2) not available – the values were below the LOD.

According to the Applicant for three of sixteen data sets it was not possible to perform the kinetic analysis for FOE Sulfonic acid, because there were no values above the LOD. Such situation was observed in the trials 30254/6 Saussay-la-Campagne, 30455/7 Fresne-L'Archeveque and 30500/6 Monheim. RMS for these trials also did not performed the kinetic assessment aimed on the determination of the persistence.

Further comparative analysis of the data sets showed that in case of four other trials – 30163/9 Monheim, 30164/7 Burscheid, 30499/9 Burscheid and 40495/0 S. Romualdo, the residues of FOE Sulfonic acid, when detected, were all lower than the LOQ. In another trial – 30162/0 Kirchlauter practically all values for FOE Sulfonic acid, when that compound was detected in soil, were <LOQ (the exception concerned one replicate in 0-10 cm layer of DAT 90, in which the residue level was 10.20 µg/kg; however when the average was calculated the resulting value was very close to the average for values < LOQ – 7.4 µg/kg) . In the reference document “The Application of Inverse Modelling Techniques to Pesticide Leaching Models” (ref.: MAF project PL 0528), in paragraph 4.7 – *Influence of the quality of the experimental dataset*, it is stated that the handling of the values <LOQ is problematic. They use to be set either to zero or some fraction of LOQ, but there is no information about the influence of such setting on the results. RMS, being aware of the significant level of uncertainty related to the numerical values attributed to the residues <LOQ, and hence to the data sets comprising only these values as “measurables”, decided not to perform the kinetic evaluation of the data sets containing no values > LOQ. For that reason for the trials 30162/0 Kirchlauter, 30163/9 Monheim, 30164/7 Burscheid, 30499/9 Burscheid and 40495/0 S. Romualdo the kinetic examination of the data aimed on the determination of persistence kinetic endpoints for FOE Sulfonic acid was not performed because the results would bear to high level of uncertainty. For the same reason RMS is of the opinion that the results obtained in this experiment for FOE Sulfonic acid in the trials listed above should not be taken into account in the further assessment.

As a result, the analysis of the pre-processed data presented by the Applicant led to the conclusion that in case of the following eight trials it was not possible to perform the reliable kinetic analysis for FOE Sulfonic acid: 30162/0 Kirchlauter, 30163/9 Monheim, 30164/7 Burscheid, 30254/6 Saussay-la-Campagne, 30455/7 Fresne-L'Archeveque, 30499/9 Burscheid, 30500/6 Monheim and 40495/0 S. Romualdo.

The remaining data base, for which RMS performed the evaluation of the results of the kinetic analysis obtained by the Applicant for Flufenacet and FOE Sulfonic acid, comprised the following trials:

- 30159/0 Breitenfelde;
- 30248/1 Fresne-L'Archeveque;
- 30250/3 Fresne-L'Archeveque;
- 30251/1 Laudun;
- 30253/8 St. Etienne du Gres;
- 40163/3 Laudun;
- 40164/1 St. Etienne du Gres;
- 40494/2 Ravenna.

It shall be noted that of all trials listed above only one – 30159/0 Breitenfelde, was performed on bare soil, and the remaining seven on cropped soil with the test compound applied to the soil surface shortly before or after the emergence of the crop.

In case of the remaining eight trials the results of the kinetic examination obtained for Flufenacet were evaluated by the RMS.

As a next element the Applicant presented the method of the normalisation of the degradation parameters for the temperature and soil moisture, used in the study. It was stated that neither on-field daily soil temperature nor soil moisture data, necessary to normalise these parameters were available, the suitable simulation method was used to generate them.

In the study report from the field trials the data on temperature and rainfall were reported as weekly, then 10-days and finally monthly sums and averages. The utility of such weather data is limited, because the normalisation procedures in the current Guidelines recommend to use the continuous weather data, measured day-by-day. For that reason the MARS weather data base was used to provide the daily variations of these parameters. For each trial site the data taken from the data base covered the period in which it was carried out and the selected MARS grid cell was closest to the specific location of the trial. The Applicant stated that because of the dimension of the grid cells within the MARS database – 50/50 km, the weather data collected on the test site or by the weather station closest were used to calibrate the MARS data. For that purpose the mean temperature and cumulative rainfall values measured on/at the site and resulting from MARS data were calculated. Next the ratio between the cumulative rainfall and the difference between mean temperature values were determined and applied to the original MARS daily data. Finally, these corrections were implemented in PEARL via *FacPrc* and *DifTem* factors. The obtained estimated values for precipitation and temperature were used as climatic conditions on the trial sites.

The results of that estimation of the weather data, as presented in the study report, are provided below in the table B.8.1.1.2.2.1_CA-133.

According to the current Guidelines that approach is admissible, but not recommended as a first-choice solution. It may be used only when the weather data measured in daily intervals are not available, and not unconditionally – the approach is recommended only where the averaging period is short (in case of the discussed trials the duration is on average 248 days, with range 231 – 303 days) and the climatic conditions within that period are stable (in this particular case the trials cover the period from spring to winter of the same year, but for two trials they start in late autumn and last until summer of the next year, so the variability of the climatic conditions within the experimental period may be, in RMS's opinion, significant). Additionally it is recommended that the calculated weather data should be checked against the measured ones whenever that is possible.

Table B.8.1.1.2.2.1_CA-133: The climatic conditions and weather data on each trial site used in the kinetic evaluation of the data obtained in field dissipation studies for Flufenacet.

Information on the trial:			Duration of the trial after application of the test compound [days]	Weather data			
Trial number	Trial site - name	Location - country		Source of the weather data	Mars grid cell	Experimental weather data collected at trial site	
						Cumulative rainfall [mm]	Mean temperature T [°C]
30159/0	Breitenfelde	Germany	240	German Weather Service, Lübeck	64060	592	11.0
30162/0	Kirchlauter	Germany	237	Weather station in 4 km from the trial site	56060	319	11.1
30163/9	Monheim	Germany	231	Trial Station Laacherhof	58055	653	12.1
30164/7	Burscheid	Germany	239	Trial Station Höfchen	58055	839	10.6
30248/1	Fresne-L'Archeveque	France (North)	303	Meteo France Station de Boos	55047	870	9.6
30250/3	Fresne-L'Archeveque	France (North)	297	Meteo France Station de Boos	55047	778	9.4
30251/1	Laudun	France (South)	255	Meteo France Station Chusclan	43051	683	15.2
30253/8	St. Etienne du Gres	France (South)	260	Meteo France Station Chateuarenard	42051	670	14.8
30254/6	Saussay-la-Campagne	France (South)	242	Meteo France Station de Boos (76)	55047	598	12.7
30455/7	Fresne-L'Archeveque	France (North)	240	Meteo France Station de Boos (76)	55047	661	13.0
30499/9	Burscheid	Germany	234	Versuchsgut Höfchen, 41399 Burscheid	58055	695	6.3
30500/6	Monheim	Germany	240	Versuchsgut Laacherhof, 40789 Monheim	58055	815	6.3
40163/3	Laudun	France (South)	240	Meteo France	43051	658	16.8
40164/1	St. Etienne du Gres	France (South)	236	Meteo France	42051	640	18.7
40494/2	Ravenna	Italy	236	Ar. Sperim. M. Marani/Ravenna	44063	407	17.0
40495/0	S. Romualdo	Italy	236	Ar. Sperim. M. Marani/Ravenna	44063	407	17.0

Next the available data were evaluated. In the study report it was stated that due to the relative high mobility of FOE Sulfonic acid, conformed by batch sorption studies and lysimeter studies, the substantial leaching from the topsoil (0-30 cm layer) cannot be ruled out and as a result may be quantitatively relevant dissipation process, needed to be separated from degradation. As the most appropriate measure to do that the inverse modeling was applied. That was done using two modeling tools: PEST and PEARL. The selection of PEARL, used to separate degradation from other dissipative processes, in the assessment was justified in the following way (the wording of the justification is that provided by the Applicant in the study report):

- it "is a state-of-art soil transport model recommended by FOCUS for pesticides and well accepted for regulatory exposure assessment.";
- "the model used in the inverse procedure is the same which is used for later exposure assessment and guarantees thereby maximum consistency between the derivation and application of the parameters optimised."

PEST was selected being "a versatile and well-established optimization tool which can be coupled with any stand-alone models". RMS also determined that PEST is one of the recommended tools for inverse modeling listed in the reference documents used to verify the validity of this study.

The parameters that were listed to be fitted in the inverse modeling were:

- the DT₅₀ values for Flufenacet and FOE Sulfonic acid,
- the formation fraction *ff* for FOE Sulfonic acid,
- the mass applied.

The reference temperature for the DT₅₀ values was set to T = 20°C and soil moisture to 100%FC, in line with recommendations given by FOCUS. Other not optimised parameters were estimated based on the site-specific

information on soil, weather and crop according to the best practice. In case of not optimised substance-specific parameters, namely sorption parameters for Flufenacet and FOE Sulfonic values, the values were the same as reported in the EU-agreed LoEP.

Because of the constraints of the modeling tool PEARL – in that model the degradation is described by the SFO kinetic model, none of the bi-phasic models was used.

The depth of the soil profile used in the estimation was 1 metre. This assumption was made to minimise the influence of the lower boundary of the simulation domain onto the region of interest – 0-30 cm layer. It was divided into 2.5-cm layers. The lower boundary conditions was set to free drainage to represent well drained soils not affected by shallow ground water.

The soil properties for each trial were defined in line with the description of each test soil provided in the relevant study report. The last horizon was defined to reach the bottom of the simulated soil profile. Hydraulic parameters were derived from soil texture using the class pedotransfer function of Schaap and Leij and soil bulk density was estimated using the pedotransfer function implemented in PEARL.

In case of the cropped trials standard crop parameters from the FOCUS scenario Piacenza were used for each crop reported in the relevant study report. The emergence and harvest dates were set according to the agricultural practices at the specific site assuming 10-days interval between sowing and emergence. That was done also for the trial 30248/1 Fresne-L'Archeveque, initially incorrectly characterized by the Applicant as performed on bare soil.

Other parameters required for modelling were set to the FOCUS default values. The Arrhenius molar activation energy were set to 65.4 kJ/mol, corresponding to $Q_{10} = 2.58$, in line with the up-to-date FOCUS recommendations.

The output of the inverse modeling – the mass in the top 30 cm, was used as modeled results to be compared with the pre-processed measured values.

The PEARL modeling tool, used to simulate water and heat flow, was its 3.0 version. PEST software was used for optimization, consisting on the minimization of the sum of squared differences between measured and calculated data using the Gauss-Marquardt-Levenberg algorithm.

The kinetic analysis of the data was performed in line with the recommendations provided by FOCUS Kinetics guidance document. The applicant stated that for that purpose the earliest accepted version of the Guidelines – 1.0 dated on 2005, was used (n.b. RMS noticed that the date of the issuing of the report implies that the currently recommended version 2.0 of 2006 of that document should rather be used). Although FOCUS Kinetics recommends that four kinetic models – SFO, FOMC, DFOP and HS, should be considered, in practice, due to the constraints related to the PEARL model used in the inverse modeling, only SFO model was used. The weighting of data was not performed in the kinetic analysis.

The obtained fits were evaluated in line with recommendations given by FOCUS, by assessing the goodness of fit visually and statistically. The principles of that assessment were similar to those used by the Applicant in other kinetic evaluations performed for Flufenacet and its degradation products, outlined in the study summaries presented under the point B.8.1.1.2.1.1. of this Renewal Assessment Report.

Results and their discussion:

The results of the initial optimization of the kinetic parameters is presented below in the table B.8.1.1.2.2.1._CA-134. Next table – B.8.1.1.2.2.1._CA-135 presents the optimised ff values with their CIs and correlation coefficients between ff and corresponding DT_{50} value for FOE Sulfonic acid ($c(ff - DT_{50 \text{ FOE SA}})$) for the given trial. Evaluating the results the Applicant stated that for the parent compound the χ^2 error was in most cases lower than 15% and always below 20%, indicating that the fit was good. As for the degradation product – FOE Sulfonic acid, the χ^2 error was in most cases lower than 30%, what was considered to be a good result taking into account low residue levels.

The DT_{50} values for the parent compound – Flufenacet, were considered well defined, i.e. sufficiently reliable, but that was not a case for the DT_{50} values for FOE Sulfonic acid, which had large CI. Those values were also strongly correlated with the corresponding ff values, displaying as well significant level of uncertainty. To solve that problem the Applicant decided to use in the final estimation the fixed $ff = 0.26$ – the mean value obtained in the laboratory studies and reported during the first evaluation of Flufenacet for its authorization in the EU. RMS has to indicate that as a result of the repeated kinetic analysis that value was reduced to 0.195, what is close to the mean field $ff = 0.18$ obtained in the presently evaluated study report.

Table B.8.1.1.2.2.1._CA-134: The optimised parameters obtained at initial step of evaluation.

Information on the trial		Optimised parameters							
		M_0 [g a. s./ha]	Kinetic parameters for Flufenacet and their statistical evaluation			Kinetic parameters for FOE Sulfonic acid and their statistical evaluation			
			DT ₅₀ [days]		χ^2 error [%]	DT ₅₀ [days]		ff value	χ^2 error [%]
Trial number	Trial site - name		value	CI range		value	CI range		
30159/0	Breitenfelde	342	16.9	14.1 – 20.3	10.2	26.8	1.4 – 518.4	0.182	26.1
30162/0	Kirchlauter	403	33.3	23.4 – 47.4	19.5	42.5	0 - >10000	0.131	20.5
30163/9	Monheim	252	31.7	24.2 – 41.5	15.4	32.4	0.1 - >10000	0.196	26.5
30164/7	Burscheid	474	11.4	10.3 – 12.7	7.3	1000.0	0 - >10000	0.049	49.2
30248/1	Fresne-L'Archeveque	475	31.3	24.6 – 39.8	14.3	28.7	0 - >10000	0.182	35.9
30250/3	Fresne-L'Archeveque	400	32.8	28.3 – 38.1	8.8	1000.0	0 - >10000	0.113	23.7
30251/1	Laudun	591	24.5	20.7 – 28.9	10.6	1000.0	0 - >10000	0.087	26.1
30253/8	St. Etienne du Gres	435	37.5	32.9 – 42.7	8.9	49.6	0.4 – 6974.2	0.142	22.2
30254/6	Saussay-la-Campagne	164	6.0	3.9 – 9.3	11.5	Assessment not performed			
30455/7	Fresne-L'Archeveque	135	7.1	5.4 – 9.5	10.8	Assessment not performed			
30499/9	Burscheid	193	8.5	7.2 – 10.0	9.3	200.9	0 - >10000	0.212	21.0
30500/6	Monheim	157	14.7	9.5 – 22.7	13.5	Assessment not performed			
40163/3	Laudun	362	45.5	33.4 – 61.8	16.6	31.5	0 - >10000	0.261	27.7
40164/1	St. Etienne du Gres	391	40.8	30.2 – 55.1	16.1	8.6	0 - >10000	0.463	51.3
40494/2	Ravenna	481	36.6	27.8 – 48.2	14.5	336.3	0 - >10000	0.116	53.1
40495/0	S. Romualdo	540	50.7	41.6 – 61.9	10.3	33.0	0 - >10000	0.145	23.2

Table B.8.1.1.2.2.1._CA-135: The optimised parameters obtained at the initial step of evaluation – detailed data for kinetic formation fractions.

Information on the trial		Optimised parameters			
Trial number	Trial site - name	Kinetic formation fractions - ff			Correlation coefficient c(ff – DT _{50 FOE_SA})
		value	CI		
			Lower	Upper	
30159/0	Breitenfelde	0.182	-0.132	0.496	-0.8426
30162/0	Kirchlauter	0.131	-0.679	0.941	-0.8830
30163/9	Monheim	0.196	-0.665	1.057	-0.8900
30164/7	Burscheid	0.049	-0.048	0.147	-0.8676
30248/1	Fresne-L'Archeveque	0.182	-0.614	0.978	-0.8954
30250/3	Fresne-L'Archeveque	0.113	-0.283	0.508	-0.9513
30251/1	Laudun	0.087	-0.120	0.294	-0.8743
30253/8	St. Etienne du Gres	0.142	-0.168	0.453	-0.8953
30254/6	Saussay-la-Campagne	Assessment not performed			
30455/7	Fresne-L'Archeveque	Assessment not performed			
30499/9	Burscheid	0.212	0.016	0.408	-0.6638
30500/6	Monheim	Assessment not performed			
40163/3	Laudun	0.261	-0.690	1.212	-0.8763
40164/1	St. Etienne du Gres	0.463	-2.867	3.792	-0.9382
40494/2	Ravenna	0.116	-0.366	0.599	-0.8341
40495/0	S. Romualdo	0.145	-1.471	1.760	-0.9074

As a next step the optimisation procedure was repeated using the refined parameters – the kinetic formation fractions for each trial fixed to $ff = 0.26$. The graphical results of the fitting are presented below, individually for each trial, on figures B.8.1.1.2.2.1._CA-85 – B.8.1.1.2.2.1._CA-100. The numerical results of the fitting - optimised parameters and the statistical evaluation, is provided further down the report in the table B.8.1.1.2.2.1._CA-136.

11.5.2.1 Trial 30159/0, Breitenfelde, Germany

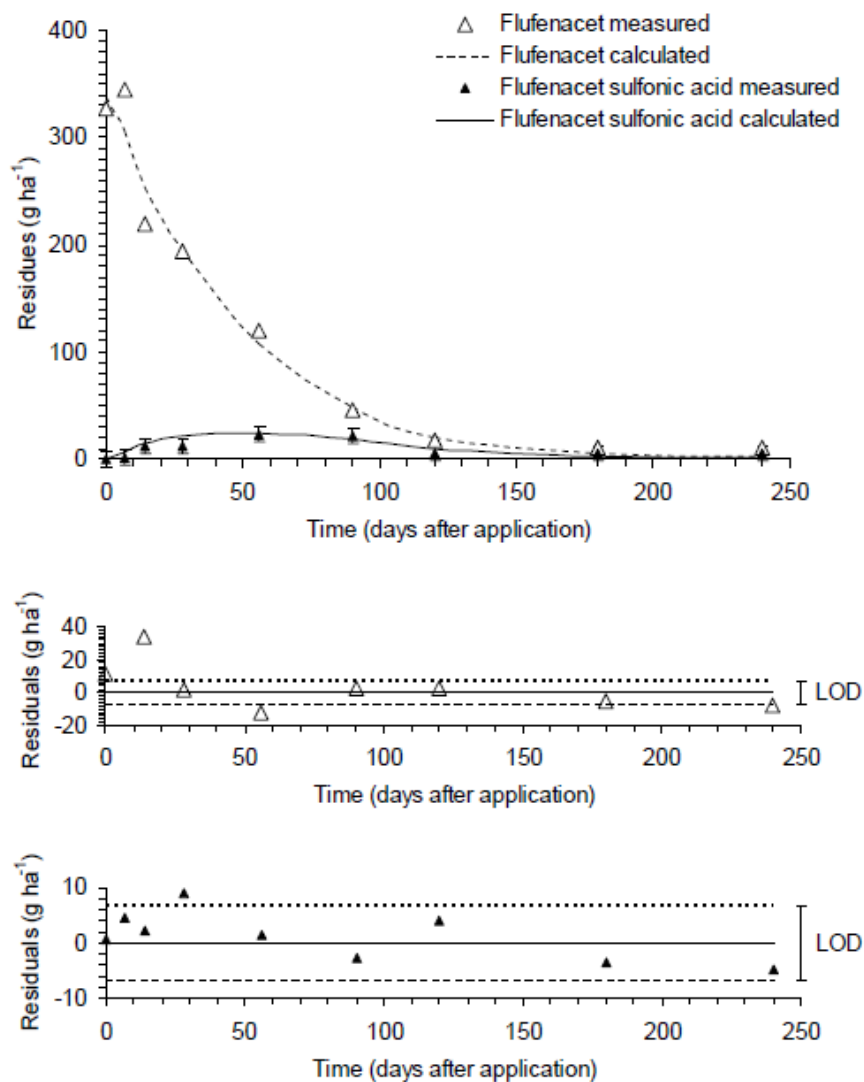


Figure 3: Modelled (solid line) and measured (symbols) residues of flufenacet and flufenacet - sulfonic acid (top), residuals of flufenacet (middle) and flufenacet - sulfonic acid (bottom) for trial 30159/0, Breitenfelde, Germany.

Figure B.8.1.1.2.2.1_CA-85: The graphical results of the kinetic analysis of the data obtained in the trial *30159/0 Breitenfelde* (copied from the study report).

11.5.2.2 Trial 30162/0, Kirchlauter, Germany

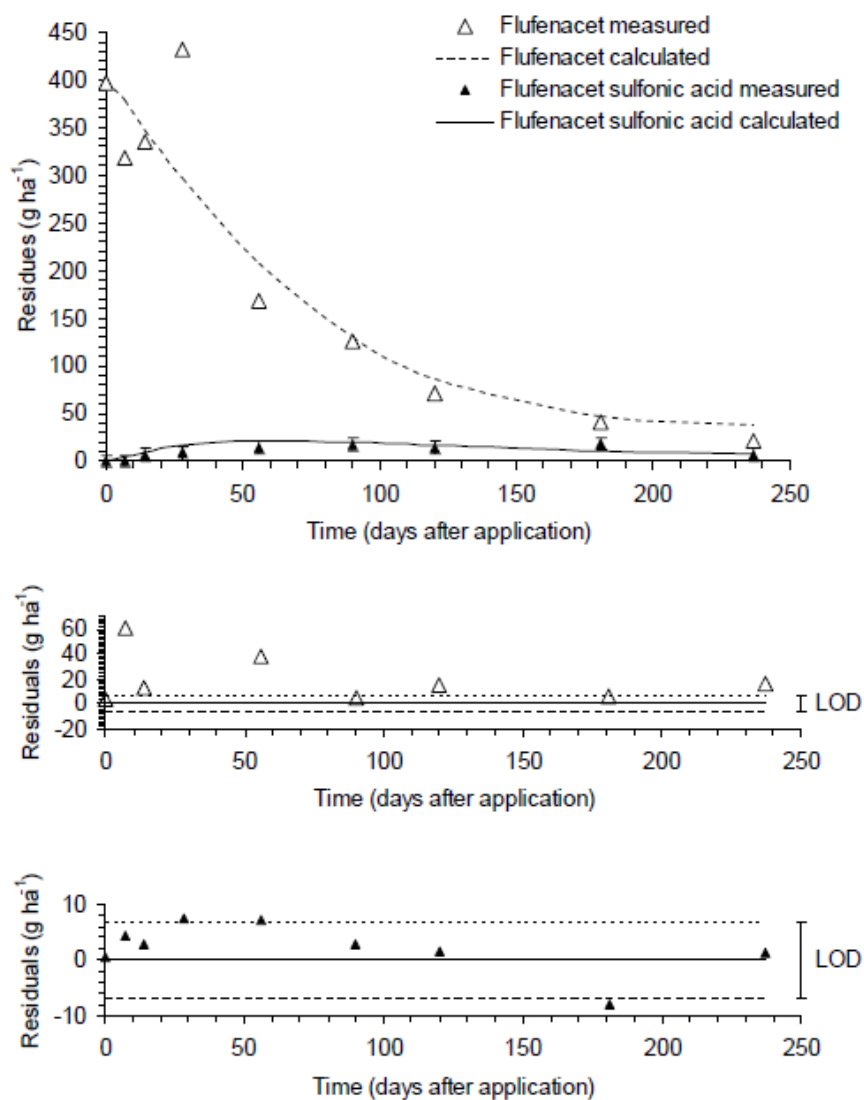


Figure 4: Modelled (solid line) and measured (symbols) residues of flufenacet and flufenacet - sulfonic acid (top), residuals of flufenacet (middle) and flufenacet - sulfonic acid (bottom) for trial 30162/0, Kirchlauter, Germany.

Figure B.8.1.1.2.2.1_CA-86: The graphical results of the kinetic analysis of the data obtained in the trial *30162/0 Kirchlauter* (copied from the study report).

11.5.2.3 Trial 30163/9, Monheim, Germany

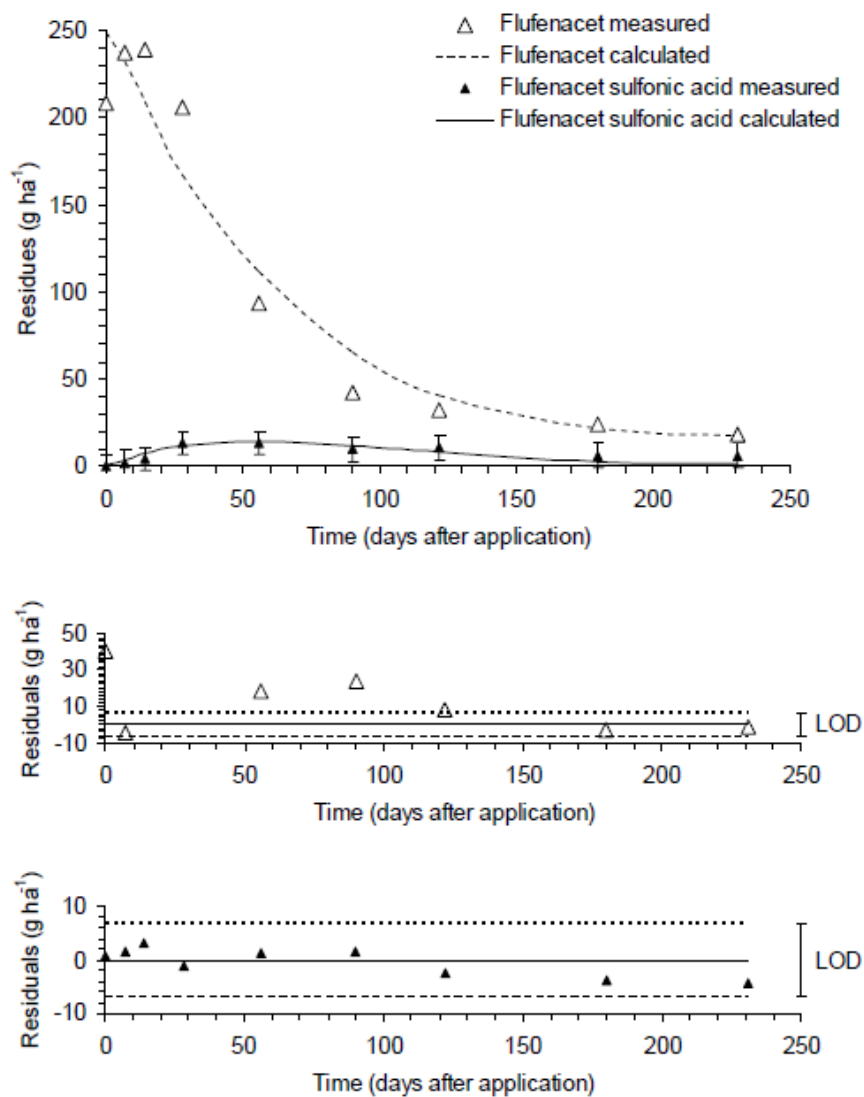


Figure 5: Modelled (solid line) and measured (symbols) residues of flufenacet and flufenacet - sulfonic acid (top), residuals of flufenacet (middle) and flufenacet - sulfonic acid (bottom) for trial 30163/9, Monheim, Germany.

Figure B.8.1.1.2.2.1._CA-87: The graphical results of the kinetic analysis of the data obtained in the trial *30163/9 Monheim* (copied from the study report).

11.5.2.4 Trial 30164/7, Burscheid, Germany

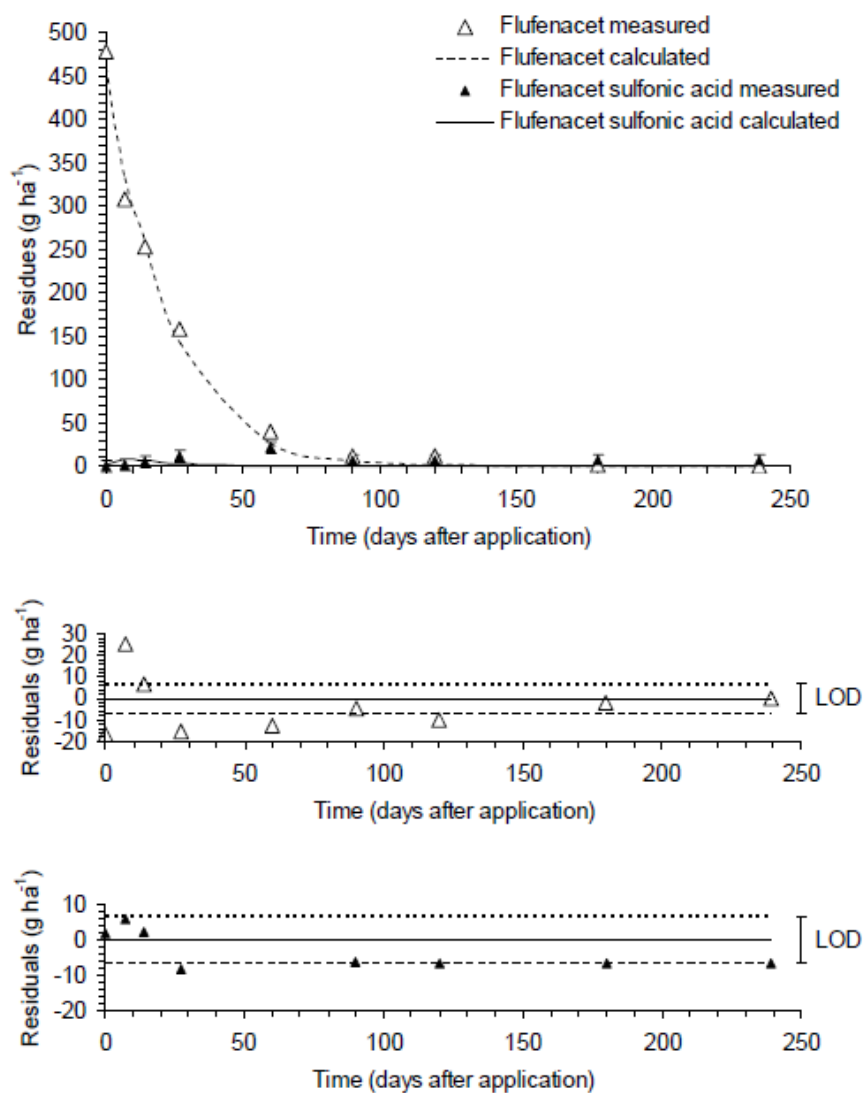


Figure 6: Modelled (solid line) and measured (symbols) residues of flufenacet and flufenacet-sulfonic acid (top), residuals of flufenacet (middle) and flufenacet-sulfonic acid (bottom) for trial 30164/7, Burscheid, Germany.

Figure B.8.1.1.2.2.1_CA-88: The graphical results of the kinetic analysis of the data obtained in the trial *30164/7 Burscheid* (copied from the study report).

11.5.2.5 Trial 30248/1, Fresne-L'Archeveque, France

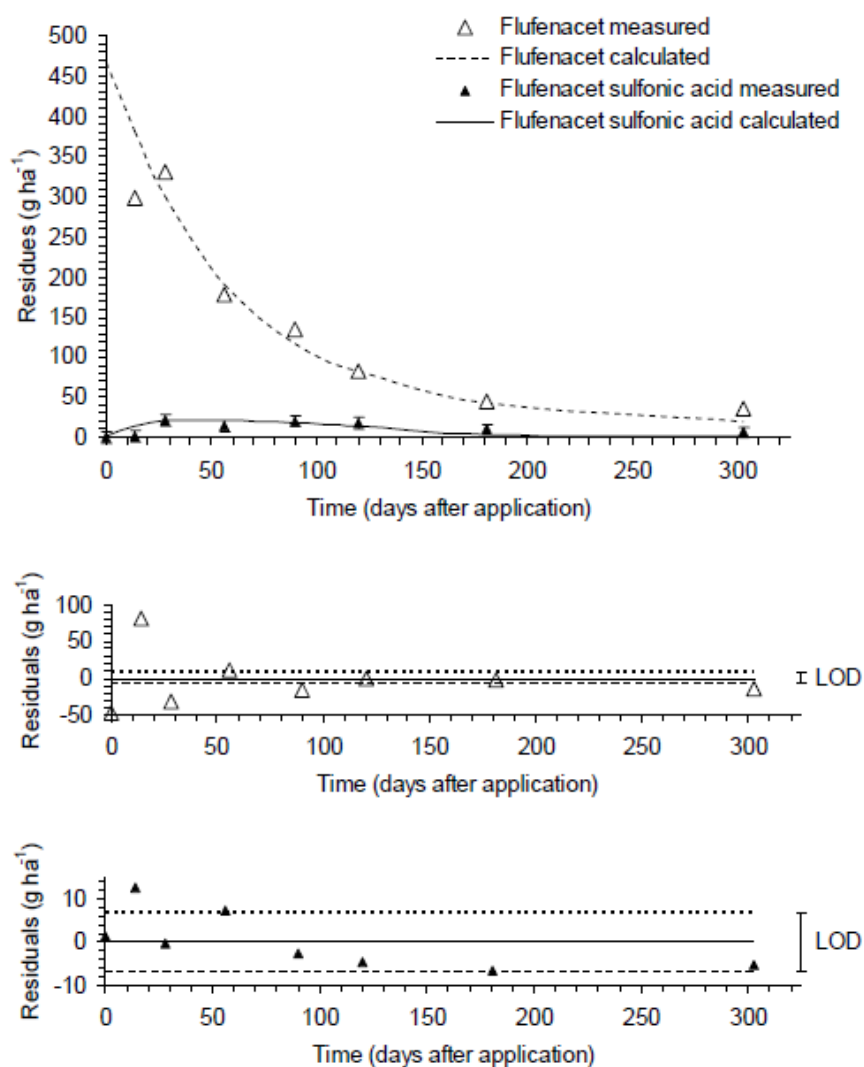


Figure 7: Modelled (solid line) and measured (symbols) residues of flufenacet and flufenacet - sulfonic acid (top), residuals of flufenacet (middle) and flufenacet - sulfonic acid (bottom) for trial 30248/1, Fresne-L'Archeveque, France.

Figure B.8.1.1.2.2.1. CA-89: The graphical results of the kinetic analysis of the data obtained in the trial 30248/1 *Fresne-L'Archeveque* (copied from the study report).

11.5.2.6 Trial 30250/3, Fresne-L'Archeveque, France

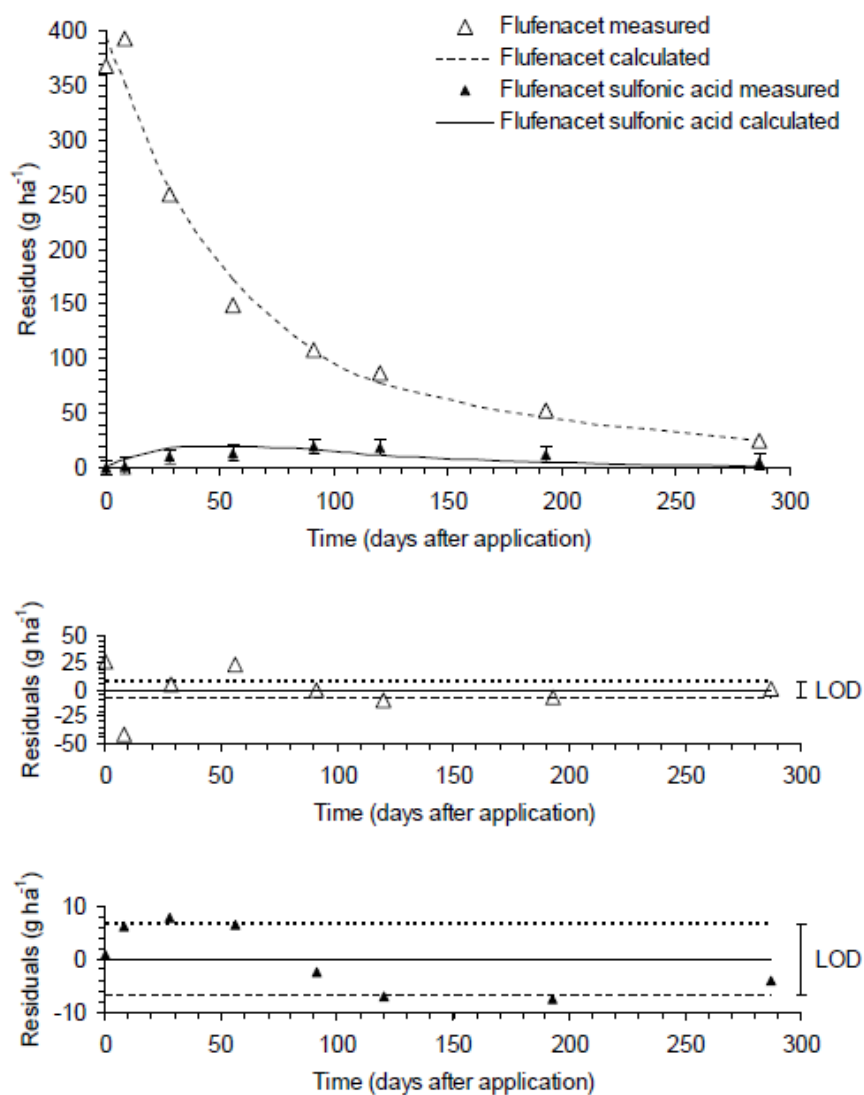


Figure 8: Modelled (solid line) and measured (symbols) residues of flufenacet and flufenacet - sulfonic acid (top), residuals of flufenacet (middle) and flufenacet - sulfonic acid (bottom) for trial 30250/3, Fresne-L'Archeveque, France.

Figure B.8.1.1.2.2.1. CA-90: The graphical results of the kinetic analysis of the data obtained in the trial 30250/3 *Fresne-L'Archeveque* (copied from the study report).

11.5.2.7 Trial 30251/1, Laudun, France

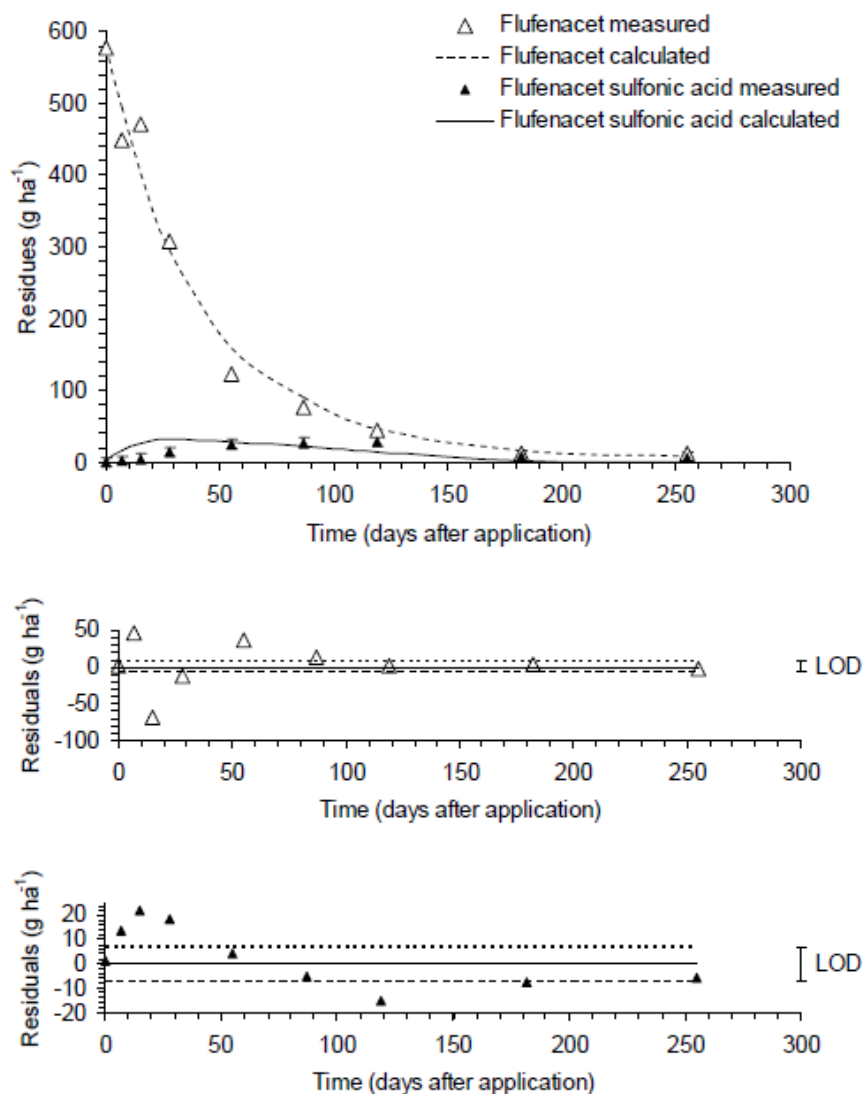


Figure 9: Modelled (solid line) and measured (symbols) residues of flufenacet and flufenacet - sulfonic acid (top), residuals of flufenacet (middle) and flufenacet - sulfonic acid (bottom) for trial 30251/1, Laudun, France.

Figure B.8.1.1.2.2.1_CA-91: The graphical results of the kinetic analysis of the data obtained in the trial *30251/1 Laudun* (copied from the study report).

11.5.2.8 Trial 30253/8, St. Etienne du Gres, France

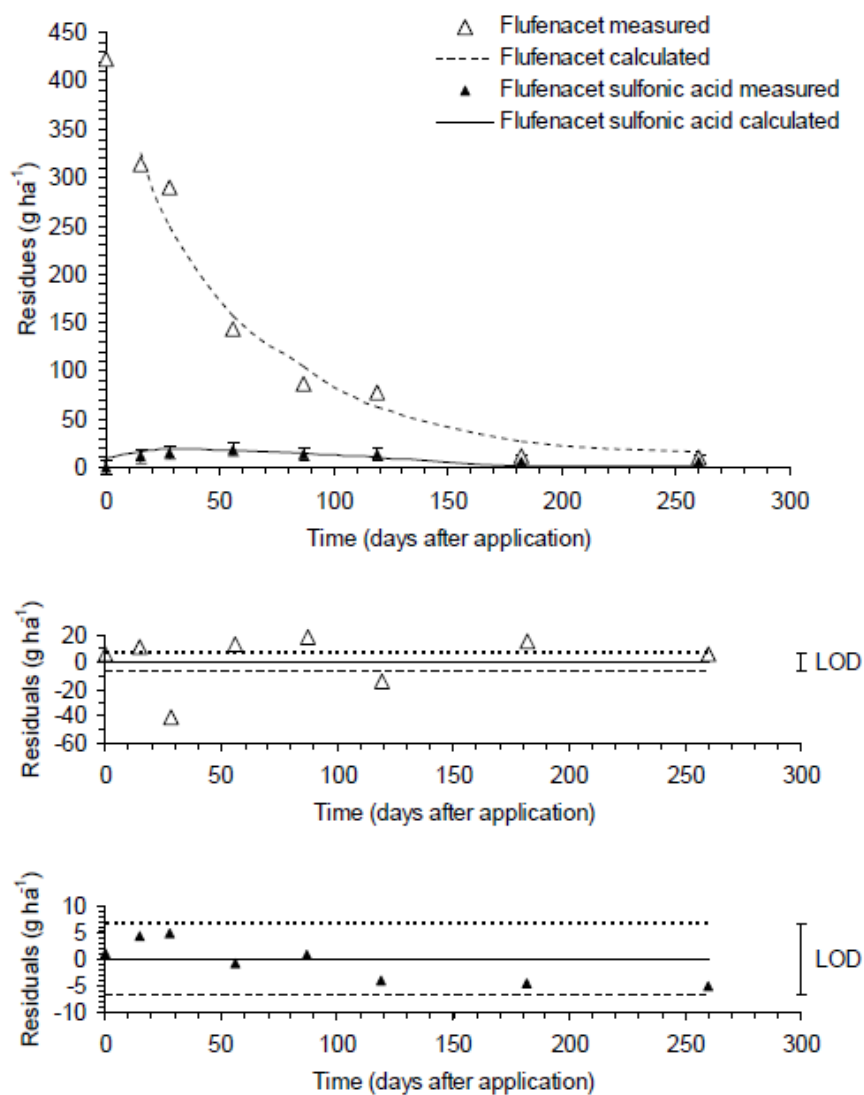


Figure 10: Modelled (solid line) and measured (symbols) residues of flufenacet and flufenacet - sulfonic acid (top), residuals of flufenacet (middle) and flufenacet - sulfonic acid (bottom) for trial 30253/8, St. Etienne du Gres, France.

Figure B.8.1.1.2.2.1._CA-92: The graphical results of the kinetic analysis of the data obtained in the trial 30253/8 *St. Etienne du Gres* (copied from the study report).

11.5.2.9 Trial 30254/6, Saussay La Campagne, France

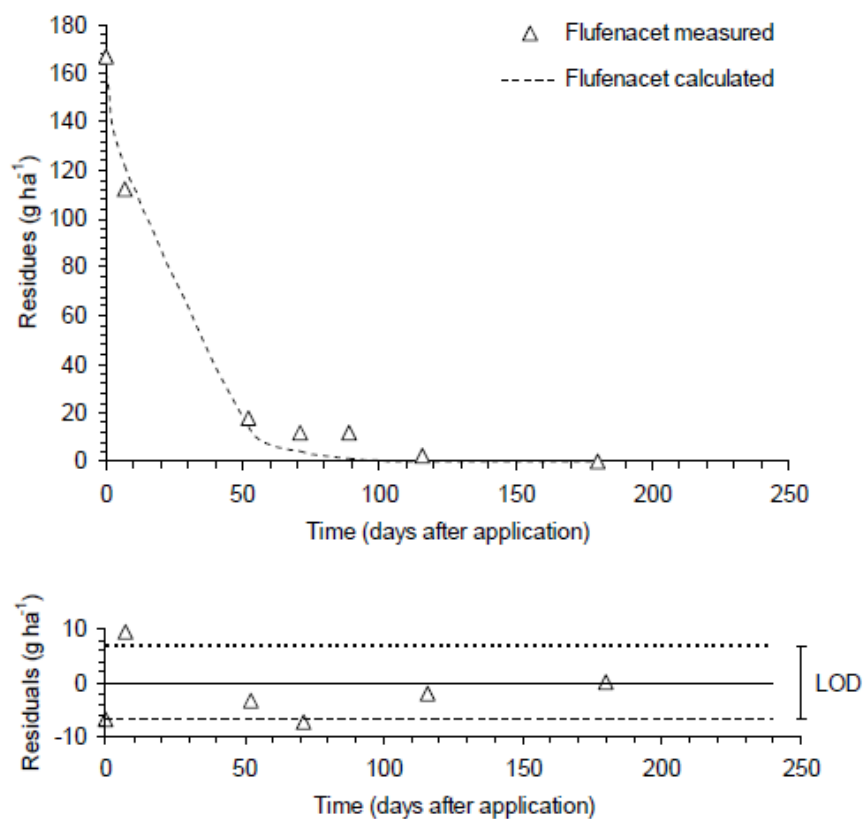


Figure 11: Modelled (solid line) and measured (symbols) residues of flufenacet (top), residuals of flufenacet (bottom) for trial 30254/6, Saussay La Campagne, France. Residues of flufenacet - sulfonic acid were always below LOD.

Figure B.8.1.1.2.2.1. CA-93: The graphical results of the kinetic analysis of the data obtained in the trial *30254/6 Saussay-la-Campagne* (copied from the study report).

11.5.2.10 Trial 30455/7, Fresne-L'Archeveque, France

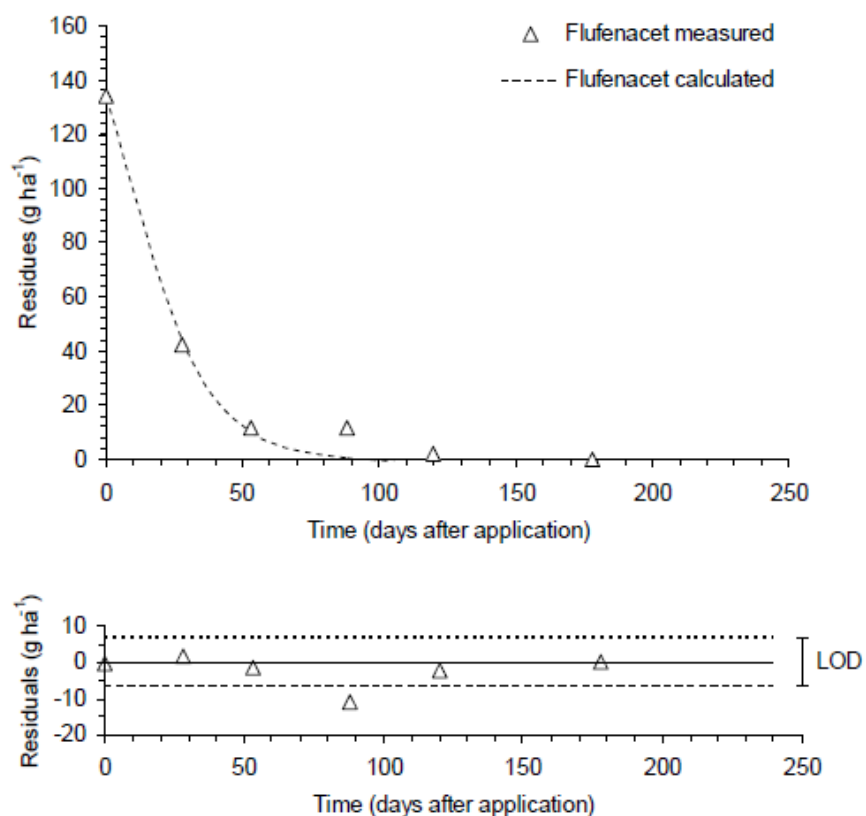


Figure 12: Modelled (solid line) and measured (symbols) residues of flufenacet (top), residuals of flufenacet (bottom) for trial 30455/7, Fresne-L'Archeveque, France. Residues of flufenacet - sulfonic acid were always below LOD.

Figure B.8.1.1.2.2.1. CA-94: The graphical results of the kinetic analysis of the data obtained in the trial 30455/7 *Fresne-L'Archeveque* (copied from the study report).

11.5.2.11 Trial 30499/9, Burscheid, Germany

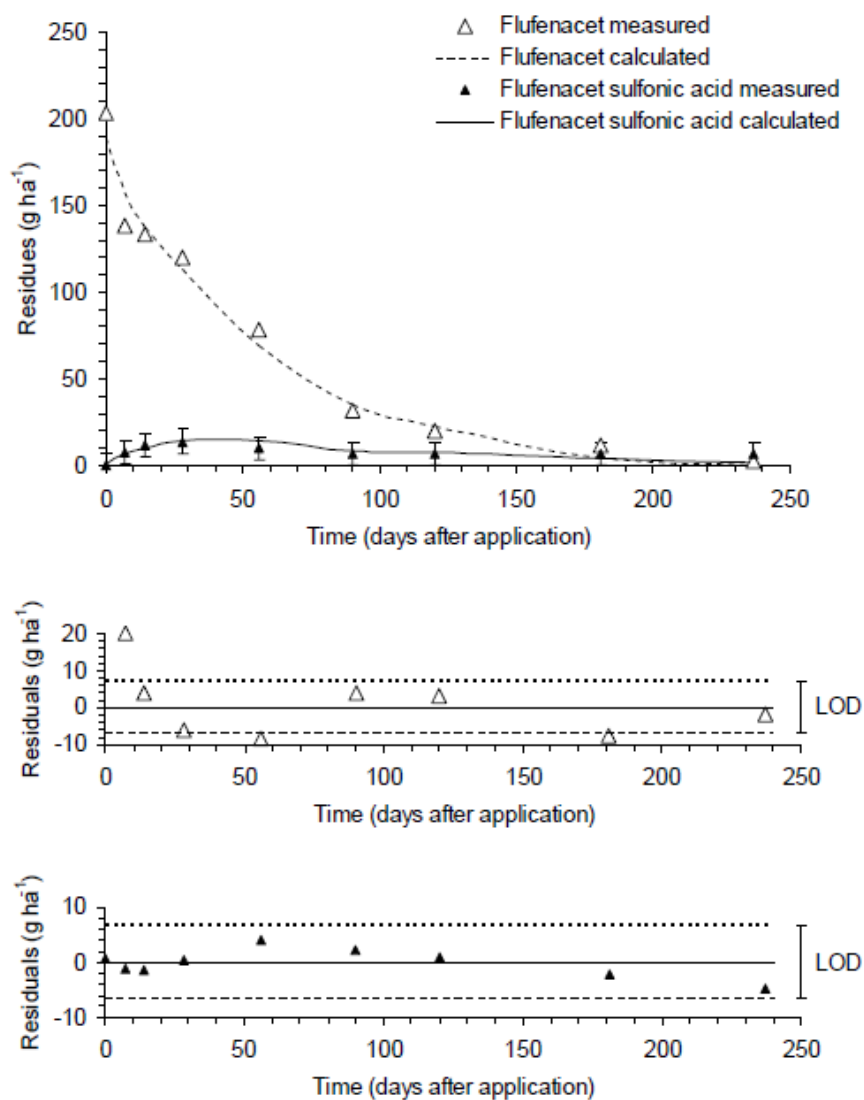


Figure 13: Modelled (solid line) and measured (symbols) residues of flufenacet and flufenacet - sulfonic acid (top), residuals of flufenacet (middle) and flufenacet - sulfonic acid (bottom) for trial 30499/9, Burscheid, Germany.

Figure B.8.1.1.2.2.1._CA-95: The graphical results of the kinetic analysis of the data obtained in the trial *30499/9 Burscheid* (copied from the study report).

11.5.2.12 Trial 30500/6, Monheim, Germany

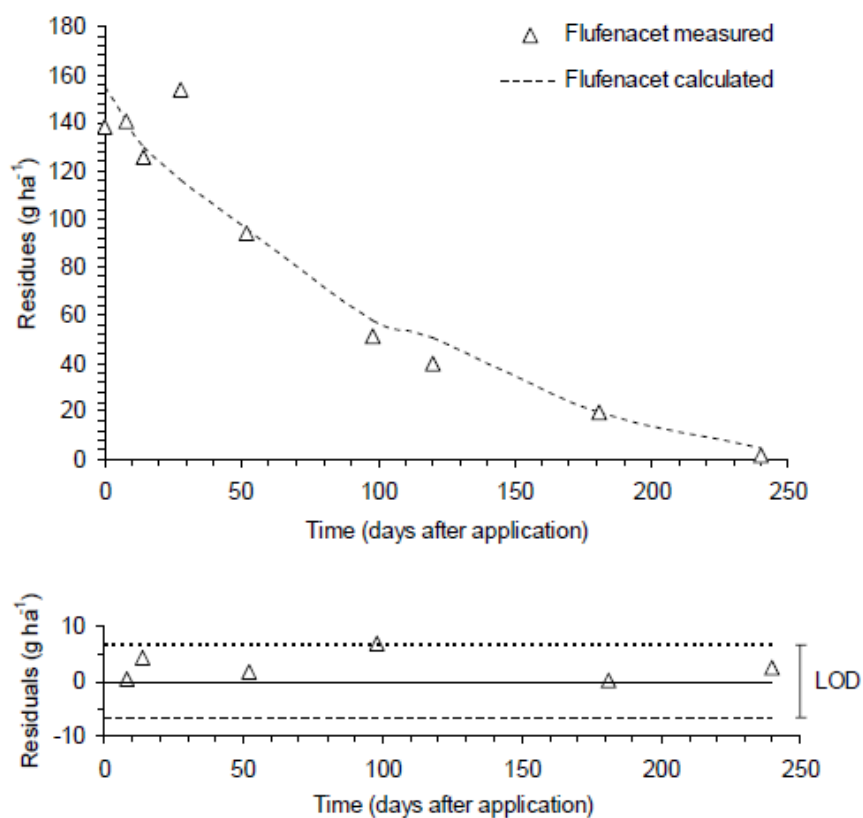


Figure 14: Modelled (solid line) and measured (symbols) residues of flufenacet (top), residuals of flufenacet (bottom) for trial 30500/6, Monheim, Germany. Residues of flufenacet - sulfonic acid were always below LOD.

Figure B.8.1.1.2.2.1._CA-96: The graphical results of the kinetic analysis of the data obtained in the trial *30500/6 Monheim* (copied from the study report).

11.5.2.13 Trial 40163/3, Laudun, France

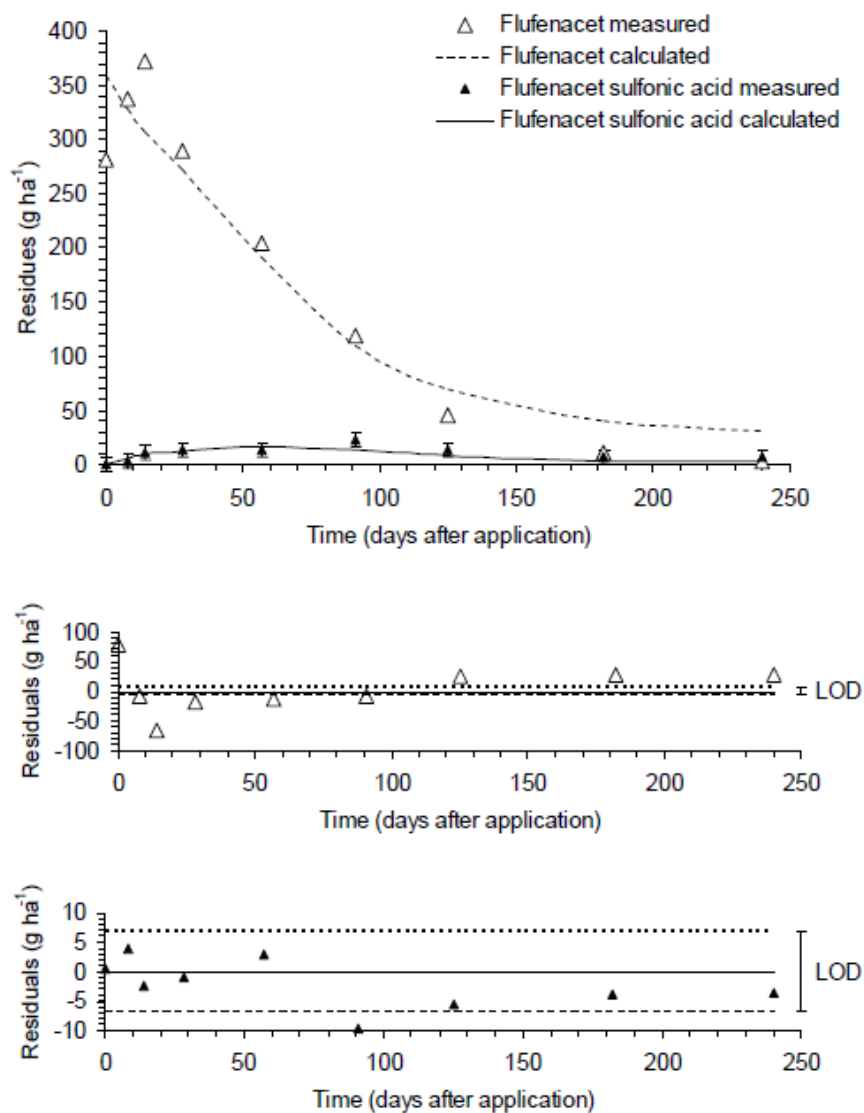


Figure 15: Modelled (solid line) and measured (symbols) residues of flufenacet and flufenacet-sulfonic acid (top), residuals of flufenacet (middle) and flufenacet-sulfonic acid (bottom) for trial 40163/3, Laudun, France.

Figure B.8.1.1.2.2.1._CA-97: The graphical results of the kinetic analysis of the data obtained in the trial *40163/3 Laudun* (copied from the study report).

11.5.2.14 Trial 40164/1, St. Etienne du Gres, France

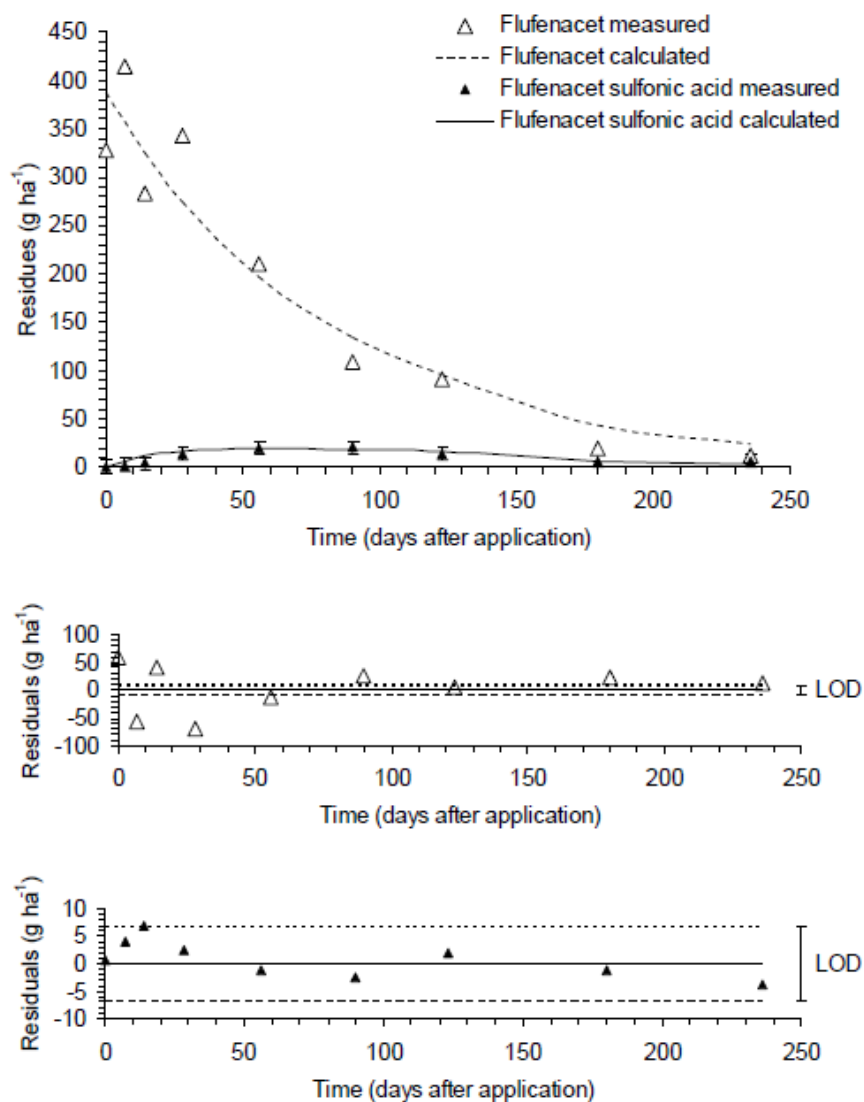


Figure 16: Modelled (solid line) and measured (symbols) residues of flufenacet and flufenacet - sulfonic acid (top), residuals of flufenacet (middle) and flufenacet - sulfonic acid (bottom) for trial 40164/1, St. Etienne du Gres, France.

Figure B.8.1.1.2.2.1._CA-98: The graphical results of the kinetic analysis of the data obtained in the trial *40164/1 St. Etienne du Gres* (copied from the study report).

11.5.2.15 Trial 40494/2, Ravenna, Italy

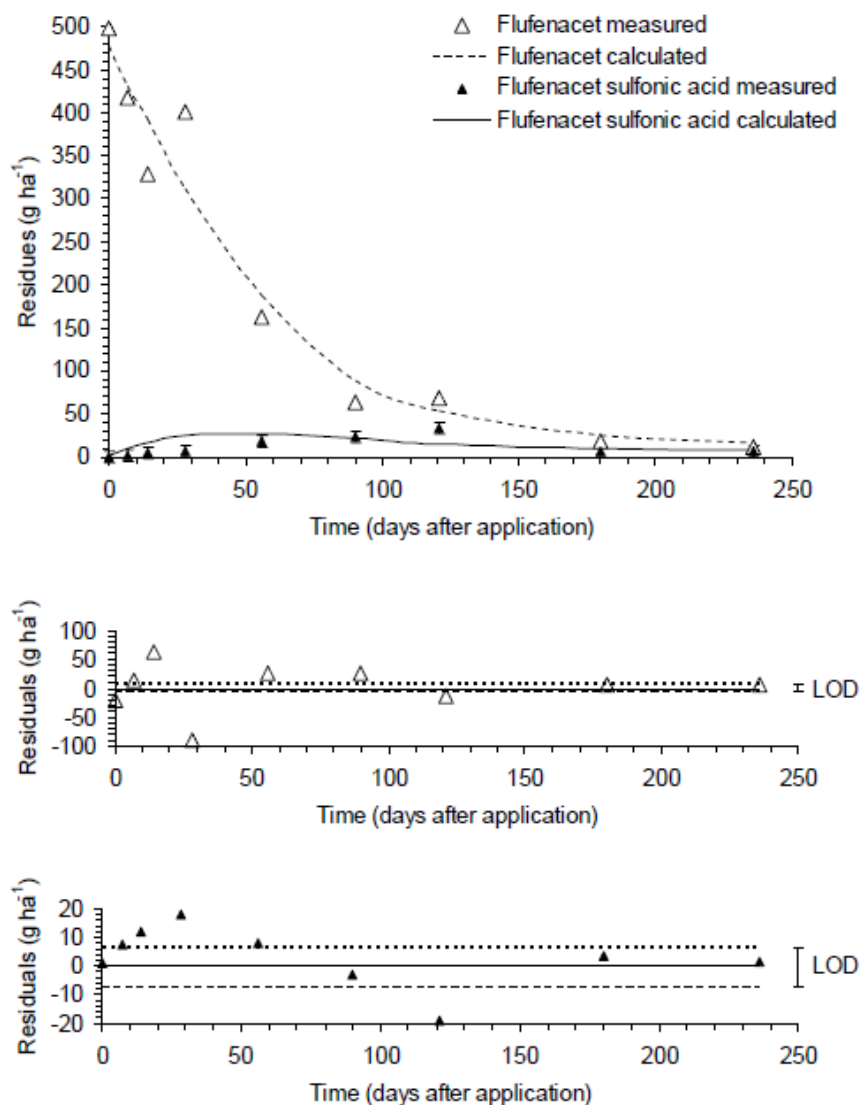


Figure 17: Modelled (solid line) and measured (symbols) residues of flufenacet and flufenacet - sulfonic acid (top), residuals of flufenacet (middle) and flufenacet - sulfonic acid (bottom) for trial 40494/2, Ravenna, Italy.

Figure B.8.1.1.2.2.1._CA-99: The graphical results of the kinetic analysis of the data obtained in the trial *40494/2 Ravenna* (copied from the study report).

11.5.2.16 Trial 40495/0, S.Romualdo, Italy

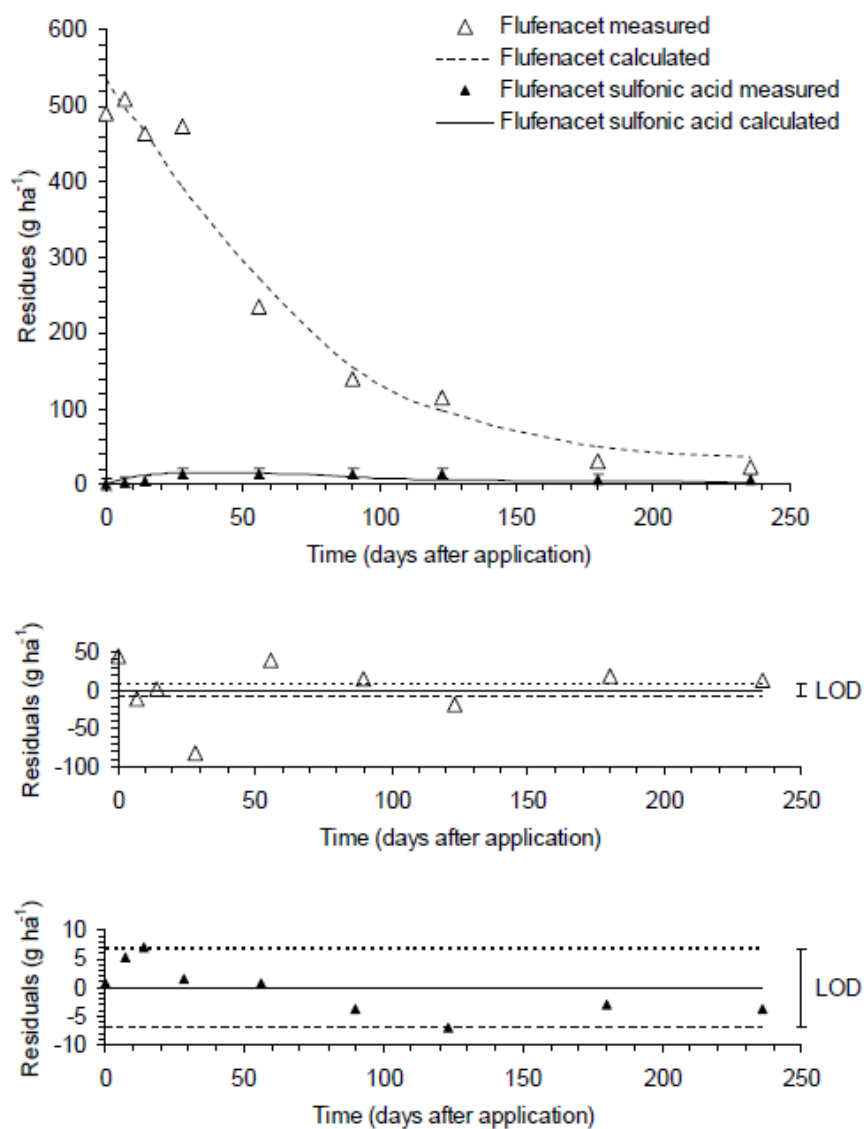


Figure 18: Modelled (solid line) and measured (symbols) residues of flufenacet and flufenacet - sulfonic acid (top), residuals of flufenacet (middle) and flufenacet - sulfonic acid (bottom) for trial 40495/0, S.Romualdo, Italy.

Figure B.8.1.1.2.2.1_CA-100: The graphical results of the kinetic analysis of the data obtained in the trial 40495/0 S. Romualdo (copied from the study report).

Table B.8.1.1.2.2.1_CA-136: The optimised parameters obtained at the final step of evaluation, as reported by the Applicant.

Information on the trial		Optimised parameters						
		M_0 [g a. s./ha]	Kinetic parameters for Flufenacet and their statistical evaluation			Kinetic parameters for FOE Sulfonic acid and their statistical evaluation		
			DT ₅₀ [days]		χ^2 error [%]	DT ₅₀ [days]		χ^2 error [%]
Trial number	Trial site - name		value	CI range		value	CI range	
30159/0	Breitenfelde	341	17.1	14.3 – 20.3	10.2	17.7	5.6 – 55.7	24.8
30162/0	Kirchlauter	402	33.3	23.5 – 47.0	19.5	19.8	1.4 – 283.7	38.1
30163/9	Monheim	252	31.8	24.6 – 41.0	15.4	20.5	1.8 – 236.0	26.9
30164/7	Burscheid	473	11.4	10.1 – 12.9	7.4	1.3	0.2 – 11.6	91.7
30248/1	Fresne-L'Archeveque	474	31.4	24.9 – 39.4	14.4	18.1	1.7 – 189.2	40.4
30250/3	Fresne-L'Archeveque	399	32.9	28.5 – 38.0	8.8	20.8	4.6 – 94.5	42.0
30251/1	Laudun	588	24.7	20.8 – 29.3	10.6	18.9	4.7 – 75.9	72.3
30253/8	St. Etienne du Gres	434	37.6	33.1 – 42.6	8.9	19.6	5.9 – 65.2	32.0
30254/6	Saussay-la-Campagne	164	6.0	3.9 – 9.3	11.5	Assessment not performed		
30455/7	Fresne-L'Archeveque	135	7.1	5.4 – 9.5	10.8	Assessment not performed		
30499/9	Burscheid	192	8.5	7.2 – 10.1	9.3	29.8	0.7 – 1198.4	23.9
30500/6	Monheim	157	14.7	9.5 – 22.7	13.5	Assessment not performed		
40163/3	Laudun	362	45.3	33.7 – 60.8	16.5	21.8	0.8 – 629.7	35.1
40164/1	St. Etienne du Gres	391	41.0	30.7 – 54.7	16.2	25.0	1.2 – 523.7	25.8
40494/2	Ravenna	483	36.2	27.9 – 47.1	14.5	41.43	2.5 – 688.0	68.8
40495/0	S. Romualdo	539	51.1	42.2 – 61.9	10.3	14.1	0.4 – 480.8	40.2

Analysing the results obtained in refined kinetic evaluation of the data the Applicant stated that the values obtained for Flufenacet changed slightly, but significant improvement was obtained for FOE Sulfonic acid. They became more reliable and consistent.

At the same time in case of the two trials – **30164/7 Burscheid** and **30251/1 Laudun**, the Applicant stated that for FOE Sulfonic acid the results cannot be considered reliable because of the insufficient goodness of fit, what is reflected in very high value of χ^2 error. Also in case of their trial 40494/2 Ravenna, the fit is not appropriate. The Applicant stated that the residues in the early phase were underestimated, while those in the medium phase overestimated (however, in the study report it was not explained what the terms “early phase” and “medium phase” meant). The χ^2 error was also high, although lower than in case of the two rejected fits. N.b the RMS noticed that in case of the trials **30251/1 Laudun** and **40494/2 Ravenna** the levels of χ^2 error were comparable – 72.3% and 68.8% respectively, what may indicate that the problems with fitting were similar, what is confirmed by very similar shape of the kinetic curve in relation to the distribution of the data points, as well as range, distribution and individual values of the residuals. RMS also noticed that in case of the trial **30251/1 Laudun** the range of CI for DT₅₀ for FOE Sulfonic acid was narrower than that determined in case of the trial **40494/2 Ravenna**. Therefore the whole approach adopted by the Applicant seems inconsistent – the results obtained for FOE Sulfonic acid in both trials shall be either rejected (in RMS's opinion recommended solution), or accepted and hence included into the data base (solution not recommended, in RMS's opinion, due to the listed above deficiencies of both fits). Finally, it shall be noted that these two trials were also identified by the RMS in course of the kinetic analysis aimed on the determination of the persistence endpoints as those for which it was not possible to obtain the reliable fit for FOE Sulfonic acid, although the available data enabled the fitting.

RMS is also of the opinion that the reliability of the results of the kinetic analysis for FOE Sulfonic acid obtained for the trials in which the detectable amounts of that compound were <LOQ are of very limited reliability because of the significant uncertainty of the input data. As a result they should not be reported and hence used to derive the averaged field DegT₅₀ value for FOE Sulfonic acid. This concerns the following five trials: **30162/2 Kirchlauter**, **30163/9 Monheim**, **30164/7 Burscheid**, **30499/9 Burscheid** and **40495/0 S. Romualdo**.

Therefore in case of FOE Sulfonic acid the results for only eight following trials should be further examined:

- 30159/0 Breitenfelde,
- 30248/1 Fresne-L'Archeveque,
- 30250/3 Fresne-L'Archeveque,
- 30251/1 Laudun,
- 30253/8 St. Etienne du Gres,
- 40163/3 Laudun,

- 40164/1 St. Etienne du Gres,
- 40494/2 Ravenna.

Of them the following should be considered as not providing the reliable kinetic endpoints for FOE Sulfonic acid – **30251/1 Laudun** and **40494/2 Ravenna**. In case of the first of them the fit for FOE sulfonic acid was identified as not reliable by the Applicant, in case of the second such conclusion was drawn by the RMS after thorough comparative analysis of the results. The conclusion is supported by the results of the kinetic analysis performed by the RMS and aimed on the identification of best-fit kinetic model and determination of the persistence endpoints.

In case of the six remaining trials the results of the fitting for FOE Sulfonic acid may be considered reliable and included into final data set, although in case of the trials **30159/0 Breitenfelde** and **40163/3 Laudun** the results should be considered with care because RMS in the kinetic analysis aimed on the identification of best-fit kinetic model and determination of the persistence endpoints was not able to obtain the reliable, robust fit for FOE Sulfonic acid.

In case of Flufenacet the results obtained for all sixteen trials may be considered reliable.

The final set of results of evaluation, with the conclusions of RMS taken into consideration, is presented below in the table B.8.1.1.2.2.1._CA-137. RMS also decided to indicate the results that should be considered with care by giving them in italics.

In the next table – B.8.1.1.2.2.1._CA-138, are provided the results of the estimation of the amounts of FOE Sulfonic acid leached below the soil depth of 30 cm. The results are given as they were provided by the Applicant in the study report. In case of the trials indicated by the RMS as not providing reliable results, the values are given in italics.

Table B.8.1.1.2.2.1._CA-137: The optimised parameters obtained at the final step of evaluation, the ultimate set of the values.

Information on the trial		Optimised parameters						
		M_0 [g a. s./ha]	Kinetic parameters for Flufenacet and their statistical evaluation			Kinetic parameters for FOE Sulfonic acid and their statistical evaluation		
			DT ₅₀ [days]		χ^2 error [%]	DT ₅₀ [days]		χ^2 error [%]
Trial number	Trial site - name		value	CI range		value	CI range	
30159/0	Breitenfelde	341	17.1	14.3 – 20.3	10.2	17.7	5.6 – 55.7	24.8
30162/0	Kirchlauter	402	33.3	23.5 – 47.0	19.5	No values > LOQ, data set not reliable as well as the fitting results		
30163/9	Monheim	252	31.8	24.6 – 41.0	15.4	No values > LOQ, data set not reliable as well as the fitting results		
30164/7	Burscheid	473	11.4	10.1 – 12.9	7.4	No values > LOQ, data set not reliable as well as the fitting results		
30248/1	Fresne-L'Archeveque	474	31.4	24.9 – 39.4	14.4	18.1	1.7 – 189.2	40.4
30250/3	Fresne-L'Archeveque	399	32.9	28.5 – 38.0	8.8	20.8	4.6 – 94.5	42.0
30251/1	Laudun	588	24.7	20.8 – 29.3	10.6	Obtained fit not reliable		
30253/8	St. Etienne du Gres	434	37.6	33.1 – 42.6	8.9	19.6	5.9 – 65.2	32.0
30254/6	Saussay-la-Campagne	164	6.0	3.9 – 9.3	11.5	No values > LOD, assessment not performed		
30455/7	Fresne-L'Archeveque	135	7.1	5.4 – 9.5	10.8	No values > LOD, assessment not performed		
30499/9	Burscheid	192	8.5	7.2 – 10.1	9.3	No values > LOQ, data set not reliable as well as the fitting results		
30500/6	Monheim	157	14.7	9.5 – 22.7	13.5	No values > LOD, assessment not performed		
40163/3	Laudun	362	45.3	33.7 – 60.8	16.5	21.8	0.8 – 629.7	35.1
40164/1	St. Etienne du Gres	391	41.0	30.7 – 54.7	16.2	25.0	1.2 – 523.7	25.8
40494/2	Ravenna	483	36.2	27.9 – 47.1	14.5	Obtained fit not reliable		
40495/0	S. Romualdo	539	51.1	42.2 – 61.9	10.3	No values > LOQ, data set not reliable as well as the fitting results		

Table B.8.1.1.2.2.1._CA-138: The results of the estimation of the amounts of FOE Sulfonic acid leached below the depth of 30 cm – as reported by the Applicant.

Information on the trial			Amount of FOE Sulfonic acid leached (% of formed)
<i>Trial number</i>	<i>Trial site - name</i>	<i>Location - country</i>	
30159/0	Breitenfelde	Germany	9.2
30162/0	Kirchlauter	Germany	1.0
30163/9	Monheim	Germany	17.0
30164/7	Burscheid	Germany	Not applicable
30248/1	Fresne-L'Archeveque	France (North)	16.8
30250/3	Fresne-L'Archeveque	France (North)	20.7
30251/1	Laudun	France (South)	Not applicable
30253/8	St. Etienne du Gres	France (South)	7.9
30254/6	Saussay-la-Campagne	France (South)	Not applicable
30455/7	Fresne-L'Archeveque	France (North)	Not applicable
30499/9	Burscheid	Germany	64.7
30500/6	Monheim	Germany	Not applicable
40163/3	Laudun	France (South)	12.9
40164/1	St. Etienne du Gres	France (South)	13.6
40494/2	Ravenna	Italy	6.4
40495/0	S. Romualdo	Italy	0.9

The results obtained for FOE Sulfonic acid were also validated by their comparison with lysimeter studies. That was done by calculating the PEC_{GW} values for that compound using the lab and field geomean DT_{50} values for FOE Sulfonic acid and the average lab ff for that compound. The calculations were carried out using modified FOCUS Hamburg scenario. The reference lysimeter data were taken from the two German lysimeter studies – by [Hellpointner; 1996] and [Hellpointner; 1997] summarized under the point B.8.1.3.3. of this Renewal Assessment Report as respectively **Study 1** and **Study 2**. The FOCUS scenario used in calculations was modified with regard to key environmental parameters – rainfall, temperature and topsoil OC content which were adjusted to the lysimeter conditions. The application and crop data were same as those recorded in the lysimeter studies. Finally, the evaluation depth was set to 1.35 m., equal to the length of the lysimeter soil cores. The model calculations were carried out using FOCUS PEARL modeling tool.

The values, which were validated this way were:

- lab mean $DT_{50} = 81.4$ days determined for FOE Sulfonic acid (n.b.: this value is not valid any more, as for FOE Sulfonic acid the refined normalized lab. geomean $DT_{50} = 40.97$ days);
- field geomean $DT_{50} = 21.7$ days determined for FOE Sulfonic acid (n.b.: this value is also not fully valid, because the recalculated geomean, after removal of the results considered not reliable, is $DT_{50} = 20.5$ days, but that difference is minimal in comparison to the change in averaged lab DT_{50} , which was reduced by the factor of 2).
- The lab mean $ff = 0.26$ (that value was also modified as a result of the repeated kinetic analysis for FOE Sulfonic acid, the results of which are presented under the point B.8.1.1.2.1.1. of this Renewal Assessment Report).

The results of the comparative analysis are presented below in the table B.8.1.1.2.2.1._CA-139. They shall be considered only as indicative, because the calculations were performed for Flufenacet applied as a parent compound, from which FOE Sulfonic acid was formed. The parametrisation for Flufenacet was also based on the endpoints defined for the previous authorization of Flufenacet in the EU, which became refined as a result of the current evaluation.

Table B.8.1.1.2.2.1_CA-139: The results of the comparison between an annual concentrations of FOE Sulfonic acid in leachates measured in lysimeter studies and calculated using FOCUS GW modeling tool.

Reference - lysimeter	Data on Application				Mean annual concentration of FOE Sulfonic acid [µg/L] in leachate:		
	Number of applications	Application time (season/year)	Application rate [g a.s./ha]	Crop	Measured – lysimeters	Modelled (PEC_{GW} calculations)	
						using lab DT_{50}	using field DT_{50}
<i>Hellpointner; 1996</i>	2	Spring/ year 1	480	Maize	1.616	11.07	3.53
		Autumn/ year 1	180	Winter wheat			
<i>Hellpointner; 1997</i>	2	Spring/ year 1	480	Maize	0.596	12.05	3.43
		Spring/ year 2	480	Maize			

The results of the comparison show that the model exposure assessment performed for FOE Sulfonic acid using the geomean field DT_{50} value determined using the inverse modelling approach will provide overestimated values in comparison to the results obtained in lysimeter studies. Therefore the geomean field DT_{50} value determined in this kinetic assessment study may be considered sufficiently conservative for the purpose of the GW modelling exposure assessment.

RMS comments and evaluation of the study:

The study in general follows the recommendations of the relevant Guidelines and the consulted reference documents. The assessment procedure is well documented. RMS however noticed that some key parameters determining the reliability of the derived kinetic endpoints are not provided – that in particular concerns the statistical evaluation of the rate constants, for which the values of the T-test, even if provided in the PEST output files are difficult to be identified.

Problematic is also normalisation of the data – the absence of the adequate climatic data forced the application of the method which is admissible, but not recommended as primary normalisation method by the current Guidelines. Additionally from the study report it is not easy to deduce how exactly it was performed, so it puts some uncertainty over it.

Finally, it has to be indicated that using the inverse modeling approach the Applicant took into account the fact that FOE Sulfonic acid is mobile in soil profile and may leach to the deeper soil layers. Therefore one of the major dissipation processes was considered in the fitting and the kinetic endpoints adequately modified in order not to take it into account. This process was demonstrated to be of a minor relevance for Flufenacet so it was not taken into account when the kinetic endpoints for that compound were derived.

However, the process that does not seem to be addressed adequately, or that was not clearly explained in the study report, was the plant uptake. The issue shall be clarified, also because half of the trials were performed on the cropped fields. It shall be also indicated that already in the former EU Assessment Report for Flufenacet, prepared by the then-RMS – France, it was stated that the dissipation of Flufenacet was faster on the cropped trial sites. That effect may not necessarily be due to the plant uptake, but this shall be clarified.

RMS also assessing the validity of the kinetic endpoints and their acceptability as input parameters in the EU modelling exposure also consulted the Ctgb checklist which may be still considered as a standard verification tool, and which is presented below.

Field studies into rate of degradation

Checklist for assessing whether a field study on pesticide persistence in soil can be used to estimate transformation rates in soil.

1. *Check that only a non-significant fraction of the dose can have leached out of the soil layers that were sampled (consider the amount of rainfall and concentration measured in the deepest sampled layer);*
2. *Check that only a non-significant fraction of the dose disappeared via processes at the soil surface such as volatilisation or photochemical transformation (consider the period between spraying and the first significant rainfall event; check additionally that there is no initial fast decline followed by a slower decline; a recovery in the field that is much lower than the dose is also an indication of losses at the soil surface);*

3. Check that the decrease of the total amount with time corresponds reasonably well with first-order kinetics (either via curve-fitting or via applying a simulation model); if there is much scatter in the relationship between total amount with time (probably due to an inadequate sampling strategy) the estimation of a transformation rate in soil may be not acceptable;
4. Check whether the soil has been characterised (organic matter, clay etc.);
5. Check whether the location can be considered representative with respect to soil type and climate for Dutch conditions;
6. Check whether meteorological data are available, and whether a correction for the difference between the actual soil temperature (mean temperature measured during the day in top soil layer) and 20°C has been made (an acceptable alternative is temperature during the day in air measured on location, or nearby weather station);
7. Check whether the dose is reported and whether the formulated product is relevant (no granulate or slow release);
8. If inverse modelling was used, check whether the model used is acceptable (see focus document: soil persistence models and EU registration, 1996);
9. Check whether analytical procedure was documented well and whether recovery was acceptable;
10. Check history of pesticide use on plot. In preceding years no active ingredient or structure analogue should be used;
11. Check method of application. Pesticide should not be applied below soil surface;
12. Check method of sampling. Method of sampling should be adequate;
13. Check influence of crop. Uptake of pesticide by crop should be negligible.

Not all points are of equal importance. Crucial points are 1, 2, 5, 6 (temperature), 7, 9, 10, 12, and 13. When a study does not meet (one of) the other points, the quality and usefulness of the study should be evaluated by expert judgement.

All points should be checked and reported. A conclusion should be drawn whether from the field study the dissipation DT_{50} can be attributed to transformation only. In the light of all available information in the dossier, it should be determined whether the field DT_{50} can be used to predict leaching of the compound.

It was stated that the kinetic evaluation in general complies with it, although it displays several deficiencies already listed above.

As a result, the RMS is of the opinion that the kinetic endpoints for Flufenacet and, in particular, FOE Sulfonic acid determined in this study may be considered as input parameters for Tier-2 modelling with refined input parameters and as such be used in refined GW, and possibly SW, modelling exposure assessment at zonal or MS levels of assessment. That however shall be done after careful examination of the study report aimed on the clarification of all listed problems identified by the RMS.

As for purpose of the current EU assessment RMS is of the opinion that the kinetic endpoints derived from this study, and in particular the DT_{50} values for FOE Sulfonic acid, bear to significant level of uncertainty to be used in GW and SW model exposure assessment.

For that reason RMS decided not to include the kinetic endpoints determined in this study into the List of EndPoints.

The final set of the results is given below in the table B.8.1.1.2.2.1._CA-140. Only the reliable fitting results are provided.

Table B.8.1.1.2.2.1_CA-140: The final results of the kinetic evaluation of the data obtained in field dissipation trials aimed on derival of the modelling endpoints for Flufenacet and FOE Sulfonic acid.

Data on the trial		Soil properties (0-30 cm layer)			Results obtained for:					
Trial code	Location; type of trial	Soil type (USDA classif.)	pH ¹⁾	OC [%]	Flufenacet			FOE Sulfonic acid		
					Kinetic model	χ^2 % error	DT ₅₀ [days] (20°C/pF2)	Kinetic model	χ^2 % error	DT ₅₀ [days] (20°C/pF2)
30159/0	Breitenfelde, Germany; bare soil	Sandy loam	6.2	1.69	SFO	10.2	17.1	SFO	24.8	17.7
30162/0	Kirchlauter, Germany; bare soil	Heavy sandy loam ⁴⁾	7.1	0.61	SFO	19.5	33.3	----	----	----
30163/9	Monheim, Germany; bare soil	Sandy loam	6.7	1.45	SFO	15.4	31.8	----	----	----
30164/7	Burscheid, Germany; bare soil	Silt loam	6.5	0.97	SFO	7.4	11.4	----	----	----
30248/1	Fresne-L'Archeveque; North France; cropped soil	Silt loam	6.0	1.11	SFO	14.4	31.4	SFO	40.4	18.1
30250/3	Fresne-L'Archeveque, North France; cropped soil	Silt loam	5.2	1.86	SFO	8.8	32.9	SFO	42.0	20.8
30251/1	Laudun, South France; cropped soil	Loam	7.6	0.62	SFO	10.6	24.7	----	----	----
30253/8	St. Etienne du Gres, South France; cropped soil	Loam	7.7	0.80	SFO	8.9	37.6	SFO	32.0	19.6
30499/9	Burscheid, Germany; bare soil	Silt loam	6.5	0.97	SFO	9.3	8.5	----	----	----
30500/6	Monheim, Germany; bare soil	Sandy loam	6.7	1.45	SFO	13.5	14.7	----	----	----
30254/6	Sausay-la-Campagne, South France; cropped soil	Silt loam	7.4	0.92	SFO	11.5	6.0	----	----	----
30455/7	Fresne-L'Archeveque; North France; cropped soil	Silt loam	6.6	1.00	SFO	10.8	7.1	----	----	----
40163/3	Laudun, South France; cropped soil	Clay loam	7.7	1.28	SFO	16.5	45.3	SFO	35.1	21.8
40164/1	St. Etienne du Gres, South France; cropped soil	Silt loam	7.7	0.96	SFO	16.2	41.0	SFO	25.8	25.0
40494/2	Ravenna, Italy; cropped soil	Silt loam	7.8	0.98	SFO	14.5	36.2	----	----	----
40495/0	S. Romualdo, Italy; cropped soil	Silty loam	7.8	1.11	SFO	10.3	51.1	----	----	----
					Geomean		22.3 (n = 16)	----	----	20.5 (n = 6)
					Median		31.6 (n = 16)	----	----	20.2 (n = 6)

Footnotes to the table:

- 1) Determined in 0.01M CaCl₂;
- 2) The DIN 19682 classification presented because the USDA classification not provided; in another report it was stated to be Sandy loam (USDA) containing 58.5% sand, 22.7% silt and 18.8% clay.

Additionally there were identified and classified as relevant three publications dealing with the issue of the field dissipation of Flufenacet. They are summarised below as **Studies 8 - 10**. It shall be indicated that although they were identified as relevant, RMS is of the opinion that they can be used only as a source of supporting data, not to be used to derive the regulatory endpoints.

Study 8:

Report: Rouchaud J.^{a)}, Neus O.^{a)}, Cools K.^{b)}, Bulcke R.^{b)} (1999): “Dissipation and mobility of the oxyacetamide flufenacet herbicide in corn and wheat crops.”; Laboratory of Phytopharmacy, Université Catholique de Louvain, B-1348 Louvain-la-Neuve, Belgium (a) and Weed Research Center, Universiteit Ghent, B-9000 Gent, Belgium; published study - published in: “Mededelingen – Faculteit Landbouwkundige en Toegepaste Biologische Wetenschappen, Universiteit Gent”, vol 64, No. 3b, 1999, pp 673 – 677.

Guidelines: None declared as this is an open-source study, therefore not submitted for the regulatory purposes.

GLP: no, not applicable – peer-reviewed scientific paper;

RMS comments: The paper presents the results of the examination of persistence of Flufenacet in soil under realistic – field conditions. The compound was performed on one trial site located in Belgium, on which cereals and maize were grown. The test compound – Flufenacet was applied to the soil as pre-emergent pesticide in application rate 600 g/ha for spring/summer crops (corn/maize) and 240 g/ha for winter crops (winter wheat). degradation was examined for two fortification levels. Although in the paper it was not indicated that the experiments were performed in line with any relevant guidelines, it can be stated that the study protocol generally complied with other, regulatory field dissipation studies. The level of detail was sufficient to evaluate the study for its validity. The study may be considered valid, and therefore is summarised below. However, RMS is of the opinion that the results it provides may be regarded only as supplementary and conformatory to the endpoints provided by the regulatory studies submitted by the Applicant and should not be used as a source of regulatory endpoints.

Summary:

The paper contains an abstract, outlining the aims of the experiment and its key results, which was made available on-line. However, due to the copyright restrictions RMS could not present it here and the readers are kindly asked to consult the relevant document. Instead, below is presented the extended summary prepared by the RMS.

Extended summary prepared by RMS:

The aim of the study was to examine the persistence and mobility of Flufenacet in soil under realistic – field conditions and on cropped field. The experiment was performed on one trial site, at Melle in Belgium. The soil on the test fields was classified as Sandy loam (55% sand, 38% silt and 7% clay), containing 2.2% OM and having pH = 6.2.

The experiment was carried out in three variants:

- on the field with spring corn as a test crop;
- on the field with summer corn as a test crop;
- on the field with winter wheat as a test crop.

The whole experiment on the trial site was initiated in Autumn 1997 by starting the variant with winter wheat as a test crop.

It was initiated by preparing the sowing bed on the test field, by tilling the soil to the depth of 10 cm. Then Next, on 21st November 1997 Flufenacet was applied to the bare soil in amount 240 g/ha, the application rate typical for winter wheat. The field was left bare (no crop cover) until the spring (early May) of the next year – 1998, to simulate failure of the Winter wheat. Then on the 7th May 1998 the field was rotary tilled and the succeeding crops – spring wheat, corn, sugar beet, oat and probably others, were sown in bands. They were grown on the test field until mid-August 1998.

The soil samples were collected from four replicate plots randomly located on the test field. They were taken at pre-defined (not reported in the paper) intervals. The soil samples from the topmost 0-10cm soil layer were

taken from each of the four plots. Additionally, from two plots were taken samples from 0-10 cm layer divided into 2-cm sections, 10-15 cm layer and 15-20 cm layer. In case of the samples taken before sowing of succeeding crops, but after the sowing bed was prepared, the soil samples were taken only from the layers 10-15 cm and 15-20 cm because the topmost layer had been disturbed by tilling. Collected soil samples were analysed separately shortly after being sampled.

The variant with the spring corn was initiated by preparing a sowing bed on the test field. That was done by rotary tilling the field firstly in November 1997 and then in late March 1998, when the sli was tilled to the depth of 10 cm. Next the test compound – Flufenacet was applied to the soil surface in application rate 600 g/ha. Then, on the 7th of May Corn was sown on the test field and grown until harvested in mid-October 1998. On the trial field four randomly located replicate plots were designated, from which at pre-defined interval soil samples from the top 0-10 cm layer were taken. Additionally from the two replicate plots soil samples from 0-10 cm, 10-15 cm and 15-20 cm layers were taken. Collected samples were analysed separately, shortly after sampling.

For the third variant – with summer corn, the whole procedure looked very similarly to that described for the variant with spring corn. The test field was prepared for sowing in late May, after what Flufenacet was applied to the soil surface at 600 g/ha. The crop was sown on the 8th June 1998 and collected in mid-October of the same year. Soil sampling procedure was identical to that described above for the variant with spring corn.

The collected soil samples were processed in a following way:

- they were extracted with the mixture acetone/water;
- the extracts were collected and the organic solvent evaporated;
- the remaining aqueous extract was partitioned with ethyl acetate, the organic phase collected, cleaned by repeated TLC and then analysed by GC and GC-MS.

The LOD for the analytical method used in the study was 3 µg Flufenacet/kg soil.

The persistence of Flufenacet in soil of the trial site was determined using the linear regression method.

The results obtained in all three variants demonstrated that the residues of Flufenacet were confined to the top 10 cm layer with little migration to the layers below that depth. The movement within 0-10 cm layer was examined only for variant with winter wheat (in fact that was the variant with bare soil). It was stated that after application the compound was confined to 0-2 cm section and one month after treatment it was detected predominantly in the section 2-4 cm, where it was recorded in highest amounts until spring of the following year. Progressive movements to the deeper sections of 0-10 cm layer: 4-6 cm section, 6-8 cm section and 8-10 cm section, was reported in the paper. The analysis of the graph illustrating that movement showed that it was not significant by comparison to the dissipation of the compound from 2-4 cm section and it decreased with depth, becoming almost insignificant for the lowest section of the layer – 8-10 cm. No significant residues of Flufenacet were detected during that period in deeper layers – 10-15 cm and 15-20 cm. The compound was also not detected in significant amounts in those layers after May tillage and sowing of succeeding crops. For the variant with winter wheat (on bare soil) the persistence of Flufenacet was not determined.

The persistence of Flufenacet in the top 0-10 cm layer of soil was determined for all three variants of the experiment. The calculations were performed using the linear regression method and the equation:

$$\ln y = kt + b$$

where:

y – concentration of Flufenacet in soil in [µg/kg];

t – time elapsing from application in [days];

k – dissipation rate constant;

The calculated half-lives, expressed as DisT₅₀ values, were:

- for the variant with winter wheat (on bare soil): DisT₅₀ = 98 ± 5 days;
- for variant with spring corn: DisT₅₀ = 74 ± 4 days;
- for variant with summer corn: DisT₅₀ = 56 ± 3 days.

On the basis of the obtained results it was stated that neither application rate (what was demonstrated in the separate trial) nor the crop cover had any significant influence on the rate of dissipation of Flufenacet on the trial site. The observed differences in the soil half-lives were attributed to the different environmental conditions recorded on the trial site, in particular temperature and soil microbial activity.

In the paper it was also stated that after 4 months of crop growing period following application of the test compound the rate of dissipation of Flufenacet increased, becoming greater than that predicted by the 1st order kinetics. That may indicate that the dissipation of Flufenacet on the trial site bore traits of a bi-phasic process.

RMS comments:

The obtained kinetic endpoints are compliant with those obtained for Flufenacet in regulatory studies. However, because of the method of their derivation they shall be considered only as indicative and not used as regulatory endpoints. The results of the study also clearly indicate that Flufenacet in field is confined to the top 10- to 20-cm layer and displays no tendency to move to the deeper soil layers. That statement conforms the

observation made in the regulatory studies aimed on the examination of the field dissipation of that compound, that Flufenacet is not expected to dissipate from the top 30-cm soil layer by leaching to the deeper ones.

However, as RMS stated at the beginning of the whole summary of the study, presenting its evaluation, the results are only conformatory and indicative. As such they cannot be reported in the EU List of End Points.

Study 9:

Report: Rouchaud J.^{a)}, Neus O.^{a)}, Cools K.^{b)}, Bulcke R.^{b)} (1999): “Flufenacet Soil Persistence and Mobility in Corn and Wheat Crops.”; Laboratory of Phytopharmacy, Université Catholique de Louvain, B-1348 Louvain-la-Neuve, Belgium (a) and Weed Research Center, Universiteit Ghent, B-9000 Gent, Belgium; published study - published in: “The Bulletin of Environmental Contamination and Toxicology”, vol 63, 1999, pp 460 – 466.

Guidelines: None declared as this is an open-source study, therefore not submitted for the regulatory purposes.

GLP: no, not applicable – peer-reviewed scientific paper;

RMS comments: The paper presents the results of the examination of persistence of Flufenacet in soil under realistic – field conditions. The compound was performed on one trial site located in Belgium, on which cereals and maize were grown. The test compound – Flufenacet was applied to the soil as pre-emergent pesticide in application rate 600 g/ha for spring/summer crops (corn/maize) and 240 g/ha for winter crops (winter wheat). degradation was examined for two fortification levels. Although in the paper it was not indicated that the experiments were performed in line with any relevant guidelines, it can be stated that the study protocol generally complied with other, regulatory field dissipation studies. Analysing its content RMS stated that it reported the results of the same study that was characterised in the previously summarised publication – **Study 8**. However, it provided more detailed information about the analytical procedure used to process the collected soil samples and the numerical results of the analysis of the residues of Flufenacet in soil. Therefore RMS decided to provide its summary focusing on the pieces of information not presented in the **Study 8**.

The level of detail was sufficient to evaluate the study for its validity. The study may be considered valid, and therefore is summarised below. However, RMS is of the opinion that the results it provides may be regarded only as supplementary and conformatory to the endpoints provided by the regulatory studies submitted by the Applicant and should not be used as a source of regulatory endpoints.

Summary:

The Editor has not provided the abstract for that publication. However the paper contained the introduction, clearly outlining the aims and scope of the research activity described in it, which may be considered a summary of the study. Due to the copyright restrictions, RMS could not present it here and the readers are kindly asked to consult the relevant document. Instead, below is presented the extended summary prepared by the RMS.

Extended summary prepared by RMS:

The aim of the study was to examine the persistence and mobility of Flufenacet in soil under realistic – field conditions and on cropped field. The experiment was performed on one trial site, at Melle in Belgium. The soil on the test fields was classified as Sandy loam (55% sand, 38% silt and 7% clay), containing 2.2% OM and having pH = 6.2.

The experiment was carried out in three variants:

- on the field with spring corn as a test crop;
- on the field with summer corn as a test crop;
- on the field with winter wheat as a test crop.

The whole experiment on the trial site was initiated in Autumn 1997 by starting the variant with winter wheat as a test crop.

It was initiated by preparing the sowing bed on the test field, by tilling the soil to the depth of 10 cm. Then Next, on 21st November 1997 Flufenacet was applied to the bare soil in amount 240 g/ha, the application rate typical for winter wheat. The field was left bare (no crop cover) until the spring (early May) of the next year – 1998, to simulate failure of the Winter wheat. Then on the 7th May 1998 the field was rotary tilled and the

succeeding crops – spring wheat, corn, sugar beet, oat and probably others, were sown in bands. They were grown on the test field until mid-August 1998.

The soil samples were collected from four replicate plots randomly located on the test field. They were taken at pre-defined (not reported in the paper) intervals. The soil samples from the topmost 0-10cm soil layer were taken from each of the four plots. Additionally, from two plots were taken samples from 0-10 cm layer divided into 2-cm sections, 10-15 cm layer and 15-20 cm layer. In case of the samples taken before sowing of succeeding crops, but after the sowing bed was prepared, the soil samples were taken only from the layers 10-15 cm and 15-20 cm because the topmost layer had been disturbed by tilling. Collected soil samples were analysed separately shortly after being sampled.

The variant with the spring corn was initiated by preparing a sowing bed on the test field. That was done by rotary tilling the field firstly in November 1997 and then in late March 1998, when the sli was tilled to the depth of 10 cm. Next the test compound – Flufenacet was applied to the soil surface in application rate 600 g/ha. Then, on the 7th of May Corn was sown on the test field and grown until harvested in mid-October 1998. On the trial field four randomly located replicate plots were designated, from which at pre-defined interval soil samples from the top 0-10 cm layer were taken. Additionally from the two replicate plots soil samples from 0-10 cm, 10-15 cm and 15-20 cm layers were taken. Collected samples were analysed separately, shortly after sampling.

For the thirs variant – with summer corn, the whole procedure looked very similarly to that described for the variant with spring corn. The test field was prepared for sowing in late May, after what Flufenacet was applied to the soil surface at 600 g/ha. The crop was sown on the 8th June 1998 and collected in mid-October of the same year. Soil sampling procedure was identical to that described above for the variant with spring corn.

The collected soil samples were processed in a following way:

- 100-g aliquots of the collected soil samples were stir-extracted with 200-mL portions of acetone/water 8:2 mixture for 1 hour at $T = 20^{\circ}\text{C}$; the collected extract was filtered;
- The extraction was repeated using the same extracting solution; that step lasted 30 minutes;
- The filtered extracts were combined, 100 mL of water was added and acetone removed by evaporation under vacuum at $T = 30^{\circ}\text{C}$;
- The remaining aqueous extract was partitioned, after addition of 15 g NaCl, with two 200-mL portions of $\text{CH}_3\text{COOC}_2\text{H}_5$; the organic phase was collected and dried by stirring for 1 hour with Na_2SO_4 at $T = 20^{\circ}\text{C}$;
- Dried ethyl-acetate extract was concentrated in a three-step procedure to 0.5 mL and the concentrate subjected to chromatographic fractionation using TLC;
- The band containing the test compound – Flufenacet (both isomers) was collected and further purified using column chromatography technique; the elution was carried out using acetone;
- The acetone extract was once again concentrated to 0.5 mL in two-step procedure and once again purified by chromatographic fractionation on TLC plates; the relevant TLC band was collected and processed in the same manner as described above;
- The final extract, having a volume of 1 mL, was subjected to GC and GC-MS analysis.

The GC analysis was performed on glass column 1.8-metre long and having the internal diameter of 2 mm and containing 5% SE30 on chromosorb W-HP 80-100 mesh. The carrier gas was N_2 flowing through the system at rate 50 mL/min. The temperature of the column oven was set to $T = 190^{\circ}\text{C}$. In case of the GC analysis the detection was performed using the ECD detector.

For GC-MS analysis chromatographic conditions were the same. The MS analysis was performed in EI (electron impact) or CI (chemical ionisation) modes. Mass spectra were recorded at 70 eV.

The determined for the whole analytical method LOD = 3 $\mu\text{g/kg}$ soil.

The detailed numerical results of the study: the soil concentrations of Flufenacet recorded at each sampling point are reported below, separately for each variant in tables B.8.1.1.2.2.1._CA-141 – B.8.1.1.2.2.1._CA-143. Analysing the results presented in the paper RMS noticed that in case of the variant with winter wheat there were a clear discrepancies in the values obtained in 0-10 cm when analysed as a whole profile and dissected into 2-cm sections. The reason for that was not given in the study report, but may be possibly attributed to the way of the processing of the results.

Table B.8.1.1.2.2.1_CA-141: The results of the study – soil concentrations of Flufenacet obtained in the variant with winter wheat (bare soil).

Sampling date		Cummulative rainfall [mm]	Soil concentration of Flufenacet [µg/kg]:						
Absolute – day/month/year	Relative – Days After Treatment		in 0-10 cm layer						in 10-15 cm layer
			total	in section:					
				0-2 cm	2-4 cm	4-6 cm	6-8 cm	8-10 cm	
22/11/1997	1	2	193	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
12/12/1997	21	67	187	514	421	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
13/01/1998	53	173	161	177	564	64	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
18/02/1998	89	204	108	97	368	59	16	n. d. ¹⁾	n. d. ¹⁾
17/03/1998	116	269	91	82	273	77	23	n. d. ¹⁾	n. d. ¹⁾
23/04/1998	153	341	68	51	167	78	37	7.2	n. d. ¹⁾
13/05/1998	173	368	65	n. a. ²⁾	n. a. ²⁾	n. a. ²⁾	n. a. ²⁾	n. a. ²⁾	5
12/06/1998	203	484	49	n. a. ²⁾	n. a. ²⁾	n. a. ²⁾	n. a. ²⁾	n. a. ²⁾	n. d. ¹⁾
28/07/1998	249	564	32	n. a. ²⁾	n. a. ²⁾	n. a. ²⁾	n. a. ²⁾	n. a. ²⁾	n. d. ¹⁾
14/08/1998	266	573	n. d. ¹⁾	n. a. ²⁾	n. a. ²⁾	n. a. ²⁾	n. a. ²⁾	n. a. ²⁾	n. d. ¹⁾

Footnotes to the table:

1) n. d. = not detected;

2) n. a. = not available.

Table B.8.1.1.2.2.1_CA-142: The results of the study – soil concentrations of Flufenacet obtained in the variant with spring corn.

Sampling date		Cummulative rainfall [mm]	Soil concentration of Flufenacet [µg/kg] in the layer:		
Absolute – day/month/year	Relative – Days After Treatment		0-10 cm	10-15 cm	15-20 cm
25/03/1998	1	0	483	n. d. ¹⁾	n. d. ¹⁾
01/04/1998	8	7	465	n. d. ¹⁾	n. d. ¹⁾
23/04/1998	30	71	397	n. d. ¹⁾	n. d. ¹⁾
13/05/1998	50	98	312	5	n. d. ¹⁾
28/05/1998	65	123	258	n. d. ¹⁾	n. d. ¹⁾
12/06/1998	80	214	227	7	n. d. ¹⁾
08/07/1998	106	258	195	n. d. ¹⁾	n. d. ¹⁾
28/07/1998	126	294	152	n. d. ¹⁾	n. d. ¹⁾
14/08/1998	143	303	103	n. d. ¹⁾	n. d. ¹⁾
02/09/1998	162	363	51	n. d. ¹⁾	n. d. ¹⁾
22/09/1998	182	466	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾

Footnotes to the table:

1) n. d. = not detected.

Table B.8.1.1.2.2.1_CA-143: The results of the study – soil concentrations of Flufenacet obtained in the variant with summer corn.

Sampling date		Cummulative rainfall [mm]	Soil concentration of Flufenacet [µg/kg] in the layer:		
Absolute – day/month/year	Relative – Days After Treatment		0-10 cm	10-15 cm	15-20 cm
28/05/1998	0	0	524	n. d. ¹⁾	n. d. ¹⁾
12/06/1998	15	91	415	n. d. ¹⁾	n. d. ¹⁾
08/07/1998	41	135	317	n. d. ¹⁾	n. d. ¹⁾
28/07/1998	61	171	240	5	n. d. ¹⁾
14/08/1998	78	180	197	7	n. d. ¹⁾
02/09/1998	97	240	154	5	n. d. ¹⁾
22/09/1998	117	343	120	n. d. ¹⁾	n. d. ¹⁾
12/10/1998	137	391	68	n. d. ¹⁾	n. d. ¹⁾
12/11/1998	168	544	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾

Footnotes to the table:

1) n. d. = not detected.

The results obtained in all three variants demonstrated that the residues of Flufenacet were confined to the top 10 cm layer with little migration to the layers below that depth. The movement within 0-10 cm layer was examined only for variant with winter wheat (in fact that was the variant with bare soil). It was stated that after application the compound was confined to 0-2 cm section and one month after treatment it was detected

predominantly in the section 2-4 cm, where it was recorded in highest amounts until spring of the following year. Progressive movements to the deeper sections of 0-10 cm layer: 4-6 cm section, 6-8 cm section and 8-10 cm section, was reported in the paper. The analysis of the graph illustrating that movement showed that it was not significant by comparison to the dissipation of the compound from 2-4 cm section and it decreased with depth, becoming almost insignificant for the lowest section of that layer – 8-10 cm. No significant residues of Flufenacet were detected during that period in deeper layers – 10-15 cm and 15-20 cm. The compound was also not detected in significant amounts in those layers after May tillage and sowing of succeeding crops. For the variant with winter wheat (on bare soil) the persistence of Flufenacet was not determined.

The persistence of Flufenacet in the top 0-10 cm layer of soil was determined for all three variants of the experiment. The calculations were performed using the linear regression method and the equation:

$$\ln y = kt + b$$

where:

y – concentration of Flufenacet in soil in [$\mu\text{g/kg}$];

t – time elapsing from application in [days];

k – dissipation rate constant;

The calculated half-lives (expressed as DisT_{50} values) were:

- for the variant with winter wheat (on bare soil): $\text{DisT}_{50} = 98 \pm 5$ days;
- for variant with spring corn: $\text{DisT}_{50} = 74 \pm 4$ days;
- for variant with summer corn: $\text{DisT}_{50} = 56 \pm 3$ days.

On the basis of the obtained results it was stated that neither application rate (what was demonstrated in the separate trial) nor the crop cover had any significant influence on the rate of dissipation of Flufenacet on the trial site. The observed differences in the soil half-lives were attributed to the different environmental conditions recorded on the trial site, in particular temperature and soil microbial activity.

In the paper it was also stated that after 4 months of crop growing period following application of the test compound the rate of dissipation of Flufenacet increased, becoming greater than that predicted by the 1st order kinetics. That may indicate that the dissipation of Flufenacet on the trial site bore traits of a bi-phasic process.

RMS comments:

The obtained kinetic endpoints are compliant with those obtained for Flufenacet in regulatory studies. However, because of the method of their derivation they shall be considered only as indicative and not used as regulatory endpoints. The results of the study also clearly indicate that Flufenacet in field is confined to the top 10- to 20-cm layer and displays no tendency to move to the deeper soil layers. That statement conforms the observation made in the regulatory studies aimed on the examination of the field dissipation of that compound, that Flufenacet is not expected to dissipate from the top 30-cm soil layer by leaching to the deeper ones.

However, as RMS stated at the beginning of the whole summary of the study, presenting its evaluation, the results are only conformatory and indicative. As such they cannot be reported in the EU List of End Points.

Study 10:

Report: Rouchaud J.^{a)}, Neus O.^{a)}, Eelen H.^{b)}, Bulcke R.^{b)} (2001): “Persistence, Mobility and Adsorption of the Herbicide Flufenacet in the Soil of Winter Wheat Crops.”; Laboratory of Phytopharmacy, Université Catholique de Louvain, B-1348 Louvain-la-Neuve, Belgium (a) and Weed Research Center, Universiteit Ghent, B-9000 Gent, Belgium; published study - published in: “The Bulletin of Environmental Contamination and Toxicology”, vol 67, 2001, pp 609 – 616.

Guidelines: None declared as this is an open-source study, therefore not submitted for the regulatory purposes.

GLP: no, not applicable – peer-reviewed scientific paper;

RMS comments: The paper presents the results of the examination of persistence of Flufenacet in soil under realistic – field conditions. The compound was performed on four trial sites located in Belgium, on which winter cereals (winter wheat) were grown. The test compound – Flufenacet was applied to the soil as post-emergent pesticide, in autumn, at application rate 240 g/ha. examined for two fortification levels. Although in the paper it was not indicated that the experiments were performed in line with any relevant guidelines, it can be stated that the study protocol generally complied with other, regulatory field dissipation studies. Analysing its content RMS stated that it reported the results of the study that continued the research project started by the experiment described in previously summarised publications – **Study 8** and **Study 9**.

The level of detail was sufficient to evaluate the study for its validity. The study may be considered valid, and therefore is summarised below. However, RMS is of the opinion

that the results it provides may be regarded only as supplementary and conformatory to the endpoints provided by the regulatory studies submitted by the Applicant and should not be used as a source of regulatory endpoints.

Summary:

The paper contains an abstract, outlining the aims of the experiment and its key results, which was made available on-line. However, due to the copyright restrictions RMS could not present it here and the readers are kindly asked to consult the relevant document. Instead, below is presented the extended summary prepared by the RMS.

Extended summary prepared by RMS:

The aim of the study was to examine the persistence and mobility of Flufenacet in soil under realistic – field conditions and on cropped field. The experiment was performed on four trial sites in Belgium: Melle, Zingem and Zevekote, located 40 km apart, and Cortil-Noirmont, 100 km-distant from Melle. The characteristic of each trial site, as provided in the paper, is given below in the table B.8.1.1.2.2.1._CA-144.

Table B.8.1.1.2.2.1._CA-144: The brief characteristic of the trial sites.

Parameter		Trial site			
		Melle	Zingem	Zevekote	Cortil-Noirmont
Soil type		Sandy loam	Loamy sand	Clay loam	Silt loam
Particle size distribution	Sand [%]	55	79	19	11
	Silt [%]	38	11	45	75
	Clay [%]	7	10	36	14
pH value		7.0	6.4	6.6	6.7
Organic matter content (OM) [%]		1.51	1.60	2.12	1.2

The organic fertilization of soil on the trial sites was following:

- on Melle trial site no organic fertilizer was used on the year when the experiment started – 1999; before that year the trial site was fertilized every second year at spring with 40 tonnes/ha of either cow slurry or cow manure;
- on Zevekote trial site no organic fertilizer was used on the year when the experiment began – 1999; before that date the trial site was fertilized every second year, in September with 40 tonnes/ha of pig slurry or 40 tonnes/ha of cow manure;
- on Zingem trial site on the year when the experiment started – 1999, the soil was fertilized with cow manure applied at rate 40 tonnes/ha in October; in the preceding years the test field was fertilized every second year with either 40 tonnes/ha of cow manure or 40 tonnes/ha of pig slurry;
- on Cortil-Noirmont on the year when the experiment started soil was organically fertilized by incorporation of the leftovers of the preceding crop (sugar beet leaves) into the soil; in preceding years the test fields were fertilized by applying onto them 40 tonnes/ha of the cow manure every fourth year.

At the beginning of the experiment – in November 1999 test fields were tilled to prepare a seed bed and winter wheat was sown. On each test field four 6 x 10 metres plot were located at random, onto which the test substance – Flufenacet, was applied. It was applied to the soil surface of the test fields at rate 240 g/ha on the following dates:

- Melle trial site: on 25th November 1999;
- Zingem trial site: on 25th November 1999;
- Zevekote trial site: on 26th November 1999;
- Cortil-Noirmont: on 26th November 1999.

Additionally at trial sites Melle and Zingem the test compound was applied to the previously untreated plots at the same application rate in early spring of the following year : on 17th March 2000 at Melle and 4th April 2000 at Zingem.

At pre-defined intervals soil samples were taken from each treated plot of each trial site. The soil sampling procedure and subsequent processing and analysis of the collected soil samples were identical to those characterised above in the **Studies 8 and 9**.

The obtained results – concentrations of Flufenacet in soil in function of time were kinetically examined to determine its persistence by calculating the half-lives. The calculations were performed using the linear regression method and the equation:

$$\ln y = kt + b$$

where:

y – concentration of Flufenacet in soil in [$\mu\text{g/kg}$];

t – time elapsing from application in [days];

k – dissipation rate constant;

In case of autumn application the kinetic examination of the data covered 5-months period, while in case of the spring application 3.5-months period.

The numerical results of the study, individually for each trial site, are presented below in tables B.8.1.1.2.2.1._CA-145 – B.8.1.1.2.2.1._CA-148. Analysing these results RMS noticed that only those results were reported only for the autumn application of the test compound – Flufenacet, onto the trial sites. Reporting the data RMS decided not to provide the SD values that followed each mean concentration.

Table B.8.1.1.2.2.1._CA-145: The results of the study – soil concentrations of Flufenacet, obtained for the trial site Melle.

Sampling date		Cummu- lative rainfall [mm]	Soil concentration of Flufenacet [µg/kg]:							
Absolute – day/month/ year	Relative – Days After Treat- ment		in 0-10 cm layer						in 10-15 cm layer	in 15-20 cm layer
			total	in section:						
				0-2 cm	2-4 cm	4-6 cm	6-8 cm	8-10 cm		
26/11/1999	1	0	198	n. a. ²⁾	n. a. ²⁾	n. a. ²⁾	n. a. ²⁾	n. a. ²⁾	n. a. ²⁾	n. a. ²⁾
23/12/1999	28	88	129	564	41	28	12	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
13/01/2000	49	177	102	279	90	71	49	22	n. d. ¹⁾	n. d. ¹⁾
07/02/2000	74	216	91	109	216	78	43	18	n. d. ¹⁾	n. d. ¹⁾
24/02/2000	91	273	79	83	136	94	55	20	5	n. d. ¹⁾
22/03/2000	117	308	61	58	55	127	36	25	11	n. d. ¹⁾
03/05/2000	159	387	32	22	34	51	30	23	15	10
29/05/2000	185	494	16	11	15	18	21	13	11	8
28/06/2000	216	520	5	n. d. ¹⁾	n. d. ¹⁾	8	10	5	5	n. d. ¹⁾
23/07/2000	241	604	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	4	3	n. d. ¹⁾	n. d. ¹⁾

Footnotes to the table:

1) n. d. = not detected;

2) n. a. = not available.

Table B.8.1.1.2.2.1._CA-146: The results of the study – soil concentrations of Flufenacet, obtained for the trial site Zevekote.

Sampling date		Cummu- lative rainfall [mm]	Soil concentration of Flufenacet [µg/kg]:							
Absolute – day/month/ year	Relative – Days After Treat- ment		in 0-10 cm layer						in 10-15 cm layer	in 15-20 cm layer
			total	in section:						
				0-2 cm	2-4 cm	4-6 cm	6-8 cm	8-10 cm		
26/11/1999	0	0	202	n. a. ²⁾	n. a. ²⁾	n. a. ²⁾	n. a. ²⁾	n. a. ²⁾	n. a. ²⁾	n. a. ²⁾
23/12/1999	27	114	131	579	51	13	12	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
13/01/2000	48	190	103	140	208	101	47	17	n. d. ¹⁾	n. d. ¹⁾
07/02/2000	73	230	90	125	191	73	44	18	n. d. ¹⁾	n. d. ¹⁾
24/02/2000	90	282	82	110	174	78	34	14	n. d. ¹⁾	n. d. ¹⁾
22/03/2000	116	302	56	67	131	47	19	13	10	n. d. ¹⁾
03/05/2000	158	399	32	20	51	46	25	16	15	5
29/05/2000	185	503	13	5	12	17	18	13	11	7
28/06/2000	216	546	9	n. d. ¹⁾	5	11	14	10	8	5
23/07/2000	241	599	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	5	3	n. d. ¹⁾	n. d. ¹⁾

Footnotes to the table:

1) n. d. = not detected;

2) n. a. = not available.

Table B.8.1.1.2.2.1._CA-147: The results of the study – soil concentrations of Flufenacet, obtained for the trial site Zingem.

Sampling date		Cummu- lative rainfall [mm]	Soil concentration of Flufenacet [µg/kg]:							
Absolute – day/month/ year	Relative – Days After Treat- ment		in 0-10 cm layer						in 10-15 cm layer	in 15-20 cm layer
			total	in section:						
				0-2 cm	2-4 cm	4-6 cm	6-8 cm	8-10 cm		
26/11/1999	1	0	189	n. a. ²⁾	n. a. ²⁾	n. a. ²⁾	n. a. ²⁾	n. a. ²⁾	n. a. ²⁾	n. a. ²⁾
23/12/1999	28	88	148	526	106	71	33	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
13/01/2000	49	177	126	198	233	105	68	25	n. d. ¹⁾	n. d. ¹⁾
07/02/2000	74	216	115	129	230	110	73	23	n. d. ¹⁾	n. d. ¹⁾
24/02/2000	91	273	104	99	237	91	64	24	n. d. ¹⁾	n. d. ¹⁾
22/03/2000	117	308	80	62	116	147	48	28	14	5
03/05/2000	159	387	58	31	47	96	91	26	21	10
29/05/2000	185	494	31	16	22	47	43	25	14	11
28/06/2000	216	520	13	9	16	17	16	10	6	7
23/07/2000	241	604	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	4	5	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾

Footnotes to the table:

- 1) n. d. = not detected;
2) n. a. = not available.

Table B.8.1.1.2.2.1._CA-148: The results of the study – soil concentrations of Flufenacet, obtained for the trial site Cortil-Noirmont.

Sampling date		Cummu- lative rainfall [mm]	Soil concentration of Flufenacet [µg/kg]:							
Absolute – day/month/ year	Relative – Days After Treat- ment		in 0-10 cm layer						in 10-15 cm layer	in 15-20 cm layer
			total	in section:						
				0-2 cm	2-4 cm	4-6 cm	6-8 cm	8-10 cm		
01/12/1999	1	0	209	n. a. ²⁾	n. a. ²⁾	n. a. ²⁾	n. a. ²⁾	n. a. ²⁾	n. a. ²⁾	n. a. ²⁾
23/12/1999	23	118	124	321	256	34	12	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾
13/01/2000	44	193	91	134	195	55	49	24	n. d. ¹⁾	n. d. ¹⁾
07/02/2000	69	226	71	70	153	57	46	23	n. d. ¹⁾	n. d. ¹⁾
25/02/2000	87	287	52	36	121	52	31	14	12	5
22/03/2000	112	326	42	34	37	89	25	24	24	12
03/05/2000	154	404	26	13	24	27	41	26	25	11
29/05/2000	185	479	10	n. d. ¹⁾	5	8	15	16	16	11
28/06/2000	216	521	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	5	8	5
23/07/2000	241	611	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾

Footnotes to the table:

- 1) n. d. = not detected;
2) n. a. = not available.

RMS, analysing the data presented in the tables above, noticed significant discrepancies between the total concentrations obtained in 0-10 cm layer and those obtained in that layer when divided into 2-cm sections. That was due to the fact that the results for the whole 0-10 cm layer were reported as averages of four replicates, while those for sections 0-2 cm, 2-4 cm, 4-6 cm, 6-8 cm and 8-10 cm as averages of the two replicate samples taken independently of the whole 0-10 cm cores.

The persistence of the test compound – Flufenacet in soil on each of the trial site was determined using the data obtained in whole 0-10 cm layer. The calculated half-lives, for convenience denominated DisT₅₀ by the RMS, together with their SD values, are provided below. They were calculated using the linear regression method and assuming the CI = 95%.

The DisT₅₀ values reported in the publication were following:

- for Melle trial site soil persistence of Flufenacet expressed as DisT₅₀ = 66 ± 3.3 days;
- for Zevekote trial site soil persistence of Flufenacet expressed as DisT₅₀ = 64 ± 3.2 days;
- for Zingem trial site soil persistence of Flufenacet expressed as DisT₅₀ = 97 ± 4.9 days;
- for Cortil-Noirmont trial site soil persistence of Flufenacet expressed as site DisT₅₀ = 54 ± 2.7 days.

Analysing the obtained results the authors stated that the trial sites were selected in such way to minimise the differences of the trial-related variables, such as soil characteristic, weather patterns, field maintenance practices and application pattern of the test compound.

It was stated that the main differences between the trial sites were:

- soil texture;
- soil OM;
- recent organic fertilization.

While no significant correlation was found between variable soil properties – texture and OM content, and persistence of Flufenacet in soil of the trial sites, such correlation was stated between the persistence of the test compound and organic fertilization practices – while the DisT_{50} values were comparable on three trial sites with no fertilization with organic fertilizer of the animal origin, on the trial site on which such practice was effectuated (Zingem), the half-life of the test compound in soil lengthened by factor of 0.5.

In case of the spring application of Flufenacet to the two trial sites – Melle and Zingem, the reported soil half-lives of Flufenacet were following:

- for Melle trial site $\text{DisT}_{50} = 44 \pm 2.2$ days;
- for Zingem trial site $\text{DisT}_{50} = 66 \pm 3.9$ days.

The longer dissipation at Zingem trial site was attributed to the fertilization with organic fertilizer of the animal origin used in autumn of the year preceding application of the test compound – Flufenacet.

It was also stated that Flufenacet when applied at spring displayed lower soil persistence than when applied in autumn, what was related to the climatic conditions on the trial sites, mainly temperature – lower in autumn and winter than at spring and summer, as well as lower soil microbial activity observed in autumn-winter period.

Another factor examined in the study and reported in the paper was soil sorption of the test compound expressed as the parameters of Freundlich sorption isotherm. The analytical protocol used in this part of the study and the obtained results will be presented under the relevant point of this Renewal Assessment Report.

RMS comments:

The obtained kinetic endpoints are compliant with those obtained for Flufenacet in regulatory studies. However, because of the method of their derivation they shall be considered only as indicative and not used as regulatory endpoints. The results of the study also clearly indicate that Flufenacet in field is confined to the top 10- to 20-cm layer and displays no tendency to move to the deeper soil layers. That statement conforms the observation made in the regulatory studies aimed on the examination of the field dissipation of that compound, that Flufenacet is not expected to dissipate from the top 30-cm soil layer by leaching to the deeper ones.

RMS analysing the tabularised results noticed the inconsistencies of the reported values, mainly concerning the sampling dates expressed in absolute (day/month/year) and relative (Days After Treatment) terms. That however had no significant impact on the results.

However, as RMS stated at the beginning of the whole summary of the study, presenting its evaluation, the results are only conformatory and indicative. As such they cannot be reported in the EU List of End Points.

The key results of the three open literature field dissipation studies are presented below in the table B.8.1.1.2.2.1._CA-149. As indicated in the RMS's comments to each summarised report, these values are only informative and as such they will not be reported in the EU list of End Points nor used anyhow in the exposure/risk assessment.

Table B.8.1.1.2.2.1._CA-149: The key results obtained in the literature studies examining the field dissipation of Flufenacet.

Data on the trial			Soil characterisation			Data on application		Soil persistence of the test compound - Flufenacet		Mobility of the test compound – Flufenacet in soil profile
<i>Trial site</i>	<i>Duration of the study – Days After application</i>	<i>Crop cover</i>	<i>Soil textural type</i>	<i>Soil pH</i>	<i>OM content</i>	<i>Application date</i>	<i>Application rate [g/ ha]</i>	<i>DisT₅₀ [days]</i>	<i>Kinetic model</i>	
Melle/ Belgium	266	Bare soil	Sandy loam	6.2	2.2	21/11/1997	240	98	1 st order, linear regression	No residues below 15 cm
Melle/ Belgium	182	Spring corn	Sandy loam	6.2	2.2	24/03/1998	600	74	1 st order, linear regression	No residues below 15 cm
Melle/ Belgium	168	Summer corn	Sandy loam	6.2	2.2	28/05/1998	600	56	1 st order, linear regression	No residues below 15 cm
Melle/ Belgium	241	Winter wheat	Sandy loam	7.0	1.5	25/11/1999	240	66	1 st order, linear regression	Residues detected down to 20 cm, but mainly confined to top 10 cm
Zingem/ Belgium	241	Winter wheat	Loamy sand	6.4	1.6	25/11/1999	240	97	1 st order, linear regression	Residues detected down to 20 cm, but mainly confined to top 10 cm
Zevekote/ Belgium	241	Winter wheat	Clay loam	6.6	2.1	26/11/1999	240	64	1 st order, linear regression	Residues detected down to 20 cm, but mainly confined to top 10 cm
Crotil-Noirmont/ Belgium	241	Winter wheat	Silt loam	6.7	1.2	01/12/2000	240	54	1 st order, linear regression	Residues detected down to 20 cm, but mainly confined to top 10 cm
Melle/ Belgium	~150	Winter wheat	Sandy loam	7.0	1.5	17/03/2000	240	44	1 st order, linear regression	No information provided
Zingem/ Belgium	~150	Winter wheat	Loamy sand	6.4	1.6	04/04/2000	240	66	1 st order, linear regression	No information provided

The key results obtained in the studies examining the field dissipation of Flufenacet and its selected major soil degradation products are presented below in the format recommended for reporting the EU-agreed End Points.

Rate of degradation field soil dissipation studies (Regulation (EU) N° 283/2013, Annex Part A, point 7.1.2.2.1 and Regulation (EU) N° 284/2013, Annex Part A, point 9.1.1.2.1)

Parent	Aerobic conditions								
Soil type (indicate if bare or cropped soil was used).	Location (country or USA state).	OC [%]	pH ^{a)}	Depth (cm)	DT ₅₀ (d) actual	DT ₉₀ (d) actual	St. (χ ²)	DT ₅₀ (d) Norm ^{b)}	Method of calculation
Sandy loam (bare soil)	Germany (Breitenfelde; 30159/0)	1.69	6.2	0-10	33.1	110.0	13.3	----	SFO
Sandy loam (bare soil)	Germany (Kirchlauter; 30162/0)	0.61	7.1	0-10	52.9	176.0	6.43	----	SFO
Sandy loam (bare soil)	Germany (Monheim; 30163/9)	1.45	6.7	0-10	48.2	160.0	16.1	----	SFO
Silt loam (bare soil)	Germany (Burscheid; 30164/7)	0.97	6.5	0-10	16.1	53.4	6.83	----	SFO
Silt loam (cropped soil)	North France (Fresne-L'Archeveque; 30248/1)	1.11	6.0	0-10	38.0	126.0	15.8	----	SFO
Silt loam (cropped soil)	North France (Fresne-L'Archeveque; 30250/3)	1.86	5.2	0-10	51.3	170.0	11.0	----	SFO
Loam (cropped soil)	South France (Laudun; 30251/1)	0.62	7.6	0-10	30.4	101.0	10.2	----	SFO
Loam (cropped soil)	South France (St. Etienne du Gres; 30253/8)	0.80	7.7	0-10	41.1	137.0	6.68	----	SFO
Silt loam (bare soil)	Germany (Burscheid; 30499/9)	0.97	6.5	0-10	31.5	140.0	7.11	----	DFOP
Sandy loam (bare soil)	Germany (Monheim; 30500/6)	1.45	6.7	0-10	68.1	226.0	5.1	----	SFO
Silt loam (cropped soil)	South France (Saussay-la-Campagne; 30254/6)	0.92	7.4	0-10	14.2	56.7	2.79	----	FOMC
Silt loam (cropped soil)	North France (Fresne-L'Archeveque ; 30455/7)	1.00	6.6	0-10	17.2	57.2	3.32	----	SFO
Clay loam (cropped soil)	South France (Laudun; 40163/3)	1.28	7.7	0-10	49.0	163.0	9.86	----	SFO
Silt loam (cropped soil)	South France (St. Etienne du Gres; 40164/1)	0.96	7.7	0-10	48.1	160.0	7.08	----	SFO
Silt loam (cropped soil)	Italy (Ravenna; 40494/2)	0.98	7.8	0-10	34.4	114.0	7.23	----	SFO
Silty loam (cropped soil)	Italy (S. Romualdo; 40495/0)	1.11	7.8	0-10	50.7	168.0	6.58	----	SFO
Geometric mean (if not pH dependent)					35.7	122.3	----	----	----
pH dependence, <i>Yes or No</i>					No				

^{a)} all values determined in 0.01 M CaCl₂;

^{b)} Normalised using a Q10 of 2.58 and Walker equation coefficient of 0.7, values are DegT50matrix

FOE Sulfonic acid		Aerobic conditions; Studies with Flufenacet dosed as precursor								
Soil type	Location	OC [%]	pH ^{a)}	Depth (cm)	DT ₅₀ (d) actual	DT ₉₀ (d) actual	St. (χ ²)	DT ₅₀ (d) Norm ^{b)}	f. f. k _f / k _{dp}	Method of calculation
Silt loam (cropped soil)	North France (Fresne-L'Archeveque; 30248/1)	1.11	6.0	0-10	60.6	201.0	23.3	----	0.094	SFO, Flufenacet as parent
Silt loam (cropped soil)	North France (Fresne-L'Archeveque; 30250/3)	1.86	5.2	0-10	75.3	250.0	9.83	----	0.119	SFO, Flufenacet as parent
Loam (cropped soil)	South France (St. Etienne du Gres; 30253/8)	0.80	7.7	0-10	30.8	102.0	12.1	----	0.142	SFO, Flufenacet as parent
Silt loam (cropped soil)	South France (St. Etienne du Gres; 40164/1)	0.96	7.7	0-10	94.9	315.0	20.5	----	0.072	SFO, Flufenacet as parent
Geometric mean (if not pH dependent)					60.4	200.4	----	----	----	----
Arithmetic mean					----	----	----	----	0.107	----
pH dependence, Yes or No						No				

^{a)} all values determined in 0.01 M CaCl₂;

^{b)} Normalised using a Q10 of 2.58 and Walker equation coefficient of 0.7 values are DegT50matrix

FOE Oxalate		Aerobic conditions; Studies with Flufenacet dosed as precursor								
Soil type	Location	OC [%]	pH ^{a)}	Depth (cm)	DT ₅₀ (d) actual	DT ₉₀ (d) actual	St. (χ ²)	DT ₅₀ (d) Norm ^{b)}	f. f. k _f / k _{dp}	Method of calculation
Loam (cropped soil)	South France (St. Etienne du Gres; 30253/8)	0.80	7.7	0-10	68.0	226.0	4.53	----	0.119	SFO, Flufenacet as parent
Geometric mean (if not pH dependent)					----	----	----	----	----	----
Arithmetic mean					----	----	----	----	----	----
pH dependence, Yes or No						No				

^{a)} all values determined in 0.01 M CaCl₂;

^{b)} Normalised using a Q10 of 2.58 and Walker equation coefficient of 0.7 values are DegT50matrix

B.8.1.1.2.2.2. – Soil residue studies

No studies were submitted in this area for the previous authorisation of Flufenacet in the EU. Instead was given the following justification for not providing them: “*Studies are neither required nor they were supplied because trigger values were not exceeded.*”. Also for the present evaluation no studies covering this data requirement were submitted and the Applicant did not justify their non-submission. However the results of the kinetic analysis of the results of soil dissipation studies, performed in line with the recommendations of FOCUS Kinetics Guideline [FOCUS; 2006], demonstrated that the justification presented in the previous Assessment Report for Flufenacet may be considered still valid.

B.8.1.1.2.2.3. – Soil accumulation studies

No studies were submitted in this area for the previous authorisation of Flufenacet in the EU. Instead was given the following justification for not providing them: “*Based on the soil dissipation studies (field) and rotational crop studies (laboratory) respective studies are not necessary and were not supplied.*”. Also for the present evaluation no studies covering this data requirement were submitted, but the Applicant provided the following justification for their non-submission: “*The accumulation potential of flufenacet was evaluated during the Annex I Inclusion. Due to the short dissipation times, soil accumulation testing is not required for flufenacet.*”

RMS is of the opinion that the justification provided by the Applicant is defensible. The results of the kinetic evaluation of the data obtained in the field dissipation trials performed by the RMS and aimed of the determination of the persistence of Flufenacet and its selected major soil degradation products in soil resulted in short dissipation times, with DT₉₀ values for Flufenacet predominantly shorter than 200 days and only in case of the trial Monheim, 30500/6, in which Flufenacet was applied in autumn (late October) to bare soil in amount 240 g/ha thbeing longer – the not normalised DT₉₀ = 226 days. Therefore it can be stated that in none of the trials was recorded the DisT₉₀ ≥ 1 year, a formal requirement for performing this type of studies set by the Commission Regulation (EU) No. 283/2013. Also in the three open-literature studies identified as relevant for the present evaluation, Flufenacet was demonstrated not to have a tendency for accumulation in soil after either autumn or spring application (please refer to the summaries of the **Studies 8-10**, presented under the point B.8.1.1.2.2.1. of this Renewal Assessment Report).

Additionally the issue of the accumulation potential for both Flufenacet and its major soil metabolites was assessed in the model soil exposure assessment presented under the point B.8.2. in the document Vol. 3. B.8_CP.

B.8.1.1.2.2.4. – Summary of the field studies.

The dissipation of Flufenacet in soil under field conditions was examined on sixteen trial sites located in the EU – in Germany, France (Northern and Southern) and Italy. The characteristic of the trial sites in presented below in the table B.8.1.1.2.2.4._CA-1. The next table – B.8.1.1.2.2.4._CA-2, provides the brief characteristic of the weather conditions recorded at each trial site during the experiment.

Table B.8.1.1.2.2.4._CA-1: The brief characteristic of field trials.

Study	Information on the trial site			Data on application		Data on crop cover		
	Trial number	Name of the trial site	Location - country	Application rate [g/ha]	Application date	Crop	Date of sowing	Sowing – days before application
[Sommer; 1995]	30159/0	Breitenfelde	Germany	480	15. 04. 1993	Bare soil	Not applicable	Not applicable
	30162/0	Kirchlauter	Germany	480	13. 04. 1993	Bare soil	Not applicable	Not applicable
	30163/9	Monheim	Germany	480	30. 04. 1993	Bare soil	Not applicable	Not applicable
	30164/7	Burscheid	Germany	480	22. 04. 1993	Bare soil	Not applicable	Not applicable
	30248/1	Fresne-L'Archeveque	France (North)	600	11. 05. 1993	Maize	04. 05. 1993	7
	30250/3	Fresne-L'Archeveque (1)	France (North)	600	27. 05. 1993	Maize	24. 05. 1993	3
	30251/1	Laudun	France (South)	600	18. 05. 1993	Sunflower	22. 04. 1993	26
	30253/8	St. Etienne du Gres	France (South)	600	17. 05. 1993	Sunflower	16. 05. 1993	1
[Sommer; 1995b]	30254/6	Saussay-la-Campagne	France (South)	240	11. 03. 1994	Winter wheat	14. 10. 1993	158
	30455/7	Fresne-L'Archeveque	France (North)	240	28. 04. 1994	Winter wheat	22. 10. 1993	169
[Sommer; 1995a]	30499/9	Burscheid	Germany	240	26. 10. 1993	Bare soil	Not applicable	Not applicable
	30500/6	Monheim	Germany	240	26. 10. 1993	Bare soil	Not applicable	Not applicable
[Sommer; 1995c]	40163/3	Laudun	France (South)	600	17. 05. 1994	Sunflower	04. 05. 1994	13
	40164/1	St. Etienne du Gres	France (South)	600	22. 04. 1994	Sunflower	16. 04. 1994	6
	40494/2	Ravenna	Italy	600	27. 04. 1994	Soybean	25. 04. 1994	2
	40495/0	S. Romualdo	Italy	600	27. 04. 1994	Soybean	26. 04. 1994	1

Table B.8.1.1.2.2.4._CA-2: The climatic conditions and weather data recorded at on each trial site.

Information on the trial:			Duration of the trial after application of the test compound [days]	Weather data			
Trial number	Trial site - name	Location - country		Source of the weather data	Mars grid cell	Experimental weather data collected at trial site	
						Cumulative rainfall [mm]	Mean temperature T [°C]
30159/0	Breitenfelde	Germany	240	German Weather Service, Lübeck	64060	592	11.0
30162/0	Kirchlauter	Germany	237	Weather station in 4 km from the trial site	56060	319	11.1
30163/9	Monheim	Germany	231	Trial Station Laacherhof	58055	653	12.1
30164/7	Burscheid	Germany	239	Trial Station Höfchen	58055	839	10.6
30248/1	Fresne-L'Archeveque	France (North)	303	Meteo France Station de Boos	55047	870	9.6
30250/3	Fresne-L'Archeveque	France (North)	297	Meteo France Station de Boos	55047	778	9.4
30251/1	Laudun	France (South)	255	Meteo France Station Chusclan	43051	683	15.2
30253/8	St. Etienne du Gres	France (South)	260	Meteo France Station Chateuaenard	42051	670	14.8
30254/6	Saussay-la-Campagne	France (South)	242	Meteo France Station de Boos (76)	55047	598	12.7
30455/7	Fresne-L'Archeveque	France (North)	240	Meteo France Station de Boos (76)	55047	661	13.0
30499/9	Burscheid	Germany	234	Versuchsgut Höfchen, 41399 Burscheid	58055	695	6.3
30500/6	Monheim	Germany	240	Versuchsgut Laacherhof, 40789 Monheim	58055	815	6.3
40163/3	Laudun	France (South)	240	Meteo France	43051	658	16.8
40164/1	St. Etienne du Gres	France (South)	236	Meteo France	42051	640	18.7
40494/2	Ravenna	Italy	236	Ar. Sperim. M. Marani/ Ravenna	44063	407	17.0
40495/0	S. Romualdo	Italy	236	Ar. Sperim. M. Marani/ Ravenna	44063	407	17.0

The residues of Flufenacet on the trial sites were determined by sampling, at pre-determined intervals, soil cores down to 30-cm or 50-cm depth. The number of sampling points was, depending on the trial site, eight or nine. The soil samples were dissected into 10-cm layers and analysed for the content of Flufenacet and its three major soil degradates – FOE Alcohol, FOE Oxalate and FOE Sulfonic acid.

The performed analysis showed that FOE Alcohol was not formed on any trial site in detectable amounts >3 µg/kg soil (LOD). Other two degradation products were detectable and, on some trial sites even quantifiable (recorded in amounts > LOQ = 10 µg/kg soil), but in none of the trials were observed in amounts higher than 30 µg/kg soil. Neither Flufenacet nor any of its degradation products were detected in deeper soil layers – below 20 cm.

The obtained results were kinetically examined in line with the recommendations of the FOCUS Work Group on the Degradation Kinetics. The results of the determination of the persistence of Flufenacet and its two quantifiable degradation products – FOE Oxalate and FOE Sulfonic acid, are presented below in three separate tables – B.8.1.1.2.2.4._CA-3 (Flufenacet), B.8.1.1.2.2.4._CA-4 (FOE Oxalate) and B.8.1.1.2.2.4._CA-5 (FOE Sulfonic acid).

Table B.8.1.2.2.4._CA-3: The persistence kinetic endpoints determined for Flufenacet in field dissipation trials.

Data on the trial		Soil properties (0-30 cm layer)			Identified best-fit model	Kinetic parameter		Evaluation of the fit		Kinetic endpoints	
Trial code	Location; type of trial	Soil type (USDA classif.)	pH ¹⁾	OC [%]		par.	value	Visual fit ²⁾ / r ³⁾	χ ² % error	DT ₅₀ [days]	DT ₉₀ [days]
30159/0	Breitenfelde, Germany; bare soil	Sandy loam	6.2	1.69	SFO	k	0.02092	A./0.9648	13.3	33.1	110.0
30162/0	Kirchlauter, Germany; bare soil	Heavy sandy loam ⁴⁾	7.1	0.61	SFO	k	0.0131	G./0.988	6.43	52.9	176.0
30163/9	Monheim, Germany; bare soil	Sandy loam	6.7	1.45	SFO	k	0.0144	A./0.9275	16.1	48.2	160.0
30164/7	Burscheid, Germany; bare soil	Silt loam	6.5	0.97	SFO	k	0.04309	G./0.9915	6.83	16.1	53.4
30248/1	Fresne-L'Archeveque, North France; cropped soil	Silt loam	6.0	1.11	SFO	k	0.01827	A./0.9536	15.8	38.0	126.0
30250/3	Fresne-L'Archeveque1, North France; cropped soil	Silt loam	5.2	1.86	SFO	k	0.01352	A./0.9672	11.0	51.3	170.0
30251/1	Laudun, South France; cropped soil	Loam	7.6	0.62	SFO	k	0.02278	A./0.9804	10.2	30.4	101.0
30253/8	St. Etienne du Gres, South France; cropped soil	Loam	7.7	0.80	SFO	k	0.01687	G./0.9902	6.68	41.1	137.0
30499/9	Burscheid, Germany; bare soil	Silt loam	6.5	0.97	DFOP	k ₁	1.501	A./0.9674	7.11	31.5	140.0
						k ₂	0.01481				
						g	0.2025				
30500/6	Monheim, Germany; bare soil	Sandy loam	6.7	1.45	SFO	k	0.01017	G./0.991	5.1	68.1	226.0
30254/6	Sausay-la-Campagne, South France; cropped soil	Silt loam	7.4	0.92	FOMC	α	4.673	G./0.9993	2.79	14.2	56.7
						β	88.960				
30455/7	Fresne-L'Archeveque; North France; cropped soil	Silt loam	6.6	1.00	SFO	k	0.04024	G./0.9989	3.32	17.2	57.2
40163/3	Laudun, South France; cropped soil	Clay loam	7.7	1.28	SFO	k	0.01451	A./0.9774	9.86	49.0	163.0
40164/1	St. Etienne du Gres, South France; cropped soil	Silt loam	7.7	0.96	SFO	k	0.01442	A./0.9892	7.08	48.1	160.0
40494/2	Ravenna, Italy; cropped soil	Silt loam	7.8	0.98	SFO	k	0.02016	G./0.991	7.23	34.4	114.0
40495/0	S. Romualdo, Italy; cropped soil	Silty loam	7.8	1.11	SFO	k	0.01368	G./0.9884	6.58	50.7	168.0

Footnotes to the table:

- 1) Determined in 0.01M CaCl₂;
- 2) Following abbreviations were used: P – Poor; A – Acceptable; G – Good;
- 3) r = correlation coefficient;
- 4) The DIN 19682 classification presented because the USDA classification not provided; in another report it was stated to be Sandy loam (USDA) containing 58.5% sand, 22.7% silt and 18.8% clay.

Table B.8.1.2.2.4._CA-4: The reliable persistence kinetic endpoints determined for FOE Oxalate in field dissipation trials.

Data on the trial		Soil properties (0-30 cm layer)			Identified best-fit model	Kinetic parameter		Evaluation of the fit		Kinetic endpoints	
Trial code	Location; type of trial	Soil type (USDA classif.)	pH ¹⁾	OC [%]		par.	value	Visual fit ^{2)/ r³⁾}	χ^2 % error	DT ₅₀ [days]	DT ₉₀ [days]
30250/3	Fresne-L'Archeveque1, North France; cropped soil	Silt loam	5.2	1.86	SFO	k	0.01091	G./0.9895	4.53	68.0	226.0

Footnotes to the table:

- 1) Determined in 0.01M CaCl₂;
 2) Following abbreviations were used: P – Poor; A – Acceptable; G – Good;
 3) r = correlation coefficient;

Table B.8.1.2.2.4._CA-5: The reliable persistence kinetic endpoints determined for FOE Sulfonic acid in field dissipation trials.

Data on the trial		Soil properties (0-30 cm layer)			Identified best-fit model	Kinetic parameter		Evaluation of the fit		Kinetic endpoints	
Trial code	Location; type of trial	Soil type (USDA classif.)	pH ¹⁾	OC [%]		par.	value	Visual fit ^{2)/ r³⁾}	χ^2 % error	DT ₅₀ [days]	DT ₉₀ [days]
30248/1	Fresne-L'Archeveque; North France; cropped soil	Silt loam	6.0	1.11	SFO	k	0.01144	A./0.7441	23.3	60.6	201.0
30250/3	Fresne-L'Archeveque1, North France; cropped soil	Silt loam	5.2	1.86	SFO	k	0.00921	G./0.9477	9.83	75.3	250.0
30253/8	St. Etienne du Gres, South France; cropped soil	Loam	7.7	0.80	SFO	k	0.02249	G./0.9379	12.1	30.8	102.0
40164/1	St. Etienne du Gres, South France; cropped soil	Silt loam	7.7	0.96	SFO	k	0.007303	A./0.9319	20.5	94.9	315.0

Footnotes to the table:

- 1) Determined in 0.01M CaCl₂;
 2) Following abbreviations were used: P – Poor; A – Acceptable; G – Good;
 3) r = correlation coefficient;

The results obtained for Flufenacet and FOE Sulfonic acid were also kinetically examined with aim to derive the kinetic endpoints suitable for modelling. The kinetic analysis was performed using the inverse modelling approach. The assessment was conditionally accepted by the RMS. However, RMS decided, because of the stated deficiencies, not to use its results in the model exposure assessment, nor to report them in the List of End Points. At the same time they may be used, at zonal or MS level, as refined input parameters in Tier 2a GW exposure assessment. The results are presented below in the table B.8.1.1.2.2.4._CA-6.

Table B.8.1.1.2.2.4._CA-6: The proposed modelling kinetic endpoints for Flufenacet and FOE Sulfonic acid determined from the data obtained in field dissipation trials using the inverse modelling approach.

Data on the trial		Soil properties (0-30 cm layer)			Results obtained for:					
Trial code	Location; type of trial	Soil type (USDA classif.)	pH ¹⁾	OC [%]	Flufenacet			FOE Sulfonic acid		
					Kinetic model	χ^2 % error	DT ₅₀ [days] (20°C/pF2)	Kinetic model	χ^2 % error	DT ₅₀ [days] (20°C/pF2)
30159/0	Breitenfelde, Germany; bare soil	Sandy loam	6.2	1.69	SFO	10.2	17.1	SFO	24.8	17.7
30162/0	Kirchlauter, Germany; bare soil	Heavy sandy loam ⁴⁾	7.1	0.61	SFO	19.5	33.3	----	----	----
30163/9	Monheim, Germany; bare soil	Sandy loam	6.7	1.45	SFO	15.4	31.8	----	----	----
30164/7	Burscheid, Germany; bare soil	Silt loam	6.5	0.97	SFO	7.4	11.4	----	----	----
30248/1	Fresne-L'Archeveque, North France; cropped soil	Silt loam	6.0	1.11	SFO	14.4	31.4	SFO	40.4	18.1
30250/3	Fresne-L'Archeveque, North France; cropped soil	Silt loam	5.2	1.86	SFO	8.8	32.9	SFO	42.0	20.8
30251/1	Laudun, South France; cropped soil	Loam	7.6	0.62	SFO	10.6	24.7	----	----	----
30253/8	St. Etienne du Gres, South France; cropped soil	Loam	7.7	0.80	SFO	8.9	37.6	SFO	32.0	19.6
30499/9	Burscheid, Germany; bare soil	Silt loam	6.5	0.97	SFO	9.3	8.5	----	----	----
30500/6	Monheim, Germany; bare soil	Sandy loam	6.7	1.45	SFO	13.5	14.7	----	----	----
30254/6	Sausay-la-Campagne, South France; cropped soil	Silt loam	7.4	0.92	SFO	11.5	6.0	----	----	----
30455/7	Fresne-L'Archeveque, North France; cropped soil	Silt loam	6.6	1.00	SFO	10.8	7.1	----	----	----
40163/3	Laudun, South France; cropped soil	Clay loam	7.7	1.28	SFO	16.5	45.3	SFO	35.1	21.8
40164/1	St. Etienne du Gres, South France; cropped soil	Silt loam	7.7	0.96	SFO	16.2	41.0	SFO	25.8	25.0
40494/2	Ravenna, Italy; cropped soil	Silt loam	7.8	0.98	SFO	14.5	36.2	----	----	----
40495/0	S. Romualdo, Italy; cropped soil	Silty loam	7.8	1.11	SFO	10.3	51.1	----	----	----
					Geomean		22.3 (n = 16)	----	----	20.5 (n = 6)
					Median		31.6 (n = 16)	----	----	20.2 (n = 6)

Footnotes to the table:1) Determined in 0.01M CaCl₂;

2) The DIN 19682 classification presented because the USDA classification not provided; in another report it was stated to be Sandy loam (USDA) containing 58.5% sand, 22.7% silt and 18.8% clay.

The soil residues studies and soil accumulation studies were not performed as the results of the field dissipation studies demonstrated that they were not required – their results clearly indicated that neither Flufenacet nor its degradation products would accumulate in soil.

Finally three relevant open-literature studies examining the dissipation of Flufenacet in soil under realistic – field conditions were identified. Their key results are presented below in the table B.8.1.1.2.2.4._CA-7.

Table B.8.1.1.2.2.4._CA-7: The key results obtained in the literature studies examining the field dissipation of Flufenacet.

Data on the trial			Soil characterisation			Data on application		Soil persistence of the test compound - Flufenacet		Mobility of the test compound – Flufenacet in soil profile
<i>Trial site</i>	<i>Duration of the study – Days After application</i>	<i>Crop cover</i>	<i>Soil textural type</i>	<i>Soil pH</i>	<i>OM content</i>	<i>Application date</i>	<i>Application rate [g/ ha]</i>	<i>DisT₅₀ [days]</i>	<i>Kinetic model</i>	
Melle/ Belgium	266	Bare soil	Sandy loam	6.2	2.2	21/11/1997	240	98	1 st order, linear regression	No residues below 15 cm
Melle/ Belgium	182	Spring corn	Sandy loam	6.2	2.2	24/03/1998	600	74	1 st order, linear regression	No residues below 15 cm
Melle/ Belgium	168	Summer corn	Sandy loam	6.2	2.2	28/05/1998	600	56	1 st order, linear regression	No residues below 15 cm
Melle/ Belgium	241	Winter wheat	Sandy loam	7.0	1.5	25/11/1999	240	66	1 st order, linear regression	Residues detected down to 20 cm, but mainly confined to top 10 cm
Zingem/ Belgium	241	Winter wheat	Loamy sand	6.4	1.6	25/11/1999	240	97	1 st order, linear regression	Residues detected down to 20 cm, but mainly confined to top 10 cm
Zevekote/ Belgium	241	Winter wheat	Clay loam	6.6	2.1	26/11/1999	240	64	1 st order, linear regression	Residues detected down to 20 cm, but mainly confined to top 10 cm
Crotil-Noirmont/ Belgium	241	Winter wheat	Silt loam	6.7	1.2	01/12/2000	240	54	1 st order, linear regression	Residues detected down to 20 cm, but mainly confined to top 10 cm
Melle/ Belgium	~150	Winter wheat	Sandy loam	7.0	1.5	17/03/2000	240	44	1 st order, linear regression	No information provided
Zingem/ Belgium	~150	Winter wheat	Loamy sand	6.4	1.6	04/04/2000	240	66	1 st order, linear regression	No information provided

B.8.1.1.3. – Summary of soil persistence (route and rate of degradation in soil)

The results of the examination of the persistence of Flufenacet in soil are presented below. The same summary is also provided in the Vol 1 and in Vol 3, B.8._CP.

1) Degradation in soil under aerobic conditions:

The route of degradation of the acetanilide herbicide Flufenacet in aerobic soil was extensively examined in eight agricultural soils – seven originating from the EU and one from US. The test compound – Flufenacet, was radiolabelled in one of the following three following positions:

- uniformly in phenyl ring – compound tested on four soils,
- position C2 in thiadiazole moiety – test performed on one soil,
- position C5 in thiadiazole moiety – examined in four soils.

These data were presented in five unpublished studies submitted specifically for the purpose of this assessment. Additionally the data relevant for determining transformation pattern of Flufenacet in aerobic soil, relevant for regulatory purposes, were found in one scientific paper, examining the degradation of Flufenacet radiolabelled uniformly in phenyl ring in two US soils. That study was based on a non-GLP regulatory study, conceived as a bridging study for laboratory and field experiments on the degradation of Flufenacet in soil. That study was verified by RMS and found acceptable. Therefore the results of the literature study based on it were included into evaluation.

The key results of the examination of transformation of Flufenacet are presented in the tabularised form below (tables B.8.1.1.3._CA-1 – B.8.1.1.3._CA-4), separately for the compound radiolabelled in phenyl ring and in thiadiazole moiety.

Table B.8.1.1.3._CA-1: The levels of mineralisation and NER fraction formed, and identified degradation products in experiments with [Phenyl-U-¹⁴C] Flufenacet.

Study	Soil		Level of mineralisation [% AR]:		Level of NER [% AR]:			Identified degradation products
	Name	Type (USDA)	After ~100 days	at the study's end	Max.	After ~100 days	at the study's end	
Kelley <i>et al.</i> ; 1995	BBA 2.2	Loamy sand	12.6 DAT 100	14.2 DAT 120	42.3 DAT 120	37.3 DAT 100	42.3 DAT 120	FOE Sulfonic acid; FOE Oxalate; FOE TGS; FOE Methylsulfoxide; FOE Methylsulfone
	Laacherhof	Silt loam	20.8 DAT 100	23.8 DAT 120	37.1 DAT 120	29.9 DAT 100	37.1 DAT 120	FOE Sulfonic acid; FOE Oxalate; FOE TGS; FOE Methylsulfoxide; FOE Methylsulfone
	Hofchen im Tal	Silt loam	10.2 DAT 100	12.0 DAT 120	58.0 DAT 120	56.2 DAT 100	58.0 DAT 120	FOE Sulfonic acid; FOE Oxalate; FOE TGS; FOE Methylsulfoxide; FOE Methylsulfone
Pangilinan & Smith; 1994	Howe	Sandy loam	2.7 DAT 91	5.9 DAT 365	17.7 DAT 271	16.3 DAT 91	16.5 DAT 365	FOE Sulfonic acid; FOE Oxalate; FOE Alcohol; FOE TGS; FOE Methylsulfoxide; FOE Chloroacetanilide;
Bloomberg <i>et al.</i> ; 2002	Fresno	Sandy loam	14.1 ¹⁾ DAT 88	14.1 ¹⁾ DAT 88	41.6 ²⁾ DAT 88	41.6 ²⁾ DAT 88	41.6 ²⁾ DAT 88	FOE Sulfonic acid; FOE Oxalate; FOE Alcohol;
	Chualar	Sandy loam	5.8 ¹⁾ DAT 88	5.8 ¹⁾ DAT 88	46.4 ²⁾ DAT 19	31.6 ²⁾ DAT 88	31.6 ²⁾ DAT 88	FOE Sulfonic acid; FOE Oxalate; FOE Alcohol;

Footnotes to the table:

- 1) Value estimated as a difference between the reported “total AR recovered” and the theoretical 100% AR;
- 2) The value is the sum of NER fraction in topsoil (0-3 cm) and subsoil (3-13 cm) for the given tie point; as in the subsoil the detected radioactivity was not further examined, but considered to represent NER fraction, in fact that value may be an overestimate;

Table B.8.1.1.3._CA-2: Concentrations and classification of soil degradation products identified in experiments with [Phenyl-U-¹⁴C] Flufenacet

Degradation product	Maximum [% AR] in soil, detected on:						Classification according to SANCO/221/2000	Justification ¹⁾
	BBA 2.2	Laacherhof	Hofchen im Tal	Howe	Fresno	Chualar		
FOE Sulfonic acid	25.4 DAT 100	26.3 DAT 100	13.5 DAT 100	7.7 DAT 180	2.4 DAT 88	1.3 DAT 88	major/relevant for GW assessment	> 10% AR
FOE Oxalate	6.6 DAT 28	15.6 DAT 28	10.0 DAT 28	26.5 DAT 365	13.0 DAT 46	7.6 DAT 88	major/relevant for GW assessment	>10% AR
FOE Alcohol	n. d.	n. d.	n. d.	2.1 DAT 44, DAT 65	8.1 DAT 88	21.2 DAT 88	major/relevant for GW assessment	>10% AR
FOE TGS	3.3 DAT 56	5.5 DAT 28	1.9 DAT 28	3.7 DAT 180	n. d. ²⁾	n. d. ²⁾	minor/not relevant for GW assessment	Not meeting any of the criteria
FOE Methyl-sulfoxide	1.1 DAT 28, DAT 56	3.5 DAT 56	1.5 DAT 56	0.6 DAT 28	n. d. ²⁾	n. d. ²⁾	minor/not relevant for GW assessment	Not meeting any of the criteria
FOE Methyl-sulfone	6.6 DAT 100	4.3 DAT 120	5.6 DAT 120	n. d.	n. d. ²⁾	n. d. ²⁾	major/relevant for GW assessment	>5% AR at study end, increasing
FOE Chloroacet-anilide	n. d. ²⁾	n. d. ²⁾	n. d. ²⁾	5.1 DAT 44	n. d. ²⁾	n. d. ²⁾	minor/not relevant for GW assessment	Not meeting any of the criteria

Footnotes to the table:

- 1) Justification based on the criteria set by the Guideline SANCO/221/2000, listed under the point 4 on page 6:
“As a minimum, degradation products must be characterized and identified by the notifiers to the extent that it is technically feasible and their relevance must be assessed, if one of the following conditions applies:
a) Metabolites, which account for more than 10% of the amount of active substance added in soil at any time during the studies; or
b) which account for more than 5% of the amount of active substance added in soil in at least two sequential measurements during the studies; or
c) for which at the end of soil degradation studies the maximum of formation is not yet reached.
- 2) Compound not detected in that soil.

Table B.8.1.1.3._CA-3: The levels of mineralisation and NER fraction formed, and identified degradation products in experiments with [Thiadiazole-¹⁴C] Flufenacet.

Study/ radiolabelling position	Soil		Level of mineralisation [% AR]:		Level of NER [% AR]:			Identified degradation products
	Name	Type (USDA)	after ~100 days	at the study's end	Max.	after ~100 days	at the study's end	
Pangilinan & Smith; 1994a [Thiadiazole-2- ¹⁴ C]	Howe	Sandy loam	31.9 DAT 90	50.9 DAT 368	6.9 DAT 270	6.2 DAT 90	6.5 DAT 368	FOE Thiadone
Hein; 2012 [Thiadiazole-5- ¹⁴ C]	Hoefchen am Hohenseh 4a	Silt loam	5.7 DAT 120	5.7 DAT 120	13.5 DAT 60	12.5 DAT 120	12.5 DAT 120	FOE Thiadone; FOE Trifluoroethane-sulfonic acid; Trifluoroacetic acid (TFA)
Hein; 2012a [Thiadiazole-5- ¹⁴ C]	Laacherhof AXXa	Loamy sand	5.6 DAT 121	5.6 DAT 121	18.6 DAT 63	17.2 DAT 121	17.2 DAT 121	FOE Thiadone; FOE 5043-Trifluoroethane-sulfonic acid; Trifluoroacetic acid (TFA)
	Dollendorf II	Clay loam	6.5 DAT 121	6.5 DAT 121	11.5 DAT 63	10.6 DAT 121	10.6 DAT 121	FOE Thiadone; FOE 5043-Trifluoroethane-sulfonic acid; Trifluoroacetic acid (TFA)
	Laacherhof Wurmwiess	Loam	4.6 DAT 121	4.6 DAT 121	18.6 DAT 35, DAT 63	17.2 DAT 121	17.2 DAT 121	FOE Thiadone; FOE 5043-Trifluoroethane-sulfonic acid; Trifluoroacetic acid (TFA)

Table B.8.1.1.3._CA-4: Concentrations and classification of soil degradation products identified in experiments with [Thiadiazole-¹⁴C] Flufenacet

Degradation product	Maximum [% AR] in soil, detected on:					Classification according to SANCO/221/2000	Justification ¹⁾
	Howe	Hoefchen am Hohenseh 4a	Laacherhof AXxa	Dollendorf II	Laacherhof Wurmweise		
FOE Thiadone	3.9 DAT 7	5.8 DAT 10	2.8 DAT 7	5.6 DAT 10	4.6 DAT	major/relevant for GW assessment	> 5% AR at two consecutive time points
FOE Trifluoroethanesulfonic acid	n. d. ²⁾	6.0 DAT 14	4.4 DAT 10	3.4 DAT 10	1.9 DAT 10	major/relevant for GW assessment	> 5% AR at two consecutive time points
TFA (Trifluoroacetic acid)	n. d. ²⁾	77.7 DAT 87	74.1 DAT 121	81.5 DAT 91	74.8 DAT 91	major/relevant for GW assessment	> 10% AR

Footnotes to the table:

- 1) Justification based on the criteria set by the Guideline SANCO/221/2000, listed under the point 4 on page 6:
“As a minimum, degradation products must be characterized and identified by the notifiers to the extent that it is technically feasible and their relevance must be assessed, if one of the following conditions applies:
a) Metabolites, which account for more than 10% of the amount of active substance added in soil at any time during the studies; or
b) which account for more than 5% of the amount of active substance added in soil in at least two sequential measurements during the studies; or
c) for which at the end of soil degradation studies the maximum of formation is not yet reached.
- 2) Compound not detected in that soil.

The transformation pattern of Flufenacet in soil was examined only on biologically viable soil. That was due to the fact that, on the basis of available results it was assumed that all transformation processes were predominantly or solely biologically-mediated. It was postulated that the initial step of the degradation was the cleavage of the test item on bridging oxygen of the thiadiazole heterocycle. The further sequence for the thiadiazole moiety is presented below:

- tautomerisation of keto-enol functional group, resulting in formation of FOE Thiadone,
- hydrolytical opening of thiadone ring and further oxidation resulting in formation of either FOE 5043-Trifluoroethanesulfonic acid or Trifluoroacetic acid (TFA), or else simple products of mineralisation and NER fraction – ultimate transformation products;
- further transformation of FOE 5043-Trifluoroethanesulfonic acid or Trifluoroacetic acid (TFA) to the simple products of mineralisation and NER fraction – ultimate transformation products.

In case of the moiety containing fluorophenyl ring next postulated step was the formation of the transient FOE Cysteine- or FOE Glutathione conjugates, undergoing subsequent quick transformation to FOE Methylsulfoxide, FOE Alcohol and FOE Chloroacetanilide. As possible side-processes were postulated direct formation of FOE Chloroacetanilide and FOE Alcohol. It shall be noted that FOE Chloroacetanilide may be not only a genuine degradation product, but also, and possibly to greater extent, analytical artefact. However, as the issue was not satisfactorily clarified, the RMS's proposal is to consider FOE Chloroacetanilide a genuine degradation product.

Additionally, as in course of evaluation FOE Alcohol was identified to be a potentially major degradation product, the additional assessment was performed to determine whether, in absence of data for that compound, the exposure assessment for FOE Alcohol may be considered to be covered by that for its immediate degradate – FOE Oxalate.

The Applicant in course of the discussion on the nature of FOE Alcohol made a following statement (the text is copied directly from the Applicant's e-mail; the “outdoor soil metabolism study” refers to the cited study by Shadrack and Kasper [1995]):

We cannot reconstruct what the reason for the accumulation or artificial formation of FOE alcohol (aka FOE hydroxy) was in that outdoor soil metabolism study, but we have several other laboratory studies, as well as EU and US field studies, which demonstrate, that FOE alcohol is a minor, transient metabolite, not accumulating at all, but rather being further oxidized quickly to FOE oxalate.

RMS having analysed the results provided by the study by Shadrack and Kasper [1995], reproduced in the publication by Bloomberg et al. [2002], noted that the compound was formed in greater amounts in Chualar soil, having lower OC content and slightly lower microbial activity of the two soils used in the experiment. Taking into account the fact that FOE Alcohol was also detected only in the study by Pangilinan and Smith [1994], performed on another soil having low OC content and microbial activity, but not in the study by Kelley et al [1995], all that may indicate that FOE Alcohol is indeed a transient, fast degrading compound, that would appear in higher amounts and for longer only in weak soils.

To further demonstrate that it was possible to cover the exposure assessment for FOE Alcohol with that for its immediate degradate – FOE Oxalate, RMS performed the comparative analysis by means of QSAR calculations, carried out with EPI Suite ver. 4.10 (September 2010) tool. The results of that assessment indicate that the properties of both compounds relevant for their environmental fate and behaviour are comparable. Therefore the exposure assessment performed for FOE Oxalate may be considered as covering that for FOE Alcohol.

The route of degradation of the acetanilide herbicide Flufenacet in anaerobic soil was examined in three soils – one from the US and two European. The test compound – Flufenacet, was radiolabelled in one of the following two positions:

- uniformly in phenyl ring – compound tested on one US soil,
- in position C5 of Thiadiazole moiety – examined in two EU soils.

The experiments performed to determine the transformation pattern of Flufenacet in soil under anaerobic conditions consisted of two phases – aerobic preincubation phase and anaerobic incubation phase. RMS decided to present the key results of the experiments taking into account both phases. In case of aerobic preincubation phase the results are given for the terminal time point of that phase.

The key results for the examination of transformation of Flufenacet in anaerobic soils in the area of formation of terminal degradation products – mineralisation expressed as CO₂ and NER fraction, are presented below in the table B.8.1.1.3._CA-5. To differentiate the results obtained for aerobic phase from those for anaerobic phase the former were shaded light grey. It shall be noted that under anaerobic conditions mineralisation, if occurred at all, was minimal. No other volatile compounds were identified during either aerobic or anaerobic phases. The level of NER formed under anaerobic conditions (net formation) was comparable to that observed in aerobic soils.

Table B.8.1.1.3._CA-5: The levels of the terminal degradation products – CO₂ and NER fraction formed in soil during examination of the transformation pattern of Flufenacet in soil under anaerobic conditions.

Study/ radiolabelling position	Soil		Results obtained for aerobic phase		Results obtained for anaerobic phase ¹⁾					
	Name	Type (USDA)	CO ₂ [%AR] – end of phase	NER [%AR] – end of phase	Mineralisation level – CO ₂ formed [% AR]			NER level [% AR]		
					Beginning of phase	Max.	Net anaero- bic ²⁾	Beginning of phase	Max.	Net anaero- bic ³⁾
Pangilinan & Smith [1994]/ ¹⁴ C-phenyl	Howe	Sandy loam	1.4 (DAT 30)	8.4 (DAT 30)	1.4 (DAT 30 DAF 0)	1.8 (DAT 210 DAF 180)	0.4	8.4 (DAT 30 DAF 0)	32.6 (DAT 210 DAF 180)	24.2 (DAT 210 DAF 180)
Heinemann [2012]/ ¹⁴ C-5- Thiadiazole	HH ⁴⁾	Silt loam	1.6 (DAT 15)	16.9 (DAT 15)	1.6 (DAT 15 DAF 0)	1.7 (DAT 105 DAF 90)	0.1	10.2 (DAT 15 DAF 0)	24.5 (DAT 135 DAF 120)	14.3 (DAT 135 DAF 120)
	DD ⁵⁾	Loam	1.9 (DAT 15)	10.1 (DAT 15)	1.8 (DAT 15 DAF 0)	1.9 (DAT 105 DAF 90)	<0.1 ⁶⁾	8.6 (DAT 15 DAF 0)	31.6 (DAT 135 DAF 120)	23.0 (DAT 135 DAF 120)

Footnotes to the table:

- 1) In case of Howe soil the results for the beginning of anaerobic phase are the same as those for the end of aerobic phase; in case of soils HH and DD they are different, because were available the results obtained immediately after generating the anaerobic conditions;
- 2) Net anaerobic is a difference between the total amount of CO₂ formed and that determined in aerobic traps for volatiles;
- 3) Net anaerobic is a difference between maximum determined level of NER and that measured at the beginning of anaerobic phase;
- 4) HH stands for *Hoefchen am Hohenseh 4a* soil;
- 5) DD stands for *Dollendorf II* soil;
- 6) At the time point where maximum CO₂ level of 2.0% AR was recorded, the amount recovered for aerobic volatile traps was 1.9% AR and from anaerobic volatile traps <0.1 AR; the slightly higher total amount may be due to either rounding or losses during extraction; in that soil the level of mineralization, expressed as recovered CO₂ in anaerobic phase was <0.1% AR;

The examination of the extracted fraction enabled the identification of one new degradate, not identified in aerobic soils – FOE Thioglycolate. All other identified degradation products were those already found in aerobic soils. On that basis it can be stated that the transformation pattern of Flufenacet in soil under anaerobic conditions would not differ significantly from that determined in aerobic soils. The key results of the profiling of degradation products in anaerobic soils are presented below in table B.8.1.1.3._CA-6. To differentiate the results obtained for aerobic phase from those for anaerobic phase the former were shaded light grey.

Table B.8.1.1.3._CA-6: The results of the profiling of Flufenacet and its degradation products.

Study/ radiolabelling position	Soil		Results obtained for aerobic phase		Results obtained for anaerobic phase ¹⁾				
	Name	Type (USDA)	Identified compound	Amount [% AR] at the end of phase	Identified compound	Amount [% AR] measured at:			Anaerobic metabolite (yes/no)
Pangilinan & Smith [1994]/ ¹⁴ C-phenyl	Howe	Sandy loam	Flufenacet	69.0 (DAT 30)	Flufenacet	69.0 (DAT 30/ DAF 0)	39.0 ⁶⁾ (DAT 210/ DAF 180)	N/A ⁸⁾	N/A ⁸⁾
			FOE Oxalate	11.2 (DAT 30)	FOE Oxalate	11.2 (DAT 30/ DAF 0)	14.5 (DAT 60/ DAF 30)	3.3 (DAT 60/ DAF 30)	Yes
			FOE Sulfonic acid	6.6 (DAT 30)	FOE Sulfonic acid	6.6 (DAT 30/ DAF 0)	6.6 (DAT 30/ DAF 0)	0.0	No
			FOE Alcohol	0.0 (DAT 30)	FOE Alcohol	0.0 (DAT 30/ DAF 0)	1.4 (DAT 153/ DAF 123)	1.4 (DAT 153/ DAF 123)	Yes
			FOE TGS ³⁾	2.6 (DAT 30)	FOE TGS ³⁾	2.6 (DAT 30/ DAF 0)	2.6 (DAT 30/ DAF 0)	0.0	No
					FOE Thioglycolate	0.0 (DAT 30/ DAF 0)	1.7 (DAT 60/ DAF 30)	1.7 (DAT 60/ DAF 30)	Yes
Heinemann [2012]/ ¹⁴ C-5- Thiadiazole	HH ⁴⁾	Silt loam	Flufenacet	30.8 (DAT 15)	Flufenacet	42.8 (DAT 15/ DASF 0)	6.4 ⁶⁾ (DAT 135/ DASF 120)	N/A ⁸⁾	N/A ⁸⁾
			FOE Thiadone	5.9 (DAT 15)	FOE Thiadone	4.8 (DAT 15/ DASF 0)	13.6 (DAT 77/ DASF 62)	8.8 (DAT 77/ DASF 62)	Yes
			FOE 5043- Trifluoroethane- sulfonic acid	2.5 (DAT 15)	FOE 5043- Trifluoroethane- sulfonic acid	5.1 (DAT 15/ DASF 0)	4.2 ⁷⁾ (DAT 48/ DASF 33)	4.2 ⁷⁾ (DAT 48/ DASF 33)	Yes
			Trifluoroacetic acid	37.5 (DAT 15)	Trifluoroacetic acid	31.4 (DAT 15/ DASF 0)	47.9 (DAT 135/ DASF 120)	16.5 (DAT 135/ DASF 120)	Yes
	DD ⁵⁾	Loam	Flufenacet	44.2 (DAT 15)	Flufenacet	35.4 (DAT 15/ DASF 0)	3.1 ⁶⁾ (DAT 135/ DASF 120)	N/A ⁸⁾	N/A ⁸⁾
			FOE Thiadone	4.3 (DAT 15)	FOE Thiadone	7.1 (DAT 15/ DASF 0)	12.4 (DAT 21/ DASF 6)	5.3 (DAT 21/ DASF 6)	Yes
			FOE 5043- Trifluoroethane- sulfonic acid	6.0 (DAT 15)	FOE 5043- Trifluoroethane- sulfonic acid	3.2 (DAT 15/ DASF 0)	3.2 (DAT 15/ DASF 0)	0.0	No
			Trifluoroacetic acid	28.0 (DAT 15)	Trifluoroacetic acid	40.4 (DAT 15/ DASF 0)	53.2 (DAT 105/ DASF 90)	12.8 (DAT 105/ DASF 90)	Yes

Footnotes to the table:

- 1) In case of Howe soil the results for the beginning of anaerobic phase are the same as those for the end of aerobic phase; in case of soils HH and DD they are different, because were available the results obtained immediately after generating the anaerobic conditions;
- 2) Net anaerobic is a difference between the maximum amount determined in anaerobic phase and that at its beginning;
- 3) FOE TGS – FOE Thioglycolate sulfoxide;
- 4) HH stands for *Hoefchen am Hohenseh 4a* soil;
- 5) DD stands for *Dollendorf II* soil;
- 6) Flufenacet is the active substance, therefore not forming in soil; as a result its concentration at the end of incubation period is given to show the level of decline;
- 7) In that soil the concentrations of FOE Trifluoroethane sulfonic acid initially decreased, to increase afterwards reaching maximum on the indicated time point; it was assumed that this maximum can be attributed totally to the amount of that compound formed under anaerobic conditions;
- 8) N/A – not applicable (parent compound);

On the basis of the results of the studies examining route of degradation of Flufenacet in soil under aerobic conditions a following transformation scheme was proposed – Figure B.8.1.1.3._CA-1 (it shall be indicated that

the scheme contains also the elements of the transformation pattern under anaerobic conditions, as the two schemes were complementary):

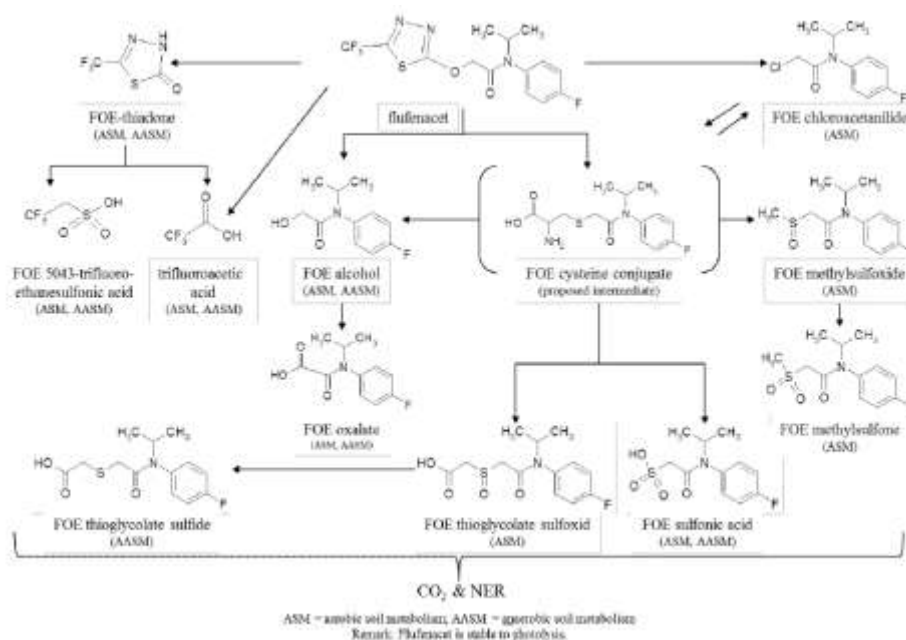


Figure B.8.1.1.3._CA-1: A postulated transformation scheme for Flufenacet in soil, as proposed by the Applicant, verified and approved by the RMS (scheme copied from the Applicant's documentation).

The degradation kinetics of Flufenacet in aerobic soil under laboratory conditions was extensively examined by the Applicant and its results presented in 26 study reports, of which 24 were found by the RMS acceptable and relevant for the current assessment. Additionally two literature studies were identified by the RMS which also provided the data on the degradation kinetics of Flufenacet in aerobic soils. These reports were found by the RMS relevant as supplementary source of data, however not suitable for deriving the regulatory endpoints.

The key results for each of the evaluated compounds are presented below, in tabularised form, individually for each of the test compounds.

a) Kinetic endpoints determined for Flufenacet:

The degradation kinetics of Flufenacet in aerobic soil was examined in ten trials using nine soils. One of the test soils – Howe, Indiana, Sandy loam soil, was used in two trials in which was used Flufenacet differently radiolabelled (either in phenyl ring or in C2 position of thiadiazole moiety), but the resulting kinetic endpoints cannot be averaged prior to calculating the overall geomean because they were derived in two separate studies, significantly differing in sample processing method.

The persistence (best-fit) kinetic endpoints obtained for Flufenacet are presented below in the table B.8.1.1.3._CA-7. The modelling endpoints are given in the table B.8.1.1.3._CA-8.

Table B.8.1.1.3._CA-7: The persistence kinetic endpoints determined for Flufenacet in aerobic soil.

Soil		Soil properties		Incubation conditions	Kinetic model	Evaluation of the fit		Kinetic parameters		Kinetic endpoints	
Soil name	Soil type (USDA)	OC	pH			χ^2 error	Visual fit ¹⁾ /R ²	Param.	Value	DT ₅₀ [days]	DT ₉₀ [days]
BBA 2,2; [Phenyl-U- ¹⁴ C] label	Loamy sand	2.58	6.2 ²⁾	20°C; 40% MWHC	SFO	8.53	A/ 0.974	<i>k</i>	0.0217	31.9	106.1
Laacherhof; [Phenyl-U- ¹⁴ C] label	Silt loam	0.9	6.2 ²⁾	20°C; 40% MWHC	SFO	11.0	G/0.978	<i>k</i>	0.0411	16.9	56
Höfchen im Tal; [Phenyl-U- ¹⁴ C] label	Silt loam	2.40	6.2 ²⁾	20°C; 40% MWHC	SFO	5.47	G/ 0.990	<i>k</i>	0.0339	20.4	67.9
Howe, Indiana; [Phenyl-U- ¹⁴ C] label	Sandy loam	0.35	6.2 ³⁾	21°C; 75% of ½ bar	SFO	2.36	G/ 0.981	<i>k</i>	0.0215	32.2	107.0
Laacherhof AXXa; [Phenyl-U- ¹⁴ C] label	Sandy loam	1.41	6.1 ⁴⁾	20°C; 50% MWHC	SFO	11.23	A/ 0.975	<i>k</i>	0.0943	7.35	24.4
Hoefchen Am Hohenseh 4a; [Thiadiazole-5- ¹⁴ C] label	Silt loam	2.5	6.7 ⁴⁾	19.1°C; 55% MWHC	SFO	4.88	G/ 0.995	<i>k</i>	0.0438	15.8	52.6
Laacherhof AXXa; [Thiadiazole-5- ¹⁴ C] label	Loamy sand	2.4	6.1 ⁴⁾	19.9°C; 55% MWHC	SFO	3.03	G/ 0.997	<i>k</i>	0.0349	19.85	65.9
Dollendorf II; [Thiadiazole-5- ¹⁴ C] label	Clay loam	5.3	7.2 ⁴⁾	19.9°C; 55% MWHC	SFO	4.67	G/ 0.994	<i>k</i>	0.0425	16.3	54.2
Laacherhof Wurmwiese; [Thiadiazole-5- ¹⁴ C] label	Loam	2.2	5.4 ⁴⁾	19.9°C; 55% MWHC	SFO	4.27	G/ 0.994	<i>k</i>	0.0465	14.9	49.5
Howe, Indiana; [Thiadiazole-2- ¹⁴ C] label	Sandy loam	0.35	6.2 ³⁾	21°C; 75% of ½ bar	SFO	2.80	A/ 0.940	<i>k</i>	0.0120	57.6	191.42

Footnotes to the table:

1) The abbreviations used to describe the visual fit: G. – good, A. – acceptable, P. – poor;

2) Declared to be measured in CaCl₂/Water;

3) Measured in distilled water;

4) Measured in CaCl₂

The DT₅₀ = **57.6 days** value, determined in Howe, Indiana Sandy loam soil treated with [Thiadiazole-2-¹⁴C] Flufenacet was identified as appropriate input parameter for soil exposure assessment.

Table B.8.1.1.3._CA-8: The modelling kinetic endpoints determined for Flufenacet in aerobic soil.

Soil		Soil properties		Incubation conditions	Kinetic model	Evaluation of the fit		Kinetic parameters		Kinetic endpoints	
Soil name	Soil type (USDA)	OC	pH			χ^2 error	Visual fit ¹⁾ /R ²	Param.	Value	DT ₅₀ [days]	DT ₉₀ [days]
BBA 2,2; [Phenyl-U- ¹⁴ C] label	Loamy sand	2.58	6.2 ²⁾	20°C; 40% MWHC	SFO	8.53	A/ 0.974	k	0.0217	31.9	106.1
Laacherhof; [Phenyl-U- ¹⁴ C] label	Silt loam	0.9	6.2 ²⁾	20°C; 40% MWHC	SFO	11.0	G/0.978	k	0.0500	13.86	45.92
Höfchen im Tal; [Phenyl-U- ¹⁴ C] label	Silt loam	2.40	6.2 ²⁾	20°C; 40% MWHC	SFO	5.47	G/ 0.990	k	0.0339	20.44	67.9
Howe, Indiana; [Phenyl-U- ¹⁴ C] label	Sandy loam	0.35	6.2 ³⁾	21°C; 75% of ½ bar	SFO	2.36	G/ 0.981	k	0.0332	20.90	69.44
Laacherhof AXXa; [Phenyl-U- ¹⁴ C] label	Sandy loam	1.41	6.1 ⁴⁾	20°C; 50% MWHC	SFO	11.23	A/ 0.975	k	0.0985	7.04	23.37
Hoefchen Am Hohenseh 4a; [Thiadiazole-5- ¹⁴ C] label	Silt loam	2.5	6.7 ⁴⁾	19.1°C; 55% MWHC	SFO	4.88	G/ 0.995	k	0.0451	15.36	51.02
Laacherhof AXXa; [Thiadiazole-5- ¹⁴ C] label	Loamy sand	2.4	6.1 ⁴⁾	19.9°C; 55% MWHC	SFO	3.03	G/ 0.997	k	0.0356	19.45	64.58
Dollendorf II; [Thiadiazole-5- ¹⁴ C] label	Clay loam	5.3	7.2 ⁴⁾	19.9°C; 55% MWHC	SFO	4.67	G/ 0.994	k	0.0447	15.49	51.52
Laacherhof Wurmweise; [Thiadiazole-5- ¹⁴ C] label	Loam	2.2	5.4 ⁴⁾	19.9°C; 55% MWHC	SFO	4.27	G/ 0.994	k	0.0474	14.61	48.51
Howe, Indiana; [Thiadiazole-2- ¹⁴ C] label	Sandy loam	0.35	6.2 ³⁾	21°C; 75% of ½ bar	SFO	2.80	A/ 0.940	k	0.0185	37.40	124.23
Geometric mean (n = 10)									0.0387	17.89	59.42
Median (n = 10)									0.0402	17.47	58.05

Footnotes to the table:

- 1) The abbreviations used to describe the visual fit: G. – good, A. – acceptable, P. – poor;
- 2) Declared to be measured in CaCl₂/Water;
- 3) Measured in distilled water;
- 4) Measured in CaCl₂

For GW and SW model exposure assessment the **geomean DT₅₀ = 17.89 days** and **geomean k = 0.0387 [days⁻¹]** are the kinetic endpoints recommended as input parameters.

b) Kinetic endpoints determined for FOE Sulfonic acid:

The degradation kinetics of FOE Sulfonic acid in aerobic soil was examined in seventeen trials on the same number of the test soils. The experiments were performed in two variants – four trials with soils treated with Flufenacet (active substance) and the remaining thirteen trials with soils treated with FOE Sulfonic acid.

The performed kinetic analysis resulted in a data base consisting of twelve reliable kinetic endpoints, all determined in trials in which the test soils were treated with FOE Sulfonic acid. In case of the experiments on soils treated with Flufenacet it was not possible to obtain reliable kinetic endpoints characterising degradation of FOE Sulfonic acid in soil because decline of that compound was not observed. As a result, the default values – DT₅₀ = 1000 days and DT₉₀ > 1000 days, were proposed for these trials. These values, due to their nature and uncertainty related to them, were not used either as input parameters in soil exposure assessment or to calculate normalised mean values used subsequently in GW/SW exposure assessment. They are however provided in the table presenting the persistence endpoints, as with them are associated reliable kinetic formation fractions for FOE Sulfonic acid, recommended to be used in GW exposure assessment. RMS however decided not to provide them in the table presenting the kinetic endpoints recommended for modelling.

In case of the kinetic analysis of the data obtained in Laacherhof IIIA Silt loam soil in the study by [Hellpointner; 1996], it was not possible to obtain a reliable kinetic fit and hence kinetic endpoints. For that reason the trial was removed from both summary table presenting persistence and modelling endpoints.

The persistence (best-fit) kinetic endpoints obtained for FOE Sulfonic acid are presented below in the table B.8.1.1.3._CA-9. The modelling endpoints are given in the table B.8.1.1.3._CA-10.

Table B.8.1.1.3._CA-9: The persistence kinetic endpoints determined for FOE Sulfonic acid in aerobic soil.

Soil		Soil properties		Incubation conditions	Kinetic model	Evaluation of the fit		Kinetic parameters		Kinetic endpoints		
Soil name	Soil type (USDA)	OC	pH ¹⁾			χ^2 error	Vis. fit ²⁾	Par.	Value	DT ₅₀ [days]	DT ₉₀ [days]	Kinetic formation fraction ff
BBA 2.2	Loamy sand	2.58	6.2 ^{a)}	20 ⁰ C; 40% MWHC	SFO	15.4	G	k	n. d. ³⁾	1000	>1000	0.257
Laacherhof	Silt loam	0.9	7.3 ^{a)}	20 ⁰ C; 40% MWHC	SFO	8.42	G	k	n. d. ³⁾	1000	>1000	0.272
Höfchen im Tal	Silt loam	2.40	5.8 ^{a)}	20 ⁰ C; 40% MWHC	SFO	6.56	G	k	n. d. ³⁾	1000	>1000	0.143
Howe, Indiana;	Sandy loam	0.35	6.2 ^{b)}	21 ⁰ C; 75% of 1/3 bar	SFO	6.28	G	k	n. d. ³⁾	1000	>1000	0.108
BBA 2.1	Sand	0.57	5.3 ^{c)}	20 ± 2 ⁰ C; 75% of 1/3 bar	SFO	1.78	G	k	2.18 E-3	318	1060	n. a. ⁴⁾
BBA 2.2	Loamy sand	2.48	6.3 ^{c)}	20 ± 2 ⁰ C; 75% of 1/3 bar	SFO	1.88	G	k	3.28 E-3	211	701	n. a. ⁴⁾
Laacherhof AXXa	Sandy loam	1.47	6.3 ^{c)}	20 ± 2 ⁰ C; 40% MWHC	SFO	3.05	G	k	0.0111	62.31	206.99	n. a. ⁴⁾
Laacherhof AIII	Silt loam	0.88	6.8 ^{c)}	20 ± 2 ⁰ C; 40% MWHC	SFO	3.03	G	k	0.0115	60.26	200.18	n. a. ⁴⁾
Laacherhof AXXa	Loamy sand	1.7	6.2 ^{c)}	19.6 ⁰ C; 55% MWHC	SFO	1.28	G	k	9.45 E-3	73.38	243.77	n. a. ⁴⁾
Dollendorf II	Loam	4.6	7.0 ^{c)}	19.6 ⁰ C; 55% MWHC	SFO	5.59	G	k	0.1033	6.71	22.30	n. a. ⁴⁾
Hoefchen Am Hohenseh 4a;	Silt loam	2.0	6.1 ^{c)}	19.6 ⁰ C; 55% MWHC	SFO	7.68	G	k	0.0242	28.58	94.95	n. a. ⁴⁾
Wurm-wiese	Sandy loam	1.8	5.0 ^{c)}	19.6 ⁰ C; 55% MWHC	SFO	3.66	G	k	0.0139	49.77	165.32	n. a. ⁴⁾
Hanscheider Hof	Loam	2.8	5.6 ^{c)}	19.9 ⁰ C; 55% MWHC	SFO	3.25	G	k	0.02539	27.30	90.70	n. a. ⁴⁾
Frankenforst	Silt loam	1.8	6.8 ^{c)}	19.9 ⁰ C; 55% MWHC	SFO	6.41	G	k	0.03181	21.79	72.39	n. a. ⁴⁾
LUFA 2.3	Sandy loam	1.1	6.8 ^{c)}	19.9 ⁰ C; 55% MWHC	SFO	1.45	G	k	0.0108	63.87	212.16	n. a. ⁴⁾
LUFA 6S	Clay	1.9	7.0 ^{c)}	19.9 ⁰ C; 55% MWHC	SFO	6.49	G	k	0.01838	37.71	125.28	n. a. ⁴⁾
Arithmetic mean for ff (n = 4)												0.195

Footnotes to the table:

- 1) Measured in:
 - CaCl₂/water for values marked a);
 - distilled water for results marked b);
 - 0.01M CaCl₂ for results marked c);
- 2) The abbreviations used to describe the visual fit: G – good, A – acceptable, P – poor;
- 3) Value not determined – the decline phase not reached;
- 4) Value not available – the test compound applied as parent.

The DT₅₀ = **318 days** value, determined in BBA 2.1 Sand soil treated with FOE Sulfonic acid was identified as appropriate input parameter for soil exposure assessment.

Table B.8.1.1.3._CA-10: The modelling kinetic endpoints determined for FOE Sulfonic acid in aerobic soil.

Soil		Soil properties		Incubation conditions	Kinetic model	Evaluation of the fit		Kinetic parameters		Kinetic endpoints		
Soil name	Soil type (USDA)	OC	pH ¹⁾			χ^2 error	Vis. fit ²⁾	Par.	Value	DT ₅₀ [days]	DT ₉₀ [days]	Kinetic formation fraction <i>ff</i>
BBA 2.2	Loamy sand	2.58	6.2 ^{a)}	20 ⁰ C; 40% MWHC	SFO	15.4	G	<i>k</i>	n. d. ³⁾	n. d. ³⁾	n. d. ³⁾	0.257
Laacherhof	Silt loam	0.9	7.3 ^{a)}	20 ⁰ C; 40% MWHC	SFO	8.42	G	<i>k</i>	n. d. ³⁾	n. d. ³⁾	n. d. ³⁾	0.272
Höfchen im Tal	Silt loam	2.40	5.8 ^{a)}	20 ⁰ C; 40% MWHC	SFO	6.56	G	<i>k</i>	n. d. ³⁾	n. d. ³⁾	n. d. ³⁾	0.143
Howe, Indiana;	Sandy loam	0.35	6.2 ^{b)}	21 ⁰ C; 75% of 1/3 bar	SFO	6.28	G	<i>k</i>	n. d. ³⁾	n. d. ³⁾	n. d. ³⁾	0.108
BBA 2.1	Sand	0.57	5.3 ^{c)}	20 ± 2 ⁰ C; 75% of 1/3 bar	SFO	1.78	G	<i>k</i>	2.66 E-3	260.76	869.2	n. a. ⁴⁾
BBA 2.2	Loamy sand	2.48	6.3 ^{c)}	20 ± 2 ⁰ C; 75% of 1/3 bar	SFO	1.88	G	<i>k</i>	3.28 E-3	211.00	701	n. a. ⁴⁾
Laacherhof AXXa	Sandy loam	1.47	6.3 ^{c)}	20 ± 2 ⁰ C; 40% MWHC	SFO	3.05	G	<i>k</i>	0.0139	49.85	165.59	n. a. ⁴⁾
Laacherhof AIII	Silt loam	0.88	6.8 ^{c)}	20 ± 2 ⁰ C; 40% MWHC	SFO	3.03	G	<i>k</i>	0.0172	40.37	134.12	n. a. ⁴⁾
Laacherhof AXXa	Loamy sand	1.7	6.2 ^{c)}	19.6 ⁰ C; 55% MWHC	SFO	1.28	G	<i>k</i>	9.84 E-3	70.44	234.02	n. a. ⁴⁾
Dollendorf II	Loam	4.6	7.0 ^{c)}	19.6 ⁰ C; 55% MWHC	SFO	5.59	G	<i>k</i>	0.1109	6.25	20.77	n. a. ⁴⁾
Hoefchen Am Hohenseh 4a;	Silt loam	2.0	6.1 ^{c)}	19.6 ⁰ C; 55% MWHC	SFO	7.68	G	<i>k</i>	0.0269	25.79	85.68	n. a. ⁴⁾
Wurm-wiese	Sandy loam	1.8	5.0 ^{c)}	19.6 ⁰ C; 55% MWHC	SFO	3.66	G	<i>k</i>	0.0145	47.78	158.71	n. a. ⁴⁾
Hanscheider Hof	Loam	2.8	5.6 ^{c)}	19.9 ⁰ C; 55% MWHC	SFO	3.25	G	<i>k</i>	0.0256	27.03	89.79	n. a. ⁴⁾
Frankenforst	Silt loam	1.8	6.8 ^{c)}	19.9 ⁰ C; 55% MWHC	SFO	6.41	G	<i>k</i>	0.0321	21.57	70.68	n. a. ⁴⁾
LUFA 2.3	Sandy loam	1.1	6.8 ^{c)}	19.9 ⁰ C; 55% MWHC	SFO	1.45	G	<i>k</i>	0.0110	63.23	210.04	n. a. ⁴⁾
LUFA 6S	Clay	1.9	7.0 ^{c)}	19.9 ⁰ C; 55% MWHC	SFO	6.49	G	<i>k</i>	0.02158	32.11	106.60	n. a. ⁴⁾
Geometric mean (n = 12)									0.0154	45.11	149.74	----
Median (n = 12)									0.0159	44.08	146.42	----
Arithmetic mean for <i>ff</i> (n = 4)												0.195

Footnotes to the table:

- 1) Measured in:
 - CaCl₂/water for values marked a);
 - distilled water for results marked b);
 - (0.01M) CaCl₂ for results marked c);
- 2) The abbreviations used to describe the visual fit: G. – good, A. – acceptable, P. – poor;
- 3) Value not determined – the decline phase not reached;
- 4) Value not available – the test compound applied as parent.

For GW and SW model exposure assessment the **geomean DT₅₀ = 45.11 days** and **geomean *k* = 0.0154 [days⁻¹]** are the kinetic endpoints recommended as input parameters. The corresponding recommended *ff* value is ***ff* = 0.195** (arithmetic mean) for Flufenacet as a precursor.

c) Kinetic endpoints determined for FOE Oxalate:

The degradation kinetics of FOE Oxalate in aerobic soil was examined in four trials on the same number of the test soils. The experiments were performed with soils treated with Flufenacet (active substance).

The performed kinetic analysis resulted in a data base consisting of three reliable kinetic endpoints. In case of the experiment in Howe, Indiana, Sandy loam soil it was not possible to obtain reliable kinetic endpoints characterising degradation of FOE Oxalate because the decline of that compound was not observed. As a result, the default values – DT₅₀ = 1000 days and DT₉₀ > 1000 days, were proposed for that trial. These values, due to

their nature and uncertainty related to them, were not used either as input parameters in soil exposure assessment or to calculate normalised mean values used subsequently in GW/SW exposure assessment. They are however provided in the table presenting the persistence endpoints, as with them are associated reliable kinetic formation fraction for FOE Oxalate, recommended to be used in GW exposure assessment. RMS however decided not to provide them in the table presenting the kinetic endpoints recommended for modelling.

The persistence (best-fit) kinetic endpoints obtained for FOE Oxalate are presented below in the table B.8.1.1.3._CA-11. The modelling endpoints are given in the table B.8.1.1.3._CA-12.

Table B.8.1.1.3._CA-11: The persistence kinetic endpoints determined for FOE Oxalate in aerobic soil.

Soil		Soil properties		Incubation conditions	Kinetic model	Evaluation of the fit		Kinetic parameters		Kinetic endpoints		
Soil name	Soil type (USDA)	OC	pH ¹⁾			χ^2 error	Vis. fit ²⁾	Par.	Value	DT ₅₀ [days]	DT ₉₀ [days]	Kinetic formation fraction ff
BBA 2.2	Loamy sand	2.58	6.2 ^{a)}	20°C; 40% MWHC	SFO	25.2	A	k	0.1011	6.9	22.8	0.448
Laacherhof	Silt loam	0.9	7.3 ^{a)}	20°C; 40% MWHC	SFO	12.7	G	k	0.0366	18.9	62.9	0.422
Höfchen im Tal	Silt loam	2.40	5.8 ^{a)}	20°C; 40% MWHC	SFO	10.5	G	k	0.0530	13.09	43.48	0.350
Howe, Indiana;	Sandy loam	0.35	6.2 ^{b)}	21°C; 75% of 1/3 bar	SFO	3.99	G	k	n. d. ³⁾	1000	>1000	0.484
Arithmetic mean for ff (n = 4)												0.426

Footnotes to the table:

- 1) Measured in:
- CaCl₂/water for values marked a);
- distilled water for results marked b);
- 2) The abbreviations used to describe the visual fit: G. – good, A. – acceptable, P. – poor;
- 3) Value not determined – the decline phase not reached;

The DT₅₀ = **18.9 days** value, determined in Laacherhof Silt loam soil was identified as appropriate input parameter for soil exposure assessment.

Table B.8.1.1.3._CA-12: The modelling kinetic endpoints determined for FOE Oxalate in aerobic soil.

Soil		Soil properties		Incubation conditions	Kinetic model	Evaluation of the fit		Kinetic parameters		Kinetic endpoints		
Soil name	Soil type (USDA)	OC	pH ¹⁾			χ^2 error	Vis. fit ²⁾	Par.	Value	DT ₅₀ [days]	DT ₉₀ [days]	Kinetic formation fraction ff
BBA 2.2	Loamy sand	2.58	6.2 ^{a)}	20°C; 40% MWHC	SFO	25.2	A	k	0.1011	6.7	22.8	0.448
Laacherhof	Silt loam	0.9	7.3 ^{a)}	20°C; 40% MWHC	SFO	12.7	G	k	0.0447	15.5	51.58	0.422
Höfchen im Tal	Silt loam	2.40	5.8 ^{a)}	20°C; 40% MWHC	SFO	10.5	G	k	0.0530	13.09	43.48	0.350
Howe, Indiana;	Sandy loam	0.35	6.2 ^{b)}	21°C; 75% of 1/3 bar	SFO	3.99	G	k	n. d. ³⁾	n. d. ³⁾	n. d. ³⁾	0.484
Geometric mean (n = 3)									0.0639	11.08	37.12	----
Arithmetic mean for ff (n = 4)												0.426

Footnotes to the table:

- 1) Measured in:
- CaCl₂/water for values marked a);
- distilled water for results marked b);
- 2) The abbreviations used to describe the visual fit: G. – good, A. – acceptable, P. – poor;
- 3) Value not determined – the decline phase not reached;

For GW and SW model exposure assessment the **geomean DT₅₀ = 11.08 days** and **geomean k = 0.0639 [days⁻¹]** are the kinetic endpoints recommended as input parameters. The corresponding recommended ff value is **ff = 0.426** (arithmetic mean) for Flufenacet as a precursor.

d) Kinetic endpoints determined for FOE Methylsulfone:

The degradation kinetics of FOE Methylsulfone in aerobic soil was examined in eleven trials using the same number of the test soils. The experiments were performed in two variants – three trials with soils treated with Flufenacet (active substance) and the remaining eight trials with soils treated with FOE Methylsulfone.

The performed kinetic analysis resulted in a data base consisting of nine reliable kinetic endpoints, one with soil treated with Flufenacet as a precursor of FOE Methylsulfone and remaining eight with soils treated with FOE Methylsulfone. In case of two trials on soils treated with Flufenacet – BBA 2.2 Loamy sand soil and Hoefchen im Tal Silt loam soil, it was not possible to obtain reliable kinetic endpoints characterising degradation of FOE Methylsulfone in soil, because decline of that compound was not observed. As a result, the default values – $DT_{50} = 1000$ days and $DT_{90} > 1000$ days, were proposed for these trials. These values, due to their nature and uncertainty related to them, were not used either as input parameters in soil exposure assessment or to calculate normalised mean values used subsequently in GW/SW exposure assessment. They are however provided in the table presenting the persistence endpoints, as with them are associated reliable kinetic formation fractions for FOE Methylsulfone, recommended to be used in GW exposure assessment. RMS however decided not to provide them in the table presenting the kinetic endpoints recommended for modelling.

The persistence (best-fit) kinetic endpoints obtained for FOE Methylsulfone are presented below in the table B.8.1.1.3._CA-13. The modelling endpoints are given in the table B.8.1.1.3._CA-14.

Table B.8.1.1.3._CP-13: The persistence kinetic endpoints determined for FOE Methylsulfone in aerobic soil.

Soil		Soil properties		Incubation conditions	Kinetic model	Evaluation of the fit		Kinetic parameters		Kinetic endpoints		
Soil name	Soil type (USDA)	OC	pH ¹⁾			χ^2 error	Vis. fit ²⁾	Par.	Value	DT_{50} [days]	DT_{90} [days]	Kinetic formation fraction <i>ff</i>
BBA 2.2	Loamy sand	2.58	6.2 ^{a)}	20°C; 40% MWHC	SFO	28.5	G	<i>k</i>	n. d. ³⁾	1000	>1000	0.061
Laacherhof	Silt loam	0.9	7.3 ^{a)}	20°C; 40% MWHC	SFO	14.4	G	<i>k</i>	3.99 E-3	174	576	0.096
Hoefchen im Tal	Silt loam	2.40	5.8 ^{a)}	20°C; 40% MWHC	SFO	17.3	G	<i>k</i>	n. d. ³⁾	1000	>1000	0.052
Laacherhof AXXa	Loamy sand	1.7	6.2 ^{b)}	19.6°C; 55% MWHC	SFO	3.37	G	<i>k</i>	1.61 E-2	43.14	143.32	n. a. ⁴⁾
Dollendorf II	Loam	4.6	7.0 ^{b)}	19.6°C; 55% MWHC	SFO	3.04	G	<i>k</i>	2.98 E-2	23.30	77.41	n. a. ⁴⁾
Hoefchen Am Hohenseh 4a;	Silt loam	2.0	6.1 ^{b)}	19.6°C; 55% MWHC	SFO	3.58	G	<i>k</i>	1.58 E-2	43.84	145.64	n. a. ⁴⁾
Wurm-wiese	Sandy loam	1.8	5.0 ^{b)}	19.6°C; 55% MWHC	SFO	3.32	G	<i>k</i>	7.21 E-3	96.13	319.32	n. a. ⁴⁾
Hanscheider Hof	Loam	2.8	5.6 ^{b)}	19.9°C; 55% MWHC	SFO	2.11	G	<i>k</i>	8.40 E-3	82.53	274.14	n. a. ⁴⁾
Frankenforst	Silt loam	1.8	6.8 ^{b)}	19.9°C; 55% MWHC	SFO	2.88	G	<i>k</i>	0.01083	63.98	212.53	n. a. ⁴⁾
LUFA 2.3	Sandy loam	1.1	6.8 ^{b)}	19.9°C; 55% MWHC	SFO	2.10	G	<i>k</i>	4.72 E-3	146.78	487.60	n. a. ⁴⁾
LUFA 6S	Clay	1.9	7.0 ^{b)}	19.9°C; 55% MWHC	SFO	1.70	G	<i>k</i>	4.25 E-3	163.06	541.68	n. a. ⁴⁾
Arithmetic mean for <i>ff</i> (n = 3)												0.070

Footnotes to the table:

- 1) Measured in:
- CaCl₂/water for values marked a);
- (0.01M) CaCl₂ for results marked b);
- 2) The abbreviations used to describe the visual fit: G. – good, A. – acceptable, P. – poor;
- 3) Value not determined – the decline phase not reached;
- 4) Value not available – the test compound applied as parent.

The $DT_{50} = 174$ days value, determined in Laacherhof Silt loam soil was identified as appropriate input parameter for soil exposure assessment.

Table B.8.1.1.3._CA-14: The modelling kinetic endpoints determined for FOE Methylsulfone in aerobic soil.

Soil		Soil properties		Incubation conditions	Kinetic model	Evaluation of the fit		Kinetic parameters		Kinetic endpoints		
Soil name	Soil type (USDA)	OC	pH ¹⁾			χ^2 error	Vis. fit ²⁾	Par.	Value	DT_{50} [days]	DT_{90} [days]	Kinetic formation fraction ff
BBA 2.2	Loamy sand	2.58	6.2 ^{a)}	20°C; 40% MWHC	SFO	28.5	G	k	n. d. ³⁾	n. d. ³⁾	n. d. ³⁾	0.061
Laacherhof	Silt loam	0.9	7.3 ^{a)}	20°C; 40% MWHC	SFO	14.4	G	k	4.86 E-3	142.68	472.32	0.096
Höfchen im Tal	Silt loam	2.40	5.8 ^{a)}	20°C; 40% MWHC	SFO	17.3	G	k	n. d. ³⁾	n. d. ³⁾	n. d. ³⁾	0.052
Laacherhof AXXa	Loamy sand	1.7	6.2 ^{b)}	19.6°C; 55% MWHC	SFO	3.37	G	k	1.66 E-2	41.85	139.00	n. a. ⁴⁾
Dollendorf II	Loam	4.6	7.0 ^{b)}	19.6°C; 55% MWHC	SFO	3.04	G	k	3.07 E-2	22.60	75.09	n. a. ⁴⁾
Hoefchen Am Hohensch 4a;	Silt loam	2.0	6.1 ^{b)}	19.6°C; 55% MWHC	SFO	3.58	G	k	1.63 E-2	42.52	141.23	n. a. ⁴⁾
Wurm-wiese	Sandy loam	1.8	5.0 ^{b)}	19.6°C; 55% MWHC	SFO	3.32	G	k	7.43 E-3	93.25	309.74	n. a. ⁴⁾
Hanscheider Hof	Loam	2.8	5.6 ^{b)}	19.9°C; 55% MWHC	SFO	2.11	G	k	8.48 E-3	81.70	271.40	n. a. ⁴⁾
Frankenforst	Silt loam	1.8	6.8 ^{b)}	19.9°C; 55% MWHC	SFO	2.88	G	k	1.09 E-2	63.34	210.40	n. a. ⁴⁾
LUFA 2.3	Sandy loam	1.1	6.8 ^{b)}	19.9°C; 55% MWHC	SFO	2.10	G	k	4.77 E-3	145.31	482.72	n. a. ⁴⁾
LUFA 6S	Clay	1.9	7.0 ^{b)}	19.9°C; 55% MWHC	SFO	1.70	G	k	4.99 E-3	138.83	461.19	n. a. ⁴⁾
Geometric mean (n = 9)									9.55 E-3	72.57	240.99	----
Median (n = 9)									8.48 E-3	81.70	271.40	----
Arithmetic mean for ff (n = 3)												0.070

Footnotes to the table:

- 1) Measured in:
- CaCl₂/water for values marked a);
- (0.01M) CaCl₂ for results marked b);
- 2) The abbreviations used to describe the visual fit: G. – good, A. – acceptable, P. – poor;
- 3) Value not determined – the decline phase not reached;
- 4) Value not available – the test compound applied as parent.

For GW and SW model exposure assessment the **median $DT_{50} = 81.70$ days** and **median $k = 0.00848$ [days⁻¹]** are the kinetic endpoints recommended as input parameters. The corresponding recommended ff value is **$ff = 0.070$** (arithmetic mean) for Flufenacet as a precursor.

e) Kinetic endpoints determined for FOE Thiadone:

The degradation kinetics of FOE Thiadone in aerobic soil was examined in eight trials using the equal number of the test soils. The experiments were performed in two variants – five trials with soils treated with Flufenacet (active substance) and the remaining eight trials with soils treated with FOE Methylsulfone.

The performed kinetic analysis resulted in a data base consisting of eight reliable kinetic endpoints, four with soil treated with Flufenacet as a precursor of FOE Thiadone and three with soils treated with FOE Thiadone. In case of one trial on soil treated with Flufenacet – Howe, Indiana Sandy loam soil, it was not possible to obtain reliable fit for FOE Thiadone in combination with the parent compound. Such fit however was obtained when the data were kinetically analysed for FOE Thiadone alone using the top-down approach. That solution however implied that no reliable value for kinetic formation fraction in that trial could be obtained and reported. RMS decided not to report the default value $ff = 1.00$, proposed by the Applicant. The persistence (best-fit) kinetic endpoints obtained for FOE Thiadone are presented below in the table B.8.1.1.3._CA-15. The modelling endpoints are given in the table B.8.1.1.3._CA-16.

Table B.8.1.1.3._CA-15: The persistence kinetic endpoints determined for FOE Thiadone in aerobic soil.

Soil		Soil properties		Incubation conditions	Kinetic model	Evaluation of the fit		Kinetic parameters		Kinetic endpoints		
Soil name	Soil type (USDA)	OC	pH			χ^2 error	Vis. fit ¹⁾	Par.	Value	DT ₅₀ [days]	DT ₉₀ [days]	Kinetic formation fraction ff
Hoefchen Am Hohenseh 4a;	Silt loam	2.5	6.7 ²⁾	19.1 ⁰ C; 55% MWHC	SFO	16.42	G	k	0.6110	1.13	3.77	0.913
Laacherhof AXA;	Loamy sand	2.4	6.1 ²⁾	19.9 ⁰ C; 55% MWHC	SFO	15.65	G	k	0.5087	1.36	4.53	0.524
Dollendorf II;	Clay loam	5.3	7.2 ²⁾	19.9 ⁰ C; 55% MWHC	SFO	16.36	G	k	0.2438	2.84	9.45	0.438
Laacherhof Wurm-wiese;	Loam	2.2	5.4 ²⁾	19.9 ⁰ C; 55% MWHC	SFO	14.73	G	k	0.3490	1.99	6.60	0.404
Howe, Indiana;	Sandy loam	0.35	6.2 ³⁾	21 ⁰ C; 75% of 1/3 bar	SFO	4.95	G	k	0.0435	15.9	52.9	n. d. ⁵⁾
Iowa	Loamy sand	1.91	7.2 ⁴⁾	20 ⁰ C; 75% of 1/3 bar	SFO	6.72	A	k	0.3494	1.98	6.59	n. d. ⁶⁾
Indiana	Sandy loam	1.28	6.5 ⁴⁾	20 ⁰ C; 75% of 1/3 bar	SFO	5.67	A	k	0.4945	1.40	4.66	n. d. ⁶⁾
Nebraska	Silt loam	1.66	7.7 ⁴⁾	20 ⁰ C; 75% of 1/3 bar	SFO	3.71	A	k	0.2363	2.93	9.74	n. d. ⁶⁾
Arithmetic mean for ff (n = 3)												0.570

Footnotes to the table:

- 1) The abbreviations used to describe the visual fit: G. – good, A. – acceptable, P. – poor;
- 2) Measured in 0.01M CaCl₂;
- 3) Measured in distilled water;
- 4) Medium for measuring pH not given;
- 5) Value not available – kinetic endpoints determined using the top-down approach;
- 6) Value not available – the test compound applied as parent.

The DT₅₀ = **15.9 days** value, determined in Howe, Indiana Sandy loam soil was identified as appropriate input parameter for soil exposure assessment.

Table B.8.1.1.3._CA-16: The modelling kinetic endpoints determined for FOE Thiadone in aerobic soil.

Soil		Soil properties		Incubation conditions	Kinetic model	Evaluation of the fit		Kinetic parameters		Kinetic endpoints		
Soil name	Soil type (USDA)	OC	pH			χ^2 error	Vis. fit ¹⁾	Par.	Value	DT ₅₀ [days]	DT ₉₀ [days]	Kinetic formation fraction ff
Hoefchen Am Hohenseh 4a;	Silt loam	2.5	6.7 ²⁾	19.1 ⁰ C; 55% MWHC	SFO	16.42	G	k	0.6301	1.10	3.66	0.913
Laacherhof AXA;	Loamy sand	2.4	6.1 ²⁾	19.9 ⁰ C; 55% MWHC	SFO	15.65	G	k	0.5212	1.33	4.44	0.524
Dollendorf II;	Clay loam	5.3	7.2 ²⁾	19.9 ⁰ C; 55% MWHC	SFO	16.36	G	k	0.2567	2.70	8.98	0.438
Laacherhof Wurm-wiese;	Loam	2.2	5.4 ²⁾	19.9 ⁰ C; 55% MWHC	SFO	14.73	G	k	0.3555	1.95	6.47	0.404
Howe, Indiana;	Sandy loam	0.35	6.2 ³⁾	21 ⁰ C; 75% of 1/3 bar	SFO	4.95	G	k	0.0672	10.32	34.33	n. d. ⁵⁾
Iowa	Loamy sand	1.91	7.2 ⁴⁾	20 ⁰ C; 75% of 1/3 bar	SFO	6.72	A	k	0.5458	1.27	4.22	n. d. ⁶⁾
Indiana	Sandy loam	1.28	6.5 ⁴⁾	20 ⁰ C; 75% of 1/3 bar	SFO	5.67	A	k	0.7702	0.90	2.98	n. d. ⁶⁾
Nebraska	Silt loam	1.66	7.7 ⁴⁾	20 ⁰ C; 75% of 1/3 bar	SFO	3.71	A	k	0.3027	2.29	7.60	n. d. ⁶⁾
Geometric mean (n = 8)									0.3557	1.95	6.48	----
Median (n = 8)									0.4384	1.64	5.46	----
Arithmetic mean for ff (n = 3)												0.570

Footnotes to the table:

- 1) The abbreviations used to describe the visual fit: G. – good, A. – acceptable, P. – poor;
- 2) Measured in 0.01M CaCl₂;
- 3) Measured in distilled water;
- 4) Medium for measuring pH not given;
- 5) Value not available – kinetic endpoints determined using the top-down approach;
- 6) Value not available – the test compound applied as parent.

For GW and SW model exposure assessment the **geomean DT₅₀ = 1.95 days** and **geomean k = 0.3557 [days⁻¹]** are the kinetic endpoints recommended as input parameters. The corresponding recommended *ff* value is ***ff* = 0.570** (arithmetic mean) for Flufenacet as a precursor.

f) Kinetic endpoints determined for FOE 5043-Trifluoroethanesulfonic acid (TFESA):

The degradation kinetics of FOE 5043-Trifluoroethanesulfonic acid (TFESA) in aerobic soil was examined in four trials using the equal number of the test soils. The experiments were performed with soils treated with Flufenacet (active substance).

The performed kinetic analysis resulted in a data base consisting of four reliable kinetic endpoints. In case of two trials – on the Dollendorf II Clay loam soil and Laacherhof Wurmwielse Loam soil it was not possible to obtain reliable kinetic fits for the whole transformation scheme, therefore the top-down approach was used. RMS however decided to keep the determined values of kinetic formation fraction *ff*. The persistence (best-fit) kinetic endpoints obtained for FOE 5043-Trifluoroethanesulfonic acid (TFESA) are presented below in the table B.8.1.1.3._CA-17. The modelling endpoints are given in the table B.8.1.1.3._CA-18.

Table B.8.1.1.3._CA-17: The persistence kinetic endpoints determined for FOE 5043-Trifluoroethanesulfonic acid in aerobic soil.

Soil		Soil properties		Incubation conditions	Kinetic model	Evaluation of the fit		Kinetic parameters		Kinetic endpoints		
Soil name	Soil type (USDA)	OC	pH ¹⁾			χ^2 error	Vis. fit ²⁾	Par.	Value	DT ₅₀ [days]	DT ₉₀ [days]	Kinetic formation fraction <i>ff</i>
Hoefchen Am Hohenseh 4a;	Silt loam	2.5	6.7	19.1 ⁰ C; 55% MWHC	SFO	5.85	G	k	0.0761	9.10	30.23	0.264
Laacherhof AXXa;	Loamy sand	2.4	6.1	19.9 ⁰ C; 55% MWHC	SFO	18.25	G	k	0.1548	4.48	14.87	0.534
Dollendorf II;	Clay loam	5.3	7.2	19.9 ⁰ C; 55% MWHC	SFO	4.31	G	k	0.0331	20.9	69.5	0.422
Laacherhof Wurm-wiese;	Loam	2.2	5.4	19.9 ⁰ C; 55% MWHC	SFO	12.3	G	k	0.3090	2.24	7.45	0.655
Arithmetic mean for <i>ff</i> (n = 3)												0.469

Footnotes to the table:

- 1) Measured in 0.01M CaCl₂;
- 2) The abbreviations used to describe the visual fit: G. – good, A. – acceptable, P. – poor;

The **DT₅₀ = 20.9 days** value, determined in Dollendorf II Clay loam soil was identified as appropriate input parameter for soil exposure assessment.

Table B.8.1.1.3._CA-18: The modelling kinetic endpoints determined for FOE 5043-Trifluoroethanesulfonic acid in aerobic soil.

Soil		Soil properties		Incubation conditions	Kinetic model	Evaluation of the fit		Kinetic parameters		Kinetic endpoints		
Soil name	Soil type (USDA)	OC	pH ¹⁾			χ^2 error	Vis. fit ²⁾	Par.	Value	DT ₅₀ [days]	DT ₉₀ [days]	Kinetic formation fraction <i>ff</i>
<i>Hoefchen Am Hohenseh 4a;</i>	Silt loam	2.5	6.7	19.1°C; 55% MWHC	SFO	5.85	G	<i>k</i>	0.0785	8.83	29.32	0.264
<i>Laacherhof AXXa;</i>	Loamy sand	2.4	6.1	19.9°C; 55% MWHC	SFO	18.25	G	<i>k</i>	0.1579	4.39	14.57	0.534
<i>Dollendorf II;</i>	Clay loam	5.3	7.2	19.9°C; 55% MWHC	SFO	4.31	G	<i>k</i>	0.0349	19.87	66.01	0.422
<i>Laacherhof Wurm-wiese;</i>	Loam	2.2	5.4	19.9°C; 55% MWHC	SFO	12.3	G	<i>k</i>	0.3165	2.19	7.30	0.655
Geometric mean (n = 4)									0.1082	6.41	21.30	----
									Arithmetic mean for <i>ff</i> (n = 3)		0.469	

Footnotes to the table:

- 1) Measured in 0.01M CaCl₂;
 2) The abbreviations used to describe the visual fit: G. – good, A. – acceptable, P. – poor;

For GW and SW model exposure assessment the **geomean DT₅₀ = 6.41 days** and **geomean *k* = 0.1082 [days⁻¹]** are the kinetic endpoints recommended as input parameters. The corresponding recommended *ff* value is ***ff* = 0.469** (arithmetic mean) for FOE Thiadone as a precursor.

g) Kinetic endpoints determined for Trifluoroacetic acid (TFA):

The degradation kinetics of Trifluoroacetic acid (TFA) in aerobic soil was examined in eight trials using the equal number of the test soils. The experiments were performed in two variants – four trials with soils treated with Flufenacet (active substance) and the remaining four trials with soils treated with TFA.

Due to the high persistence of the test compound – TFA, in none of the test soils it was possible to obtain the reliable kinetic endpoints. For that reason the default values were proposed.

Due to the difference between the modelling tools, for the persistence endpoints two sets of the default values were provided. For trials on test soils treated with Flufenacet as precursor of TFA, where the analysis performed by the Applicant was accepted, the default kinetic endpoints were: **DT₅₀ = 1000 days** and **DT₉₀ > 1000 days**. In case however of the trials with TFA applied as parent compound, for which RMS had to repeat the kinetic analysis, the kinetic endpoints were: **DT₅₀ = 10000 days** and **DT₉₀ > 10000 days** – the values returned by the applied tool. RMS considers these defaults to be representative for the persistence of TFA in soil, as that indicated the results of the examination of the fate of TFA in environment presented in the open-source literature.

However for modelling the recommended input value is **DT₅₀ = 1000 days**, because of the constraints of the current modelling tools. It shall be noted that due to the nature of the determined endpoint – a default value, its normalisation was not performed as not necessary.

For TFA a set for two kinetic formation fraction values were determined – one for formation of TFA from Flufenacet and the second for its formation from FOE Thiadone.

The persistence (best-fit) kinetic endpoints obtained for TFA Thiadone are presented below in the table B.8.1.1.3._CA-19. The modelling endpoints are given in the table B.8.1.1.3._CA-20.

Table B.8.1.1.3._CA-19: The persistence kinetic endpoints determined for Trifluoroacetic acid (TFA) in aerobic soil.

Soil		Soil properties		Incubation conditions	Kinetic model	Evaluation of the fit		Kinetic parameters		Kinetic endpoints		
Soil name	Soil type (USDA)	OC	pH ¹⁾			χ^2 error	Vis. fit ¹⁾	Par.	Value	DT ₅₀ [days]	DT ₉₀ [days]	Kinetic formation fraction $ff^{4)}$
<i>Hoefchen Am Hohenseh 4a;</i>	Silt loam	2.5	6.7	19.1 ⁰ C; 55% MWHC	SFO	10.49	G	<i>k</i>	n. d. ³⁾	1000	>1000	$ff_1 = 0.087$ $ff_2 = 0.736$
<i>Laacherhof AXx;</i>	Loamy sand	2.4	6.1	19.9 ⁰ C; 55% MWHC	SFO	10.34	G	<i>k</i>	n. d. ³⁾	1000	>1000	$ff_1 = 0.476$ $ff_2 = 0.466$
<i>Dollendorf II;</i>	Clay loam	5.3	7.2	19.9 ⁰ C; 55% MWHC	SFO	9.45	G	<i>k</i>	n. d. ³⁾	1000	>1000	$ff_1 = 0.562$ $ff_2 = 0.578$
<i>Laacherhof Wurm-wiese;</i>	Loam	2.2	5.4	19.9 ⁰ C; 55% MWHC	SFO	9.44	G	<i>k</i>	n. d. ³⁾	1000	>1000	$ff_1 = 0.596$ $ff_2 = 0.345$
<i>Hanscheider Hof</i>	Loam	2.8	5.6	19.9 ⁰ C; 55% MWHC	SFO	4.95	G	<i>k</i>	n. d. ³⁾	10000	>10000	n. d. ³⁾
<i>Frankenforst</i>	Silt loam	1.8	6.8	19.9 ⁰ C; 55% MWHC	SFO	6.72	A	<i>k</i>	n. d. ³⁾	10000	>10000	n. d. ³⁾
<i>LUFA 2.3</i>	Sandy loam	1.1	6.8	19.9 ⁰ C; 55% MWHC	SFO	5.67	A	<i>k</i>	n. d. ³⁾	10000	>10000	n. d. ³⁾
<i>LUFA 6S</i>	Clay	1.9	7.0	19.9 ⁰ C; 55% MWHC	SFO	3.71	A	<i>k</i>	n. d. ³⁾	10000	>10000	n. d. ³⁾
Arithmetic mean for ff (n = 4)												$ff_1 = 0.430$ $ff_2 = 0.531$

Footnotes to the table:

- 1) Measured in 0.01M CaCl₂;
- 2) The abbreviations used to describe the visual fit: G. – good, A. – acceptable, P. – poor;
- 3) n. d. – not determined
- 4) ff_1 – kinetic formation fraction for formation of TFA from Flufenacet; ff_2 – kinetic formation fraction for formation of TFA from FOE Thiadone.

The default **DT₅₀ = 10000 days** value was identified as appropriate input parameter for soil exposure assessment.

Table B.8.1.1.3._CA-20: The modelling kinetic endpoints determined for Trifluoroacetic acid (TFA) in aerobic soil.

Soil		Soil properties		Incubation conditions	Kinetic model	Evaluation of the fit		Kinetic parameters		Kinetic endpoints		
Soil name	Soil type (USDA)	OC	pH ¹⁾			χ^2 error	Vis. fit ¹⁾	Par.	Value	DT ₅₀ [days]	DT ₉₀ [days]	Kinetic formation fraction $ff^{4)}$
Hoefchen Am Hohenseh 4a;	Silt loam	2.5	6.7	19.1 ⁰ C; 55% MWHC	SFO	10.49	G	k	n. d. ³⁾	1000	>1000	$ff_1 = 0.087$ $ff_2 = 0.736$
Laacherhof AXXa;	Loamy sand	2.4	6.1	19.9 ⁰ C; 55% MWHC	SFO	10.34	G	k	n. d. ³⁾	1000	>1000	$ff_1 = 0.476$ $ff_2 = 0.466$
Dollendorf II;	Clay loam	5.3	7.2	19.9 ⁰ C; 55% MWHC	SFO	9.45	G	k	n. d. ³⁾	1000	>1000	$ff_1 = 0.562$ $ff_2 = 0.578$
Laacherhof Wurm-wiese;	Loam	2.2	5.4	19.9 ⁰ C; 55% MWHC	SFO	9.44	G	k	n. d. ³⁾	1000	>1000	$ff_1 = 0.596$ $ff_2 = 0.345$
Hanscheider Hof	Loam	2.8	5.6	19.9 ⁰ C; 55% MWHC	SFO	4.95	G	k	n. d. ³⁾	1000	>1000	n. d. ³⁾
Frankenforst	Silt loam	1.8	6.8	19.9 ⁰ C; 55% MWHC	SFO	6.72	A	k	n. d. ³⁾	1000	>1000	n. d. ³⁾
LUFA 2.3	Sandy loam	1.1	6.8	19.9 ⁰ C; 55% MWHC	SFO	5.67	A	k	n. d. ³⁾	1000	>1000	n. d. ³⁾
LUFA 6S	Clay	1.9	7.0	19.9 ⁰ C; 55% MWHC	SFO	3.71	A	k	n. d. ³⁾	1000	>1000	n. d. ³⁾
Geometric mean (n = 8)										1000	>1000	----
Arithmetic mean for ff (n = 4)												$ff_1 = 0.430$ $ff_2 = 0.531$

Footnotes to the table:

- 1) Measured in 0.01M CaCl₂;
- 2) The abbreviations used to describe the visual fit: G. – good, A. – acceptable, P. – poor;
- 3) n. d. – not determined
- 4) ff_1 – kinetic formation fraction for formation of TFA from Flufenacet; ff_2 – kinetic formation fraction for formation of TFA from FOE Thiadone.

For GW and SW model exposure assessment the default **DT₅₀ = 1000 days** is a kinetic endpoint recommended as input parameter. The corresponding recommended ff values are $ff_1 = 0.430$ (arithmetic mean) for Flufenacet as a precursor and $ff_2 = 0.531$ (arithmetic mean) for FOE Thiadone as a precursor.

The kinetic endpoints identified by RMS as appropriate to be used in model exposure assessment for soil, groundwater and surface water compartments are summarised below in the table B.8.1.1.3._CA-21. For completeness also the maximum concentrations observed in soils are provided.

Table B.8.1.1.3._CA-21: The kinetic endpoints determined in laboratory studies on aerobic soils, recommended to be used in model exposure assessment for soil, groundwater and surface water compartments.

Compound	Compartment	Recommended endpoints					
		Maximum observed in soil		Kinetic formation fraction - ff		Persistence in soil – DT ₅₀ value	
		Observed soil maximum [%]	Remark	ff	Remark	DT ₅₀ [days]	Remark
Flufenacet	Soil	Not applicable	Not applicable – parent compound	----	Not applicable – parent compound	57.6	Longest not normalised lab value
	Groundwater			----		17.89	Normalised lab geomean value
	Surface Water			----		17.89	Normalised lab geomean value
FOE Sulfonic acid	Soil	26.5	Recommended for simple modelling ¹⁾	0.195	Precursor: flufenacet; to be used in complex modelling ²⁾	318	Longest not normalised lab value
	Groundwater	----	Not applicable	0.195	Precursor: flufenacet;	45.11	Normalised lab geomean value
	Surface Water	26.5	To be used in calculations at Steps 1 and 2	0.195	Precursor: flufenacet; to be used in Step 3-4 assessment	45.11	Normalised lab geomean value
FOE Oxalate	Soil	26.3	Recommended for simple modelling ¹⁾	0.426	Precursor: flufenacet; to be used in complex modelling ²⁾	18.9	Longest not normalised lab value
	Groundwater	----	Not applicable	0.426	Precursor: flufenacet;	11.08	Normalised lab geomean value
	Surface Water	26.3	To be used in calculations at Steps 1 and 2	0.426	Precursor: flufenacet; to be used in Step 3-4 assessment	11.08	Normalised lab geomean value
FOE Methylsulfone	Soil	6.6	Recommended for simple modelling ¹⁾	0.070	Precursor: flufenacet; to be used in complex modelling ²⁾	174	Longest not normalised lab value
	Groundwater	----	Not applicable	0.070	Precursor: flufenacet;	81.70	Normalised lab median value
	Surface Water	6.6	To be used in calculations at Steps 1 and 2	0.070	Precursor: flufenacet; to be used in Step 3-4 assessment	81.70	Normalised lab median value
FOE Thiadone	Soil	5.8	Recommended for simple modelling ¹⁾	0.570	Precursor: flufenacet; to be used in complex modelling ²⁾	15.9	Longest not normalised lab value
	Groundwater	----	Not applicable	0.570	Precursor: flufenacet;	1.95	Normalised lab geomean value
	Surface Water	5.8	To be used in calculations at Steps 1 and 2	0.570	Precursor: flufenacet; to be used in Step 3-4 assessment	1.95	Normalised lab geomean value
FOE 5043-Trifluoroethane-sulfonic acid	Soil	6.0	Recommended for simple modelling ¹⁾	0.469	Precursor: Thiadone; to be used in complex modelling ²⁾	20.9	Longest not normalised lab value
	Groundwater	----	Not applicable	0.469	Precursor: Thiadone;	6.41	Normalised lab geomean value
	Surface Water	6.0	To be used in calculations at Steps 1 and 2	0.469	Precursor: Thiadone; to be used in Step 3-4 assessment	6.41	Normalised lab geomean value
Trifluoroacetic acid (TFA)	Soil	81.5	Recommended for simple modelling ¹⁾	0.430	Precursor: flufenacet; to be used in complex modelling ²⁾	10000	Longest lab value (default)
				0.531	Precursor: Thiadone; to be used in complex modelling ²⁾		
	Groundwater	----	Not applicable	0.430	Precursor: flufenacet;	1000	FOCUS default for non-degrading compounds
				0.531	Precursor: Thiadone;		
	Surface Water	81.5	To be used in calculations at Steps 1 and 2	0.430	Precursor: flufenacet; to be used in Step 3-4 assessment	1000	FOCUS default for non-degrading compounds
				0.531	Precursor: Thiadone; to be used in Step 3-4 assessment		

Footnotes to the table:

- 1) By the term “simple modelling” are understood calculations performed using simple models with metabolites applied as parent;
- 2) The term “complex models” concerns calculations performed using more sophisticated tools, e.g. ESCAPE, in which metabolites are calculated as formed from their precursor (parent compound or preceding degradation product).

Additionally the results of the determination of the rate of degradation of Flufenacet in aerobic soils incubated under controlled (laboratory) conditions were provided by two literature studies. The key results of these two studies are provided below in the table B.8.1.1.3_CA-22. These results shall be considered as indicative and for that reason were not used to derive the regulatory endpoints.

Table B.8.1.1.3_CA-22: The key results of the relevant publications examining the rate of degradation of Flufenacet in aerobic soils.

Study	Test soil	Key soil properties			Incubation conditions		Fortification level [µg a. s./g soil]	Kinetic endpoints – DT ₅₀ [days]		Method of calculation
		Soil type (USDA)	pH	OC [%]	T [°C]	Soil moisture		T=25°C; FC	T=20°C; FC	
<i>Gupta, Gajbhiye, Agnihotri [2001]</i>	Sandy loam	Sandy loam	7.1	0.34	25	FC	1	9.3	13.4	1 st order, linear regression, r =0.99
							10	13.0	20.4	1 st order, linear regression, r =0.99
<i>Gupta, Gajbhiye, [2002]</i>	Dehli sandy loam	US Loamy sand	7.69	0.50	25	FC	1	10.1	15.8	1 st order, linear regression, r =0.99
							10	13.0	20.4	1 st order, linear regression, r =0.99
	Ranchi sandy loam	US Sandy clay loam	5.54	0.04	25	FC	1	10.5	16.5	1 st order, linear regression, r =0.99
							10	21.3	33.4	1 st order, linear regression, r =0.99
	Nagpur clayey soil	US Clay	8.25	0.40	25	FC	1	31.0	48.6	1 st order, linear regression, r =0.99
							10	29.2	45.8	1 st order, linear regression, r =0.94

2) Degradation in soil under anaerobic conditions:

The route of degradation of the acetanilide herbicide Flufenacet in anaerobic soil was examined in three soils – one from the US and two European. The test compound – Flufenacet, was radiolabelled in one of the following two positions:

- uniformly in phenyl ring – compound tested on one US soil,
- in position C5 of Thiadiazole moiety – examined in two EU soils.

The experiments performed to determine the transformation pattern of Flufenacet in soil under anaerobic conditions consisted of two phases – aerobic preincubation phase and anaerobic incubation phase. RMS decided to present the key results of the experiments taking into account both phases. In case of aerobic preincubation phase the results are given for the terminal time point of that phase.

The key results for the examination of transformation of Flufenacet in anaerobic soils in the area of formation of terminal degradation products – mineralisation expressed as CO₂ and NER fraction, are presented below in the table B.8.1.1.3_CA-23. To differentiate the results obtained for aerobic phase from those for anaerobic phase the former were shaded light grey. It shall be noted that under anaerobic conditions mineralisation, if occurred at all, was minimal. No other volatile compounds were identified during either aerobic or anaerobic phases. The level of NER formed under anaerobic conditions (net formation) was comparable to that observed in aerobic soils.

Table B.8.1.1.3._CA-23: The levels of the terminal degradation products – CO₂ and NER fraction formed in soil during examination of the transformation pattern of Flufenacet in soil under anaerobic conditions.

Study/ radiolabelling position	Soil		Results obtained for aerobic phase		Results obtained for anaerobic phase ¹⁾					
	Name	Type (USDA)	CO ₂ [%AR] – end of phase	NER [%AR] – end of phase	Mineralisation level – CO ₂ formed [% AR]			NER level [% AR]		
					Beginning of phase	Max.	Net anaero- bic ²⁾	Beginning of phase	Max.	Net anaero- bic ³⁾
Pangilinan & Smith [1994]/ ¹⁴C-phenyl	Howe	Sandy loam	1.4 (DAT 30)	8.4 (DAT 30)	1.4 (DAT 30 DAF 0)	1.8 (DAT 210 DAF 180)	0.4	8.4 (DAT 30 DAF 0)	32.6 (DAT 210 DAF 180)	24.2 (DAT 210 DAF 180)
Heinemann [2012]/ ¹⁴C-5- Thiadiazole	HH ⁴⁾	Silt loam	1.6 (DAT 15)	16.9 (DAT 15)	1.6 (DAT 15 DAF 0)	1.7 (DAT 105 DAF 90)	0.1	10.2 (DAT 15 DAF 0)	24.5 (DAT 135 DAF 120)	14.3 (DAT 135 DAF 120)
	DD ⁵⁾	Loam	1.9 (DAT 15)	10.1 (DAT 15)	1.8 (DAT 15 DAF 0)	1.9 (DAT 105 DAF 90)	<0.1 ⁶⁾	8.6 (DAT 15 DAF 0)	31.6 (DAT 135 DAF 120)	23.0 (DAT 135 DAF 120)

Footnotes to the table:

- 1) In case of Howe soil the results for the beginning of anaerobic phase are the same as those for the end of aerobic phase. In case of soils HH and DD they are different, because there were available the results obtained immediately after generating the anaerobic conditions;
- 2) "Net anaerobic" is a difference between the total amount of CO₂ formed and that determined in aerobic traps for volatiles;
- 3) "Net anaerobic" is a difference between maximum determined level of NER and that measured at the beginning of anaerobic phase;
- 4) HH stands for *Hoefchen am Hohenseh 4a* soil;
- 5) DD stands for *Dollendorf II* soil;
- 6) At the time point where maximum CO₂ level of 2.0% AR was recorded, the amount recovered for aerobic volatile traps was 1.9% AR and from anaerobic volatile traps <0.1 AR. The slightly higher total amount may be due to either rounding or losses during extraction. In that soil the level of mineralization, expressed as recovered CO₂ in anaerobic phase was <0.1% AR;

The examination of the extracted fraction enabled the identification of one new degradate, not identified in aerobic soils – FOE Thioglycolate. All other identified degradation products were those already found in aerobic soils. On that basis it can be stated that the transformation pattern of Flufenacet in soil under anaerobic conditions would not differ significantly from that determined in aerobic soils. The key results of the profiling of degradation products in anaerobic soils are presented below in table B.8.1.1.3._CA-24. To differentiate the results obtained for aerobic phase from those for anaerobic phase the former were shaded light grey.

Table B.8.1.1.3._CA-24: The results of the profiling of Flufenacet and its degradation products.

Study/ radiolabelling position	Soil		Results obtained for aerobic phase		Results obtained for anaerobic phase ¹⁾				
	Name	Type (USDA)	Identified compound	Amount [% AR] at the end of phase	Identified compound	Amount [% AR] measured at:			Anaerobic metabolite (yes/no)
Pangilinan & Smith [1994]/ ¹⁴ C-phenyl	Howe	Sandy loam	Flufenacet	69.0 (DAT 30)	Flufenacet	69.0 (DAT 30/ DAF 0)	39.0 ⁶⁾ (DAT 210/ DAF 180)	N/A ⁸⁾	N/A ⁸⁾
			FOE Oxalate	11.2 (DAT 30)	FOE Oxalate	11.2 (DAT 30/ DAF 0)	14.5 (DAT 60/ DAF 30)	3.3 (DAT 60/ DAF 30)	Yes
			FOE Sulfonic acid	6.6 (DAT 30)	FOE Sulfonic acid	6.6 (DAT 30/ DAF 0)	6.6 (DAT 30/ DAF 0)	0.0	No
			FOE Alcohol	0.0 (DAT 30)	FOE Alcohol	0.0 (DAT 30/ DAF 0)	1.4 (DAT 153/ DAF 123)	1.4 (DAT 153/ DAF 123)	Yes
			FOE TGS ³⁾	2.6 (DAT 30)	FOE TGS ³⁾	2.6 (DAT 30/ DAF0)	2.6 (DAT 30/ DAF0)	0.0	No
					FOE Thioglycolate	0.0 (DAT 30/ DAF 0)	1.7 (DAT 60/ DAF 30)	1.7 (DAT 60/ DAF 30)	Yes
Heinemann [2012]/ ¹⁴ C-5- Thiadiazole	HH ⁴⁾	Silt loam	Flufenacet	30.8 (DAT 15)	Flufenacet	42.8 (DAT 15/ DASF 0)	6.4 ⁶⁾ (DAT 135/ DASF 120)	N/A ⁸⁾	N/A ⁸⁾
			FOE Thiadone	5.9 (DAT 15)	FOE Thiadone	4.8 (DAT 15/ DASF 0)	13.6 (DAT 77/ DASF 62)	8.8 (DAT 77/ DASF 62)	Yes
			FOE 5043- Trifluoroethane- sulfonic acid	2.5 (DAT 15)	FOE 5043- Trifluoroethane- sulfonic acid	5.1 (DAT 15/ DASF 0)	4.2 ⁷⁾ (DAT 48/ DASF 33)	4.2 ⁷⁾ (DAT 48/ DASF 33)	Yes
			Trifluoroacetic acid	37.5 (DAT 15)	Trifluoroacetic acid	31.4 (DAT 15/ DASF 0)	47.9 (DAT 135/ DASF 120)	16.5 (DAT 135/ DASF 120)	Yes
	DD ⁵⁾	Loam	Flufenacet	44.2 (DAT 15)	Flufenacet	35.4 (DAT 15/ DASF 0)	3.1 ⁶⁾ (DAT 135/ DASF 120)	N/A ⁸⁾	N/A ⁸⁾
			FOE Thiadone	4.3 (DAT 15)	FOE Thiadone	7.1 (DAT 15/ DASF 0)	12.4 (DAT 21/ DASF 6)	5.3 (DAT 21/ DASF 6)	Yes
			FOE 5043- Trifluoroethane- sulfonic acid	6.0 (DAT 15)	FOE 5043- Trifluoroethane- sulfonic acid	3.2 (DAT 15/ DASF 0)	3.2 (DAT 15/ DASF 0)	0.0	No
			Trifluoroacetic acid	28.0 (DAT 15)	Trifluoroacetic acid	40.4 (DAT 15/ DASF 0)	53.2 (DAT 105/ DASF 90)	12.8 (DAT 105/ DASF 90)	Yes

Footnotes to the table:

- 1) In case of Howe soil the results for the beginning of anaerobic phase are the same as those for the end of aerobic phase. In case of soils HH and DD they are different, because were available the results obtained immediately after generating the anaerobic conditions;
- 2) "Net anaerobic" is a difference between the maximum amount determined in anaerobic phase and that at its beginning;
- 3) FOE TGS – FOE Thioglycolate sulfoxide;
- 4) HH stands for *Hoefchen am Hohenseh 4a* soil;
- 5) DD stands for *Dollendorf II* soil;
- 6) Flufenacet is the active substance, therefore not forming in soil. For that reason its concentration at the end of incubation period is given to show the level of decline;
- 7) In that soil the concentrations of FOE Trifluoroethane sulfonic acid initially decreased, to increase afterwards reaching maximum on the indicated time point. It was assumed that this maximum can be attributed totally to the amount of that compound formed under anaerobic conditions;
- 8) N/A – not applicable (parent compound);

The results of the determination of transformation pathway of Flufenacet in anaerobic soil demonstrated that it would not significantly differ, qualitatively and quantitatively, from that observed in aerobic soil.

The degradation products that may require further consideration for the risk assessment are the same as identified during examination of the degradation pattern of Flufenacet in aerobic soil: FOE Oxalate, FOE

Thiadone and Trifluoroacetic acid. The proposed whole transformation pattern determined during examination of degradation of Flufenacet in anaerobic soil, is presented below on figure B.8.1.1.3._CA-2.

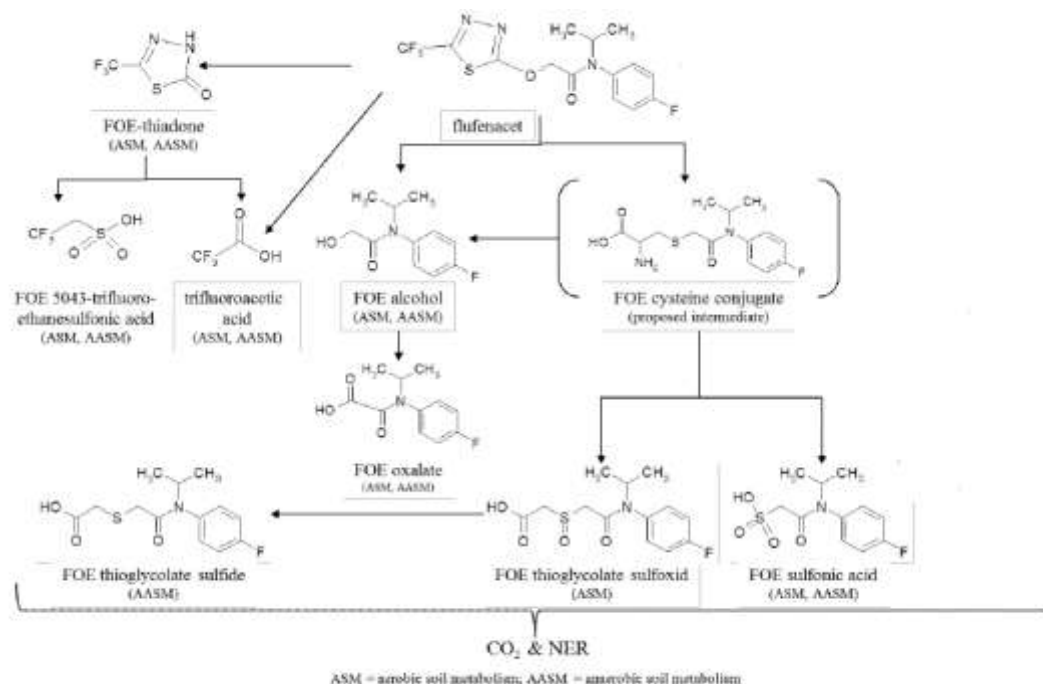


Figure B.8.1.1.3._CA-2: The proposed degradation scheme for Flufenacet in anaerobic soil, including initial aerobic stage. **ASM** stands for transformation under aerobic conditions and **AASM** for that under anaerobic conditions (scheme copied from the Applicant's documentation, modified by the RMS).

The determination of the kinetic parameters of the process of degradation of Flufenacet in anaerobic soil was performed for the results obtained in two studies, on three soils using the test compound radiolabelled in two different positions:

- uniformly in phenyl ring (one test soil);
- in C5 position of thiadiazole moiety (two test soils).

The conclusions and key results are presented below, individually for each test soil.

- The conclusions and key results obtained for Sandy loam (Howe) soil treated with Phenyl-U-¹⁴C] Flufenacet (study by [Pangilinan and Smith; 1995]):

The kinetic analysis of the data for Flufenacet and its major degradation products – FOE Oxalate and FOE Sulfonic acid, obtained for Sandy loam (Howe) soil incubated under anaerobic conditions demonstrated that:

- The degradation of Flufenacet in that soil was most adequately described by DFOP kinetic model. Therefore that model should be considered as providing the kinetic endpoints describing the persistence of Flufenacet in anaerobic sandy loam soil;
- DFOP kinetic model – its slow phase, should be also considered as providing the kinetic endpoints appropriate for modelling. That conclusion is drawn by the RMS and is different from the Applicant's proposal – to consider the SFO kinetic model as a source of the kinetic endpoints appropriate for modelling. That conclusion is based on the fact that DFOP fit was superior to SFO both when the fitting was performed for the parent compound alone and for the parent and degradation products.
- It was not possible to obtain the reliable kinetic fit for either of the degradation products – FOE Oxalate and FOE Sulfonic acid kinetically examined together with parent. Slightly better results were obtained when the data for these two compounds were fitted alone using the top-down approach. In both cases SFO was identified as returning visually and statistically reliable fits with reliable parameters. RMS however is of the opinion that the kinetic endpoints derived from those fits should be considered indicative with regard to the persistence of both compounds in anaerobic sandy loam soil and cannot be further used to

derive any modelling endpoints. It shall be also noted that it was not possible to derive reliable kinetic formation fractions for either FOE Oxalate or FOE Sulfonic acid.

The proposed set of the kinetic endpoints derived from that study is following:

- Flufenacet, persistence endpoints: $DT_{50} = 229.63$ days, $DT_{90} = 895.64$ days, DFOP model ($k_1 = 0.9976$ days⁻¹, $k_2 = 2.416 \text{ E-}3$ days⁻¹, $g = 0.1291$);
 - Flufenacet, modelling endpoints not normalised: $k = 2.416 \text{ E-}3$ [days⁻¹], $DT_{50} = 286.90$ days, $DT_{90} = 953.06$ days, SFO (slow phase DFOP);
 - Flufenacet, modelling endpoints normalized for temperature: $k = 2.205 \text{ E-}3$ [days⁻¹], $DT_{50} = 314.35$ days, $DT_{90} = 1044.26$ days, SFO (slow phase DFOP);
 - FOE Oxalate, persistence endpoints (indicative): $DT_{50} = 311$ days, $DT_{90} = 1030$ days, SFO model – top-down approach ($k = 0.002233$ days⁻¹);
 - FOE Sulfonic acid, persistence endpoints (indicative): $DT_{50} = 352$ days, $DT_{90} = 1170$ days, SFO model – top-down approach ($k_1 = 0.001986$ days⁻¹).
- The conclusions and key results obtained for Silt loam (Hoefchen am Hohenseh 4a) soil treated with [Thiadiazole-5-¹⁴C]Flufenacet (study by [Heinemann; 2012]):

The kinetic analysis of the data for Flufenacet and its major degradation products – FOE Thiadone, FOE-5043 Trifluoroethanesulfonic acid and Trifluoroacetic acid, obtained for Silt loam (Hoefchen am Hohenseh 4 a) soil incubated under anaerobic conditions demonstrated that:

- The degradation of Flufenacet in that soil was most adequately described by DFOP kinetic model. Therefore that model should be considered as providing the kinetic endpoints describing the persistence of Flufenacet in anaerobic Silt loam soil;
- DFOP kinetic model – its slow phase, should be also considered as providing the kinetic endpoints appropriate for modelling.
- It was possible to obtain reliable kinetic fit and kinetic endpoints for FOE Thiadone;
- Although it was possible to obtain reliable kinetic fit for Trifluoroacetic acid, the reliable kinetic parameters describing degradation of that compound could not be derived due to the fact that the decline phase was not reached. Therefore RMS proposed to use the default DT_{50} and DT_{90} values instead of those calculated by the model;
- It was not possible to obtain the reliable kinetic fit for FOE 5043-Trifluoroethanesulfonic acid, therefore for that compound no reliable kinetic endpoints are available. RMS attributed that to the low concentrations of the compound recorded in the test system and their significant scattering, what may indicate that the compound of concern is transient and rapidly degrades in anaerobic silt loam soil.

The proposed set of the kinetic endpoints derived from that study is following:

- Flufenacet, persistence endpoints: $DT_{50} = 22.66$ days, $DT_{90} = 156.90$ days, DFOP model ($k_1 = 0.1214$ days⁻¹, $k_2 = 0.01162$ days⁻¹, $g = 0.3810$);
 - Flufenacet, modelling endpoints: $k = 0.01162$ [days⁻¹], $DT_{50} = 59.65$ days, $DT_{90} = 198.16$ days, SFO (slow phase DFOP), normalisation was not required as the experiment was carried out at $T = 20^{\circ}\text{C}$ and the correction for soil moisture was not necessary (soil was permanently flooded);
 - FOE Thiadone, persistence and modelling endpoints: $DT_{50} = 97.04$ days, $DT_{90} = 322.30$ days, $ff = 0.425$ (from parent compound), SFO model ($k = 0.0071$ days⁻¹);
 - Trifluoroacetic acid persistence endpoints (indicative): $DT_{50} = 1000$ days, $DT_{90} > 1000$ days, $ff = 0.575$ (from parent compound), SFO model;
 - FOE 5043-Trifluoroethanesulfonic acid: it was not possible to derive reliable kinetic endpoints.
- The conclusions and key results obtained for Loam (Dollendorf II) soil treated with [Thiadiazole-5-¹⁴C] Flufenacet (study by [Heinemann; 2012]):

The kinetic analysis of the data for Flufenacet and its major degradation products – FOE Thiadone, FOE-5043 Trifluoroethanesulfonic acid and Trifluoroacetic acid, obtained for Loam (Dollendorf II) soil incubated under anaerobic conditions demonstrated that:

- The degradation of Flufenacet in that soil was most adequately described by DFOP kinetic model. Therefore that model should be considered as providing the kinetic endpoints describing the persistence of Flufenacet in anaerobic Silt loam soil;
- DFOP kinetic model – its slow phase, should be also considered as providing the kinetic endpoints appropriate for modelling.
- It was possible to obtain reliable kinetic fit and kinetic endpoints for FOE Thiadone;
- Although it was possible to obtain reliable kinetic fit for Trifluoroacetic acid, the reliable kinetic parameters describing degradation of that compound could not be derived due to the fact that the well

pronounced decline phase was not reached. Therefore RMS proposed to use the default DT_{50} and DT_{90} values instead of those calculated by the model;

- It was not possible to obtain the reliable kinetic fit for FOE 5043-Trifluoroethanesulfonic acid, therefore for that compound no reliable kinetic endpoints are available. RMS attributed that to the low concentrations of the compound recorded in the test system and their significant scattering, what may indicate that the compound of concern is transient and rapidly degrades in anaerobic silt loam soil.

The proposed set of the kinetic endpoints derived from that study is following:

- Flufenacet, persistence endpoints: $DT_{50} = 13.51$ days, $DT_{90} = 110.02$ days, DFOP model ($k_1 = 0.4756$ days⁻¹, $k_2 = 0.0167$ days⁻¹, $g = 0.3745$);
- Flufenacet, modelling endpoints not normalised: $k = 0.0167$ [days⁻¹], $DT_{50} = 41.51$ days, $DT_{90} = 137.88$ days, SFO (slow phase DFOP), normalisation was not required as the experiment was carried out at $T = 20^\circ\text{C}$ and the correction for soil moisture was not necessary (soil was permanently flooded);
- FOE Thiadone, persistence and modelling endpoints: $DT_{50} = 97.04$ days, $DT_{90} = 322.30$ days, $ff = 0.425$ (from parent compound), SFO model ($k = 0.0071$ days⁻¹);
- Trifluoroacetic acid persistence endpoints (indicative): $DT_{50} = 1000$ days, $DT_{90} > 1000$ days, $ff = 0.575$ (from parent compound), SFO model;
- FOE 5043-Trifluoroethanesulfonic acid: it was not possible to derive reliable kinetic endpoints.

Additionally the results of the determination of the rate of degradation of Flufenacet in anaerobic soils incubated under controlled (laboratory) conditions were provided by two literature studies, also providing the results for aerobic soils. Below, in the table B.8.1.1.3._CA-25 are given the key results obtained in these two studies. As already indicated, these results may be considered only as indicative and were not used to derive the regulatory endpoints.

Table B.8.1.1.3._CA-25: The key results of the relevant publications examining the rate of degradation of Flufenacet in anaerobic (submerged) soils.

Study	Test soil	Key soil properties			Incubation conditions		Fortification level [µg a. s./g soil]	Kinetic endpoints – DT_{50} [days]		Method of calculation
		Soil type (USDA)	pH	OC [%]	$T [^\circ\text{C}]$	Soil moisture		$T=25^\circ\text{C};$ FC	$T=20^\circ\text{C};$ FC	
<i>Gupta, Gajbhiye, Agnihotri [2001]</i>	Sandy loam	Sandy loam	7.1	0.34	25	FC	10	22.5	35.3	1 st order, linear regression, $r = 0.99$
<i>Gupta, Gajbhiye, [2002]</i>	Dehli sandy loam	US Loamy sand	7.69	0.50	25	FC	10	22.3	35.0	1 st order, linear regression, $r = 0.99$
	Ranchi sandy loam	US Sandy clay loam	5.54	0.04	25	FC	10	24.1	37.8	1 st order, linear regression, $r = 0.99$
	Nagpur clayey soil	US Clay	8.25	0.40	25	FC	10	30.1	47.2	1 st order, linear regression, $r = 0.93$

3) Photodegradation on the soil surface:

The soil photolysis of Flufenacet was examined in one soil – US Sandy loam, using the test compound radiolabelled in one position – uniformly at phenyl ring. The experiment was performed using soil that was demonstrated to be biologically viable throughout the whole irradiation/incubation period. Samples were irradiated with artificial light (Xenon lamp) continuously for 10.25 days, corresponding to 30 days of natural summer sunlight (conditions relevant for Phoenix, Arizona, USA). The key results of the examination are presented below in the table B.8.1.1.3._CA-26

Table B.8.1.1.3._CA-26: The key results obtained for Flufenacet in soil photolysis study

Parameter		Results obtained for:	
		Irradiated sample	Dark control
Terminal transformation products	Mineralisation (CO ₂) at the end of the study	0.2% AR; DAT ²⁾ 10.25; 30 th DNS ³⁾	0.1% AR; DAT ²⁾ 10.25; 30 th DNS ³⁾
	Max. NER level	3.2% AR; DAT ²⁾ 10.25; 30 th DNS ³⁾	4.4% AR; DAT ²⁾ 10.25; 30 th DNS ³⁾
Identified compounds	Flufenacet – amount at study's end	91.2 AR; DAT ²⁾ 10.25; 30 th DNS ³⁾	87.2 AR; DAT ²⁾ 10.25; 30 th DNS ³⁾
	FOE Oxalate – max. amount	0.6% AR; DAT ²⁾ 10.25; 30 th DNS ³⁾	4.6% AR; DAT ²⁾ 10.25; 30 th DNS ³⁾
	FOE Sulfonic acid – max. amount	0.4% AR; DAT ²⁾ 5.13; 15 th DNS ³⁾	2.2% AR; DAT ²⁾ 10.25; 30 th DNS ³⁾
	FOE Methylsulfoxide – max. amount	0.7% AR; DAT ²⁾ 10.25; 30 th DNS ³⁾	0.6% AR; DAT ²⁾ 10.25; 30 th DNS ³⁾
	FOE Alcohol – max. amount	1.0% AR; DAT ²⁾ 10.25; 30 th DNS ³⁾	0.4% AR; DAT ²⁾ 10.25; 30 th DNS ³⁾
	FOE N-isomer ¹⁾ – max. amount	1.8% AR; DAT ²⁾ 5.13; 15 th DNS ³⁾	0.3% AR; DAT ²⁾ 2.75; 8 th DNS ³⁾
Kinetics of the process	rate constant <i>k</i> [days ⁻¹]	0.0076	0.0124
	DT ₅₀ [days]	90.72	55.90

Footnotes to the table:

- 4) N-isomer of Flufenacet (for the structural formula, please refer to the table in Appendix 1 - List of Evaluated Compounds in the Vol. 3 B.8_CA);
5) DAT stands for Days After Treatment, the real sampling point in the experiment;
6) DNS – Days of Natural Sunlight, the sampling point related to the natural summer day sunlight conditions in Tucson Arizona, USA

On the basis of these results it was stated that Flufenacet is not prone to photolytical degradation on the soil surface, therefore soil photolysis will not be a relevant degradation mechanism of Flufenacet in soil. Additionally the potential of photodegradation of FOE Thiadone on soil surface was examined. Although it was demonstrated that the process might contribute to transformation of FOE Thiadone in soil, its relevance is estimated to be minimal, also because FOE Thiadone is not expected to occur on the soil surface in significant, if any, amounts.

The photolysis of Flufenacet on the soil surface was examined in one experiment using one soil. Its results were kinetically examined, in line with the recommendations given by FOCUS [2006], by the RMS. The final set of the kinetic endpoints obtained for Flufenacet as a result of that examination is presented below in the table B.8.1.1.3._CA-27.

Table B.8.1.1.3._CA-27: The definitive set of the kinetic endpoints obtained for Flufenacet in the study examining soil photolysis of that compound.

Determined parameter	Results obtained for:		
	Dark control samples	Irradiated samples	
		Values not corrected (Suntest days)	Values corrected for summer sunlight intensity (Natural sunlight days) ¹⁾
Rate constant <i>k</i> [days⁻¹]	0.0124	0.076	0.0026
DT₅₀ [days]	55.90	90.72	265.67
DT₉₀ [days]	185.68	301.36	882.55
Kinetic model	SFO	SFO	SFO

Footnotes to the table:

- 1) values calculated for conditions representative for summer sunny day in Phoenix, AZ, USA – longitude: 33° 27' N

On their basis it can be stated that Flufenacet is not expected to degrade in soil via its photolysis on the soil surface.

The conclusion drawn by the RMS from the study on the basis of the results presented above was following: “The results clearly demonstrate that the degradation of Flufenacet was slower in irradiated samples than in the dark control. On that basis it can be stated that Flufenacet is not prone to the photolysis on the soil surface, hence soil photolysis will not be a relevant mechanism of degradation of Flufenacet in soil.”.

None of the degradation products of Flufenacet requiring further assessment were formed in that study, so the kinetic analysis for them was not performed. However, for one the major soil degradation product of Flufenacet – FOE Thiadone the photodegradation of that compound on the soil surface was examined in a separate study. The results were kinetically examined by the RMS and the definitive data set is presented below in the table B.8.1.1.3._CA-28.

Table B.8.1.1.3._CA-28: The definitive set of the kinetic endpoints obtained for FOE Thiadone in the study examining its photolysis on the soil surface.

Determined parameter	Results obtained for:	
	Dark control samples	Irradiated samples
Rate constant k [days ⁻¹]	0.1612	0.2120
DT ₅₀ [days]	4.30	3.27
DT ₉₀ [days]	14.29	10.86
Kinetic model	SFO	SFO

The results demonstrate that photolysis on the soil surface might contribute to degradation of FOE Thiadone in soil.

The net rate constant of the photolysis will be:

$$k_{\text{photolysis}} = k_{\text{irrad}} - k_{\text{dark control}} = 0.2120 - 0.1612 = 0.0508 \text{ [days}^{-1}\text{]}.$$

The resulting kinetic endpoints calculated using that value are: **DT₅₀ = 13.64 days** and **DT₉₀ = 45.33 days**.

At the same time it shall be pointed out however that the probability that that compound would be found on the soil surface in any substantial amounts is minimal. For that reason the process should be considered to have minimal relevance in the overall transformation of Flufenacet in soil.

4) Soil persistence under realistic – field, conditions:

The dissipation of Flufenacet in soil under field conditions was examined on sixteen trial sites located in the EU – in Germany, France (Northern and Southern) and Italy. The characteristic of the trial sites is presented below in the table B.8.1.1.3._CA-29. The next table – B.8.1.1.3._CA-30, provides the brief characteristic of the weather conditions recorded at each trial site during the experiment.

Table B.8.1.1.3._CA-29: The brief characteristic of field trials.

Study	Information on the trial site			Data on application		Data on crop cover		
	Trial number	Name of the trial site	Location - country	Application rate [g/ha]	Application date	Crop	Date of sowing	Sowing – days before application
[Sommer; 1995]	30159/0	Breitenfelde	Germany	480	15. 04. 1993	Bare soil	Not applicable	Not applicable
	30162/0	Kirchlauter	Germany	480	13. 04. 1993	Bare soil	Not applicable	Not applicable
	30163/9	Monheim	Germany	480	30. 04. 1993	Bare soil	Not applicable	Not applicable
	30164/7	Burscheid	Germany	480	22. 04. 1993	Bare soil	Not applicable	Not applicable
	30248/1	Fresne-L'Archeveque	France (North)	600	11. 05. 1993	Maize	04. 05. 1993	7
	30250/3	Fresne-L'Archeveque (I)	France (North)	600	27. 05. 1993	Maize	24. 05. 1993	3
	30251/1	Laudun	France (South)	600	18. 05. 1993	Sunflower	22. 04. 1993	26
	30253/8	St. Etienne du Gres	France (South)	600	17. 05. 1993	Sunflower	16. 05. 1993	1
[Sommer; 1995b]	30254/6	Saussay-la-Campagne	France (South)	240	11. 03. 1994	Winter wheat	14. 10. 1993	158
	30455/7	Fresne-L'Archeveque	France (North)	240	28. 04. 1994	Winter wheat	22. 10. 1993	169
[Sommer; 1995a]	30499/9	Burscheid	Germany	240	26. 10. 1993	Bare soil	Not applicable	Not applicable
	30500/6	Monheim	Germany	240	26. 10. 1993	Bare soil	Not applicable	Not applicable
[Sommer; 1995c]	40163/3	Laudun	France (South)	600	17. 05. 1994	Sunflower	04. 05. 1994	13
	40164/1	St. Etienne du Gres	France (South)	600	22. 04. 1994	Sunflower	16. 04. 1994	6
	40494/2	Ravenna	Italy	600	27. 04. 1994	Soybean	25. 04. 1994	2
	40495/0	S. Romualdo	Italy	600	27. 04. 1994	Soybean	26. 04. 1994	1

Table B.8.1.1.3._CA-30: The climatic conditions and weather data recorded at on each trial site.

Information on the trial:			Duration of the trial after application of the test compound [days]	Weather data			
Trial number	Trial site - name	Location - country		Source of the weather data	Mars grid cell	Experimental weather data collected at trial site	
						Cumulative rainfall [mm]	Mean temperature T [°C]
30159/0	Breitenfelde	Germany	240	German Weather Service, Lübeck	64060	592	11.0
30162/0	Kirchlauter	Germany	237	Weather station in 4 km from the trial site	56060	319	11.1
30163/9	Monheim	Germany	231	Trial Station Laacherhof	58055	653	12.1
30164/7	Burscheid	Germany	239	Trial Station Höfchen	58055	839	10.6
30248/1	Fresne-L'Archeveque	France (North)	303	Meteo France Station de Boos	55047	870	9.6
30250/3	Fresne-L'Archeveque	France (North)	297	Meteo France Station de Boos	55047	778	9.4
30251/1	Laudun	France (South)	255	Meteo France Station Chusclan	43051	683	15.2
30253/8	St. Etienne du Gres	France (South)	260	Meteo France Station Chateuaenard	42051	670	14.8
30254/6	Saussay-la-Campagne	France (South)	242	Meteo France Station de Boos (76)	55047	598	12.7
30455/7	Fresne-L'Archeveque	France (North)	240	Meteo France Station de Boos (76)	55047	661	13.0
30499/9	Burscheid	Germany	234	Versuchsgut Höfchen, 41399 Burscheid	58055	695	6.3
30500/6	Monheim	Germany	240	Versuchsgut Laacherhof, 40789 Monheim	58055	815	6.3
40163/3	Laudun	France (South)	240	Meteo France	43051	658	16.8
40164/1	St. Etienne du Gres	France (South)	236	Meteo France	42051	640	18.7
40494/2	Ravenna	Italy	236	Ar. Sperim. M. Marani/Ravenna	44063	407	17.0
40495/0	S. Romualdo	Italy	236	Ar. Sperim. M. Marani/Ravenna	44063	407	17.0

The residues of Flufenacet on the trial sites were determined by sampling, at pre-determined intervals, soil cores down to 30-cm or 50-cm depth. The number of sampling points was, depending on the trial site, eight or nine. The soil samples were dissected into 10-cm layers and analysed for the content of Flufenacet and its three major soil degradates – FOE Alcohol, FOE Oxalate and FOE Sulfonic acid.

The performed analysis showed that FOE Alcohol was not formed on any trial site in detectable amounts >3 µg/kg soil (LOD). Other two degradation products were detectable and, on some trial sites even quantifiable (recorded in amounts > LOQ = 10 µg/kg soil), but in none of the trials were observed in amounts higher than 30 µg/kg soil. Neither Flufenacet nor any of its degradation products were detected in deeper soil layers – below 20 cm.

The obtained results were kinetically examined in line with the recommendations of the FOCUS Work Group on the Degradation Kinetics. The results of the determination of the persistence of Flufenacet and its two quantifiable degradation products – FOE Oxalate and FOE Sulfonic acid, are presented below in three separate tables – B.8.1.1.3._CA-31 (Flufenacet), B.8.1.1.3._CA-32 (FOE Oxalate) and B.8.1.1.3._CA-32 (FOE Sulfonic acid).

Table B.8.1.1.3._CA-31: The persistence kinetic endpoints determined for Flufenacet in field dissipation trials.

Data on the trial		Soil properties (0-30 cm layer)			Identified best-fit model	Kinetic parameter		Evaluation of the fit		Kinetic endpoints	
Trial code	Location; type of trial	Soil type (USDA classif.)	pH ¹⁾	OC [%]		par.	value	Visual fit ²⁾ / r ³⁾	χ ² % error	DT ₅₀ [days]	DT ₉₀ [days]
30159/0	Breitenfelde, Germany; bare soil	Sandy loam	6.2	1.69	SFO	k	0.02092	A./0.9648	13.3	33.1	110.0
30162/0	Kirchlauter, Germany; bare soil	Heavy sandy loam ⁴⁾	7.1	0.61	SFO	k	0.0131	G./0.988	6.43	52.9	176.0
30163/9	Monheim, Germany; bare soil	Sandy loam	6.7	1.45	SFO	k	0.0144	A./0.9275	16.1	48.2	160.0
30164/7	Burscheid, Germany; bare soil	Silt loam	6.5	0.97	SFO	k	0.04309	G./0.9915	6.83	16.1	53.4
30248/1	Fresne-L'Archeveque, North France; cropped soil	Silt loam	6.0	1.11	SFO	k	0.01827	A./0.9536	15.8	38.0	126.0
30250/3	Fresne-L'Archeveque1, North France; cropped soil	Silt loam	5.2	1.86	SFO	k	0.01352	A./0.9672	11.0	51.3	170.0
30251/1	Laudun, South France; cropped soil	Loam	7.6	0.62	SFO	k	0.02278	A./0.9804	10.2	30.4	101.0
30253/8	St. Etienne du Gres, South France; cropped soil	Loam	7.7	0.80	SFO	k	0.01687	G./0.9902	6.68	41.1	137.0
30499/9	Burscheid, Germany; bare soil	Silt loam	6.5	0.97	DFOP	k ₁	1.501	A./0.9674	7.11	31.5	140.0
						k ₂	0.01481				
						g	0.2025				
30500/6	Monheim, Germany; bare soil	Sandy loam	6.7	1.45	SFO	k	0.01017	G./0.991	5.1	68.1	226.0
30254/6	Sausay-la-Campagne, South France; cropped soil	Silt loam	7.4	0.92	FOMC	α	4.673	G./0.9993	2.79	14.2	56.7
						β	88.960				
30455/7	Fresne-L'Archeveque; North France; cropped soil	Silt loam	6.6	1.00	SFO	k	0.04024	G./0.9989	3.32	17.2	57.2
40163/3	Laudun, South France; cropped soil	Clay loam	7.7	1.28	SFO	k	0.01451	A./0.9774	9.86	49.0	163.0
40164/1	St. Etienne du Gres, South France; cropped soil	Silt loam	7.7	0.96	SFO	k	0.01442	A./0.9892	7.08	48.1	160.0
40494/2	Ravenna, Italy; cropped soil	Silt loam	7.8	0.98	SFO	k	0.02016	G./0.991	7.23	34.4	114.0
40495/0	S. Romualdo, Italy; cropped soil	Silty loam	7.8	1.11	SFO	k	0.01368	G./0.9884	6.58	50.7	168.0

Footnotes to the table:

- 1) Determined in 0.01M CaCl₂;
- 2) Following abbreviations were used: P – Poor; A – Acceptable; G – Good;
- 3) r = correlation coefficient;
- 4) The DIN 19682 classification presented because the USDA classification not provided; in another report it was stated to be Sandy loam (USDA) containing 58.5% sand, 22.7% silt and 18.8% clay.

Table B.8.1.1.3._CA-32: The reliable persistence kinetic endpoints determined for FOE Oxalate in field dissipation trials.

Data on the trial		Soil properties (0-30 cm layer)			Identified best-fit model	Kinetic parameter		Evaluation of the fit		Kinetic endpoints	
Trial code	Location; type of trial	Soil type (USDA classif.)	pH ¹⁾	OC [%]		par.	value	Visual fit ^{2)/ r³⁾}	χ^2 % error	DT ₅₀ [days]	DT ₉₀ [days]
30250/3	Fresne-L'Archeveque1, North France; cropped soil	Silt loam	5.2	1.86	SFO	k	0.01091	G./0.9895	4.53	68.0	226.0

Footnotes to the table:

- 1) Determined in 0.01M CaCl₂;
 2) Following abbreviations were used: P – Poor; A – Acceptable; G – Good;
 3) *r* = correlation coefficient;

Table B.8.1.1.3._CA-33: The reliable persistence kinetic endpoints determined for FOE Sulfonic acid in field dissipation trials.

Data on the trial		Soil properties (0-30 cm layer)			Identified best-fit model	Kinetic parameter		Evaluation of the fit		Kinetic endpoints	
Trial code	Location; type of trial	Soil type (USDA classif.)	pH ¹⁾	OC [%]		par.	value	Visual fit ^{2)/ r³⁾}	χ^2 % error	DT ₅₀ [days]	DT ₉₀ [days]
30248/1	Fresne-L'Archeveque; North France; cropped soil	Silt loam	6.0	1.11	SFO	k	0.01144	A./0.7441	23.3	60.6	201.0
30250/3	Fresne-L'Archeveque1, North France; cropped soil	Silt loam	5.2	1.86	SFO	k	0.00921	G./0.9477	9.83	75.3	250.0
30253/8	St. Etienne du Gres, South France; cropped soil	Loam	7.7	0.80	SFO	k	0.02249	G./0.9379	12.1	30.8	102.0
40164/1	St. Etienne du Gres, South France; cropped soil	Silt loam	7.7	0.96	SFO	k	0.007303	A./0.9319	20.5	94.9	315.0

Footnotes to the table:

- 1) Determined in 0.01M CaCl₂;
 2) Following abbreviations were used: P – Poor; A – Acceptable; G – Good;
 3) *r* = correlation coefficient;

The results obtained for Flufenacet and FOE Sulfonic acid were also kinetically examined with aim to derive the kinetic endpoints suitable for modelling. The kinetic analysis was performed using the inverse modelling approach. The assessment was conditionally accepted by the RMS. However, RMS decided, because of the stated deficiencies, not to use its results in the model exposure assessment, nor to report them in the List of End Points. At the same time they may be used, at zonal or MS level, as refined input parameters in Tier 2a GW exposure assessment. The results are presented below in the table B.8.1.1.3._CA-34.

Table B.8.1.1.3._CA-34: The proposed modelling kinetic endpoints for FLufenacet and FOE Sulfonic acid determined from the data obtained in field dissipation trials using the inverse modelling approach.

Data on the trial		Soil properties (0-30 cm layer)			Results obtained for:					
Trial code	Location; type of trial	Soil type (USDA classif.)	pH ¹⁾	OC [%]	Flufenacet			FOE Sulfonic acid		
					Kinetic model	χ^2 % error	DT ₅₀ [days] (20°C/pF2)	Kinetic model	χ^2 % error	DT ₅₀ [days] (20°C/pF2)
30159/0	Breitenfelde, Germany; bare soil	Sandy loam	6.2	1.69	SFO	10.2	17.1	SFO	24.8	17.7
30162/0	Kirchlauter, Germany; bare soil	Heavy sandy loam ⁴⁾	7.1	0.61	SFO	19.5	33.3	----	----	----
30163/9	Monheim, Germany; bare soil	Sandy loam	6.7	1.45	SFO	15.4	31.8	----	----	----
30164/7	Burscheid, Germany; bare soil	Silt loam	6.5	0.97	SFO	7.4	11.4	----	----	----
30248/1	Fresne-L'Archeveque, North France; cropped soil	Silt loam	6.0	1.11	SFO	14.4	31.4	SFO	40.4	18.1
30250/3	Fresne-L'Archeveque, North France; cropped soil	Silt loam	5.2	1.86	SFO	8.8	32.9	SFO	42.0	20.8
30251/1	Laudun, South France; cropped soil	Loam	7.6	0.62	SFO	10.6	24.7	----	----	----
30253/8	St. Etienne du Gres, South France; cropped soil	Loam	7.7	0.80	SFO	8.9	37.6	SFO	32.0	19.6
30499/9	Burscheid, Germany; bare soil	Silt loam	6.5	0.97	SFO	9.3	8.5	----	----	----
30500/6	Monheim, Germany; bare soil	Sandy loam	6.7	1.45	SFO	13.5	14.7	----	----	----
30254/6	Sausay-la-Campagne, South France; cropped soil	Silt loam	7.4	0.92	SFO	11.5	6.0	----	----	----
30455/7	Fresne-L'Archeveque, North France; cropped soil	Silt loam	6.6	1.00	SFO	10.8	7.1	----	----	----
40163/3	Laudun, South France; cropped soil	Clay loam	7.7	1.28	SFO	16.5	45.3	SFO	35.1	21.8
40164/1	St. Etienne du Gres, South France; cropped soil	Silt loam	7.7	0.96	SFO	16.2	41.0	SFO	25.8	25.0
40494/2	Ravenna, Italy; cropped soil	Silt loam	7.8	0.98	SFO	14.5	36.2	----	----	----
40495/0	S. Romualdo, Italy; cropped soil	Silty loam	7.8	1.11	SFO	10.3	51.1	----	----	----
					Geomean		22.3 (n = 16)	----	----	20.5 (n = 6)
					Median		31.6 (n = 16)	----	----	20.2 (n = 6)

Footnotes to the table:3) Determined in 0.01M CaCl₂;

4) The DIN 19682 classification presented because the USDA classification not provided; in another report it was stated to be Sandy loam (USDA) containing 58.5% sand, 22.7% silt and 18.8% clay.

The soil residues studies and soil accumulation studies were not performed as the results of the field dissipation studies demonstrated that they were not required – their results clearly indicated that neither Flufenacet nor its degradation products would accumulate in soil.

Finally three relevant open-literature studies examining the dissipation of Flufenacet in soil under realistic – field conditions were identified. Their key results are presented below in the table B.8.1.1.3._CA-35.

Table B.8.1.1.3._CA-35: The key results obtained in the literature studies examining the field dissipation of Flufenacet.

Data on the trial			Soil characterisation			Data on application		Soil persistence of the test compound - Flufenacet		Mobility of the test compound – Flufenacet in soil profile
<i>Trial site</i>	<i>Duration of the study – Days After application</i>	<i>Crop cover</i>	<i>Soil textural type</i>	<i>Soil pH</i>	<i>OM content</i>	<i>Application date</i>	<i>Application rate [g/ ha]</i>	<i>DisT₅₀ [days]</i>	<i>Kinetic model</i>	
Melle/ Belgium	266	Bare soil	Sandy loam	6.2	2.2	21/11/1997	240	98	1 st order, linear regression	No residues below 15 cm
Melle/ Belgium	182	Spring corn	Sandy loam	6.2	2.2	24/03/1998	600	74	1 st order, linear regression	No residues below 15 cm
Melle/ Belgium	168	Summer corn	Sandy loam	6.2	2.2	28/05/1998	600	56	1 st order, linear regression	No residues below 15 cm
Melle/ Belgium	241	Winter wheat	Sandy loam	7.0	1.5	25/11/1999	240	66	1 st order, linear regression	Residues detected down to 20 cm, but mainly confined to top 10 cm
Zingem/ Belgium	241	Winter wheat	Loamy sand	6.4	1.6	25/11/1999	240	97	1 st order, linear regression	Residues detected down to 20 cm, but mainly confined to top 10 cm
Zevekote/ Belgium	241	Winter wheat	Clay loam	6.6	2.1	26/11/1999	240	64	1 st order, linear regression	Residues detected down to 20 cm, but mainly confined to top 10 cm
Crotil-Noirmont/ Belgium	241	Winter wheat	Silt loam	6.7	1.2	01/12/2000	240	54	1 st order, linear regression	Residues detected down to 20 cm, but mainly confined to top 10 cm
Melle/ Belgium	~150	Winter wheat	Sandy loam	7.0	1.5	17/03/2000	240	44	1 st order, linear regression	No information provided
Zingem/ Belgium	~150	Winter wheat	Loamy sand	6.4	1.6	04/04/2000	240	66	1 st order, linear regression	No information provided

B.8.1.2. – Adsorption/desorption in soil

To address the issue of sorption of Flufenacet and its major soil degradation products onto soil the Applicant submitted nine study reports, of which eight were aimed on the examination of adsorption and desorption and the additional one examined the time-dependent sorption in soil of one of the degradation products of Flufenacet – FOE Sulfonic acid. All they will be summarised below under the relevant data points.

Additionally were identified four open-source publications providing the data on sorption of Flufenacet onto soil. They will be also summarised below under the relevant data points.

B.8.1.2.1. – Adsorption and desorption

To address this data point the Applicant submitted eight studies – four for the parent compound Flufenacet and another another four for its degradation products. Their summaries are provided below under the relevant data points. Additionally the RMS identified three relevant open-literature studies on soil sorption of Flufenacet include d into the RAR

B.8.1.2.1.1. – Adsorption and desorption of the active substance

The adsorption of Flufenacet onto soil was examined in four studies, two submitted for the previous authorisation of Flufenacet in the EU (studies by [Kelley and Wood; 1992] and by [Christensen and Yen; 1994]) and two newly submitted studies ([Stupp; 2010] and [Hein; 2012]). They are summarised below as **Studies 1-4**. Additionally the RMS in course of the repeated literature search identified three papers relevant for this assessment dealing with the issue of the batch sorption of Flufenacet onto soil. They are summarised further down this section of the Report as **Studies 5 – 7**.

Study 1:

Report: Kelley I., Wood S., (1992): “Adsorption/Desorption of FOE 5043 to Soil.”; Miles Inc., Agriculture Division, Research and Development Department, P. O. Box 4913, Kansas City, Missouri 64120, USA; Miles Study No. F3182101, Miles Report No. 103903, 30 September 1992; updated by study report: Kelley I., Wood S., (1993): Addendum to Miles Report No. 103903: Adsorption/Desorption of FOE 5043 to Soil.”; Miles Report No.103903-1, 13 September 1993; study reference number: M-002202-01-1;

Guidelines: The study was performed to comply with the following Guidelines:

- US. EPA Guidelines (1982), Subdivision N, Section 163-1 for adsorption/desorption of chemicals.

GLP: Yes;

RMS comments: The study had been evaluated for the previous authorisation of Flufenacet in the EU, by its inclusion into the Annex I of the Directive 91/414/EEC. Its summary can be found under the point B.7.2.1.1, in section B.7 of the Annex B to the Monograph prepared by the RMS – France, for Flufenacet. For the present authorisation in the EU the study was evaluated for its compliance with OECD Guideline for the Testing of Chemicals 106 – Adsorption-Desorption Using a Batch Equilibrium Method. Additionally the study was checked for its validity against the US EPA Fate, Transport and Transformation Test Guidelines OPPTS 835.1230 – Adsorption/Desorption (Batch Equilibrium) and OPPTS 835.1220 – Sediment and Soil Adsorption/Desorption Isotherm as well as SETAC Guidance Document “Procedures for Assessing the Environmental Fate and Ecotoxicity of Pesticides.”. Also consulted was the Guideline which was declared in the study report to be a reference document – US EPA Guideline 163-1 for determining the adsorption/desorption of chemicals. Finally, RMS consulted the evoked above Assessment Report for Flufenacet prepared by the then RMS-France and the Review Report for the active substance Flufenacet, in particular the List of Endpoints in the area of soil sorption. That was done because of the following problems related to the study protocol were identified:

- of the five test soils used in the experiment two displayed very low OC content: Howe (IN) Loamy sand/Sandy loam (OC = 0.23%) and Vero Beach (FL) Sand (OC = 0.17%) and according to the provisions of the OECD Guideline 106 (and US EPA OPPTS

835.1220 Guideline) such soils are not recommended to be used in the examination of the soil sorption because the low OC content they display may disturb the results (correlation between adsorption and organic content); the problem and resulting acceptability of the results obtained for these two soils will be discussed in details in the summary of the study;

- in case of one of the test soils – Howe (IN) Loamy sand/Sandy loam soil its classification in the study report was changed from Loamy sand to Sandy loam on the basis of the triplicate analysis of its properties performed by the same laboratory in three consecutive years; the problem and resulting acceptability of the results obtained for that soil will be discussed in details in the summary of the study;
- in the preliminary test HgCl_2 was used as a sterilising agent; the problem will be discussed in details in the summary of the study;

In general however, despite the problems listed above, RMS found the study acceptable, and possible to be used for the regulatory purposes. The study is summarised below.

Summary:

The aim of the was to examine the process of the equilibrium sorption – adsorption and desorption, of Flufenacet onto soil. The study was performed using five test soils – four originating form the US and one European soil. Their characteristic is provided below in the table B.8.1.2.1.1._CA-1.

Table B.8.1.2.1.1._CA-1: The characteristic of soils used in the study.

Parameter		Soil				
		<i>Stanley (307)</i>	<i>Hagerstown (318)</i>	<i>Howe (395)²⁾</i>	<i>Vero Beach (396)</i>	<i>Monheim (3253)</i>
Soil origin		Kansas, USA	Maryland, USA	Indiana, USA	Florida, USA	Germany, Europe
Soil type	<i>Applicant</i>	Silt loam	Clay loam	Loamy sand	Sand	Sandy loam
	<i>RMS (USDA)</i>	Silt loam	Clay loam	Loamy sand	Sand	Sandy loam
Particle size distribution	Sand [%]	17	21	78	94	72
	Silt [%]	66	50	17	3	23
	Clay [%]	17	29	5	3	5
Soil pH		5.9	6.4	6.4	5.0	6.4
Organic matter content (OM) [%]		2.9	2.2	0.4	0.3	2.41 ³⁾
Organic carbon content (OC) [%] ¹⁾		1.68	1.28	0.23	0.17	1.4 ⁴⁾
CEC [meq/100 g]		26.0	21.0	7.4	3.8	8.0

Footnotes to the table:

- 1) recalculated by the RMS from organic matter content using the following equation: $\text{OM} = 1.724 \text{ OC}$; with exception of Monheim Sandy loam test soil;
- 2) As reported in the study report and in the Assessment Report prepared by the RMS – France for the first authorisation of Flufenacet in the EU;
- 3) Value recalculated by the RMS from OC content using the following equation: $\text{OM} = 1.724 \text{ OC}$;
- 4) Measured value.

The four US soils were selected in accordance with the US EPA Guideline 163-1, recommending that:

- the experiment should be performed on at least four soils, such as agricultural sand, sandy loam, silt loam, clay or clay loam, each having pH within the range 4-8;
- at least one of the test soils should have an organic matter content lower than or equal to 1%, and in such case sand or sandy loam is preferred;
- one of the test soils should also be used in other experiments examining the environmental fate and behaviour of the test compound, and in particular aerobic soil metabolism study; the preferred soil is sandy loam.

The test soils meet these criteria, although in case of two of them – Vero Beach Sand soil and Howe Loamy sand soil, the same cannot be stated when the acceptability criteria of the OECD 106 Guideline are applied – the OC content is lower than the recommended 0.3%.

The fifth soil, Monheim Sandy loam soil, was included into the set because it was used in one of the lysimeter studies. The soil meets all acceptability criteria listed in US EPA Guideline 163-1 and in OECD Guideline 106.

It shall be indicated that in case of the two US soils – Vero Beach Sand soil and Howe Loamy sand soil the OC content was lower than 0.3% recommended by OECD 106 Guideline as minimal soil OC content. That recommendation was explained by the fact that soils with less than 0.3% OC content may disturb correlation between OC and adsorption. For that reason the results for both soils should not be taken into consideration in calculation of the averaged sorption parameters for Flufenacet.

However, it shall be indicated that the Howe loamy sand soil was used in two studies examining the route and rate of degradation of Flufenacet in soil under aerobic conditions. Both studies were found acceptable in course

of the current evaluation, despite the deficiencies displayed by the test soil. As a result, in order to maintain the consistency of the evaluation, RMS proposes to consider the adsorption parameters obtained for Flufenacet in this soil reliable, also because the level of adsorption of Flufenacet onto this soil was higher than recommended as minimum 20%.

In case of Vero Beach Sand soil it shall be indicated that it was also used in another study, aimed on the examination of the soil sorption of several degradation products of Flufenacet – FOE Oxalate, FOE Sulfonic acid, FOE Thiadone, FOE Methylsulfoxide and FOE Alcohol. There that soil displayed similar deficiency – very low OC content. In RMS's opinion, to maintain the representativeness of the adsorption parameters determined for the metabolites listed above – the Vero Beach Sand soil was one of four test soils used in the experiment and the evoked study is a sole study examining soil sorption of the compounds listed above that was submitted for the purpose of the current evaluation, the results obtained for that soil should be kept in the data base. Therefore, to maintain the consistency of the evaluation, also for Flufenacet they should not be excluded just on the basis of soil characteristic.

In case of Howe Loamy sand soil an additional problem was identified – its proper identification with regard to the USDA textural class. The Applicant in the study report classified that soil as Loamy sand to subsequently change that classification, in the Addendum to the study issued on 13th September 1993, to Sandy loam. The proposal was based on the results of the repeated analysis of the properties of the test soil performed by two laboratories – Agvise in 1991 and 1992, and A&L Great Lakes Laboratories in 1993, demonstrating that the test soil was rather Sandy loam. However, it shall be pointed out that the results of the analysis performed in February 1992, the year in which the evaluated soil sorption study was also performed, showed that the test soil was Loamy sand. As nowhere in the study report it was stated that in the repeated analysis the same batch was subjected to characterisation, it may be assumed that the results were obtained for three different soil batches sampled on the same field and representing spatial variability of soil on the sampling area. Also assuming that the analysed sample came from the same batch as soil samples used in the examination of the soil sorption of Flufenacet, it seems appropriate to classify the test soil Howe as Loamy sand and not Sandy loam. For that reason RMS decided to keep the classification presented in the main study report and not in its amendment.

The test soils were air-dried and sieved through 2-mm sieve before being used. No other information with regard to soil sampling and handling procedure prior to the beginning of the experiment was given in the study report.

The test compound – Flufenacet, was used in two forms: as radiolabelled and as a non-radiolabelled compound.

The radiolabelled test compound was [Phenyl-¹⁴C]-Flufenacet, having a specific activity 60.0 mCi/mmol and radiochemical purity of 98%. Its structural formula, with radiolabelling position marked by an asterisk, is shown below on figure B.8.1.2.1.1._CA-1.

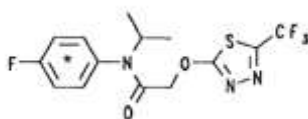


Figure B.8.1.2.1.1._CA-1: The structural formula of the test compound. The radiolabelling position is indicated by the asterisk (*) (copied from the study report).

The non-radiolabelled test substance used in the experiment had a chemical purity of 94.8%.

The water solubility of the test compound, determined for the purpose of this study was approx. 42 ppm at T = 20°C.

The experiment consisted of the following stages:

- 1) **Initial Preliminary Test**, carried out to determine the optimum soil:solution ratio and the stability of the test compound in soil;
- 2) **Second Preliminary Test** in which the equilibration time, i.e. time necessary for adsorption to reach a plateau, was determined for each test soil;
- 3) The **Definitive Test** in which the Adsorption and Desorption isotherms for Flufenacet in each test soil were determined;

The main aim of the Initial Preliminary Test was to determine the optimum soil:solution ratio at which maximum adsorption of Flufenacet onto soil occurred. Additionally the stability of the test item in soil was examined. The examination was performed using a one test soil – Stanley (307) Silt loam soil, having the highest OC content – 1.68%. The test solution was 0.01M CaCl₂ aqueous solution containing 25 ppm of the radiolabelled test item – Flufenacet. It was prepared in duplicate – one replicate containing HgCl₂ and another

without that compound. HgCl_2 was added, in amount to grant a rate of 1.8 mmol/kg soil, as soil sterilising agent. The specific activity of the test solution was 1869 dpm/ μg in case of the test solution with HgCl_2 and 2290 dpm/ μg in case of that not containing it.

The tested soil:solution ratios were: 1:5, 1:10, 1:20 and 1:50. In case of the ratios 1:5, 1:10 and 1:20 1-g portions of the test soil were used. The amounts of the test solution were: 5 mL for 1:5 ratio, 10 mL for 1:10 ratio and 20 mL for 1:20 ratio. For testing 1:50 soil:solution ratio 0.4 g portions of the test soil and 20 mL of test solution were used. The examination was performed in 20-mL culture tubes.

For each tested soil:solution ratio and test solution variant triplicate samples were prepared. They were shaken continuously for 21 hours at constant $T = 24 \pm 1^\circ\text{C}$. After that period the samples were centrifuged for 30 minutes at 4000 rpm, clear supernatants decanted into 10-mL graduated cylinders and their volume recorded. The triplicate 100- μL aliquots were taken for the determination of the radioactivity content, and then the supernatants were pooled before being further processed by extraction – transfer of the test compound to the aqueous phase before subsequent chromatographic (TLC and HPLC) analysis. At that stage of the experiment the most appropriate extraction method of the aqueous supernatant was determined. That was done in a following way:

- one portion of supernatant was extracted three times with CH_2Cl_2 ;
- another portion was extracted once with $\text{CH}_3\text{COOC}_2\text{H}_5$ (ethyl acetate);
- the third portion was passed through C_{18} SPE column and eluted with MeOH.

Organic extracts were evaporated to dryness and residues redissolved in MeOH prior to chromatographic – TLC and HPLC, analysis. The aim of the chromatographic analysis performed at that stage was to determine the extent of the would-be degradation of the test compound and identify and quantify the degradation products.

The most efficient organic extraction method identified at that stage was that with $\text{CH}_3\text{COOC}_2\text{H}_5$, subsequently used in remaining stages of the experiment.

The optimum soil:solution ratio determined at this stage of the experiment and subsequently used in the further examination of the equilibrium sorption of Flufenacet onto soil was 1:5.

The aim of the Second Preliminary Test was to determine the time required to reach the equilibrium concentration, i.e. the equilibration time after which the adsorption changed by less than 5% within 24 hours. The experiment was performed using all five test soils and the optimum soil:solution ratio determined at previous stage. For that purpose 1-g samples of test soils – 19 for each test soil, were weighed into 10-mL borosilicate glass centrifuge tubes equipped with teflon-lined caps. Soil samples were pre-equilibrated for 2 hours with the appropriate amounts of blank, sterile 0.01 M CaCl_2 solution decanted at the end of equilibration period. After that the appropriate amounts of the test solution – either blank 0.01 M CaCl_2 solution or the 0.01 M CaCl_2 solution containing 25 ppm Flufenacet, were added. All samples were then shaken for the predefined time, up to 48 hours, on a laboratory rotator at 20 rpm. The shaker was placed in the incubator set to the constant $T = 22 \pm 1^\circ\text{C}$.

The test solution containing Flufenacet was prepared in the following way: 0.06 mg of ^{14}C -Flufenacet and 6.19 mg of the non-radiolabelled Flufenacet were weighed to 250-mL volumetric flask and dissolved in small amount of CH_3CN (<1%). The solution was brought to volume with the appropriate amount of sterile 0.01M CaCl_2 aq. Then the solution was radioassayed by LSC. Its specific activity was determined to be 4059 dpm/ μg Flufenacet.

For each test soil and the solution with the test compound the samples were taken, in duplicate, after 2, 4, 8, 16 and 24 hours and after 48 hours, in triplicate. Also for each time point single samples with the blank solution were taken for analysis.

Additionally in that experiment five test vessels containing only the appropriate amount of test solution (soilless samples) were set and sampled at the same time points as above in order to determine the possible adsorption of the test compound to the vessel.

The samples were centrifuged for 30 minutes at 4300 rpm at $T = 20^\circ\text{C}$. The clear supernatants were decanted and their volume recorded. Three 200- μL aliquots of each supernatant were analysed for radioactivity content by LSC.

The supernatants of the samples collected after 48 hour of shaking were pooled, extracted three times with $\text{CH}_3\text{COOC}_2\text{H}_5$, organic extracts collected, evaporated to almost dryness and residue redissolved in 1 mL of $\text{CH}_3\text{COOC}_2\text{H}_5$ before being analysed by TLC.

The remaining soil pellets were dried under the gentle stream of N_2 and their triplicate aliquots analysed for the radioactivity content, after combustion, by LSC.

For the following three test soils: Stanley Silt loam, Howe Loamy sand and Monheim Sandy loam, the optimum equilibration time was determined to be 24 hours while for the remaining two test soils – Hagerstown Clay loam and Vero Beach Sand the optimum equilibration time was 48 hours.

The definitive test was carried out to obtain Freundlich sorption isotherms for the processes of adsorption and desorption of Flufenacet in soil and to determine Freundlich isotherm parameters for these processes: the sorption constants – $K_{F\text{ ads}}$ and $K_{F\text{ des}}$ and corresponding $1/n$ values.

The experiment was performed for all five test soils and for the following nominal concentrations of the test item – Flufenacet, in 0.01 M $\text{CaCl}_2\text{ aq}$ test solution: 0.04 ppm, 2.1 ppm, 10.5 ppm 15.8 ppm and 21 ppm.

The test solutions listed above were prepared in the following way:

- Firstly the solution having the concentration 21 ppm – stock solution, was prepared by dissolving the appropriate amount of Flufenacet in sterile 0.01 M $\text{CaCl}_2\text{ aq}$. Small amount of CH_3CN (<1%) was added to the volumetric flask to facilitate solubility and grant homogeneity of the solution. The specific radioactivity of that solution was measured by LSC and was determined to be 4770 dpm/ μg Flufenacet.
- Next the solutions having concentrations 15.8 ppm, 10.5 ppm and 2.1 ppm were prepared by diluting the stock solution in volumetric flasks with the appropriate amounts of 0.01M $\text{CaCl}_2\text{ aq}$. The dilution factors were 0.75, 0.5 and 0.1 respectively.
- The test solution having the lowest concentration of the test item – 0.04 ppm was prepared by dissolving 40 μg of [^{14}C]-Flufenacet in 1000 mL of 0.01M $\text{CaCl}_2\text{ aq}$ in a volumetric flask. The obtained solution had a specific activity, determined by LSC, of 366639 dpm/ μg Flufenacet.

The determination of Freundlich sorption isotherms was carried out in a following way:

- The examination of the adsorption began with weighing to the test vessels, of the same kind as used at preceding step (10-mL disposable borosilicate glass centrifuge tubes), 1-g samples of each test soil. Test vessels were prepared in triplicate for each combination of the test soil and test solution.
- The so prepared soil samples were pre-equilibrated with the appropriate amount of 0.01 M $\text{CaCl}_2\text{ aq}$ solution in the same manner as described for the preceding step.
- Next the appropriate test solutions were introduced to the test vessels in such amount to obtain soil:solution ratio 1:5. So prepared samples were equilibrated for either 24 hours (Stanley Silt loam, Howe Loamy sand and Monheim Sandy loam test soils) or 48 hours (Hagerstown Clay loam and Vero Beach Sand test soils), by constant rotating at 20 rpm, in the darkness and at $T = 22^\circ\text{C}$. Alongside them were equilibrated blank samples, containing each test soil and sterile 0.01M $\text{CaCl}_2\text{ aq}$ solution, and 5 tubes containing the test solutions.
- After equilibration test vessels were centrifuged for 45 min at 4300 rpm (at constant $T = 20^\circ\text{C}$). Triplicate aliquots of supernatants were analysed for radioactivity content and the pH of each supernatant was measured. Next, supernatants were decanted into graduated 5-mL centrifuge tubes, their volumes recorded and conductivity measured. Finally supernatants from replicate samples were pooled and extracted with three portions of $\text{CH}_3\text{COOC}_2\text{H}_5$. The organic extracts were processed in the same way as described for Second Preliminary Test and then analysed by TLC.
- To examine the desorption isotherm the appropriate amount of sterile blank 0.01M $\text{CaCl}_2\text{ aq}$ solution was added to each test vessel after decantation of the test solution. So prepared samples were equilibrated in the same way as described above for the adsorption phase. After that time the test vessels were centrifuged, three 200- μL aliquots of each supernatant radioassayed, pH of each supernatant determined and supernatants decanted to measure their volume. They were then processed in the same way as supernatants obtained at the step examining the adsorption.
- Soil samples left after decantation were dried under the gentle stream of N_2 , ground to a fine powder and three aliquots of each of them were analysed, after combustion, for the radioactivity content using LSC.

The LSC analyses of liquid and solid samples were performed using Packard Tri-Carb Model 4640 LS counter.

Liquid samples were analysed directly, after mixing their 100- μL or 200- μL aliquots with 15 mL of the Ultima Gold Liquid Scintillation cocktail. The parameters of the analysis were following:

- for solutions having the initial specific activity of 366639 dpm/ μg :
 - average sample counting size: 0.2 mL;
 - sample counting time: 5 min.;
 - average background: 35 cpm;
 - average counting efficiency: 95%;
 - Lowest Acceptable Gross Count Rate (LAGC): 64 cpm;
 - Lowest Acceptable Net Count Rate (LANC) – 32 cpm;
 - minimum sensitivity: $5.0 \text{ E-}4$ ppm;
 - greatest probable error (GPE): 8.8%.
- for solutions having the initial specific activity of 4769 dpm/ μg
 - average sample counting size: 0.2 mL;

- sample counting time: 5 min.;
- average background: 35 cpm;
- average counting efficiency: 95%;
- Lowest Acceptable Gross Count Rate (LAGC): 70 cpm;
- Lowest Acceptable Net Count Rate (LANC) – 35 cpm;
- minimum sensitivity: 3.9 E-2 ppm;
- greatest probable error (GPE): 8.8%.

Solid samples were analysed in a following way: the whole portion was oxidised and the evolved $^{14}\text{CO}_2$ trapped in a mixture of 6 mL Carbosorb and 15 mL Perma Fluor V. The parameters of the analysis were following:

- for samples having the initial specific activity of 366639 dpm/ μg :
 - average sample counting size: 0.1 g;
 - sample counting time: 5 min.;
 - average background: 35 cpm;
 - average counting efficiency: 95%;
 - Lowest Acceptable Gross Count Rate (LAGC): 70 cpm;
 - Lowest Acceptable Net Count Rate (LANC): 35 cpm;
 - minimum sensitivity: 1.0 E-3 ppm;
 - greatest probable error (GPE): 8.8%.
- for samples having the initial specific activity of 4769 dpm/ μg :
 - average sample counting size: 0.1 g;
 - sample counting time: 5 min.;
 - average background: 35 cpm;
 - average counting efficiency: 95%;
 - Lowest Acceptable Gross Count Rate (LAGC): 70 cpm;
 - Lowest Acceptable Net Count Rate (LANC) – 35 cpm;
 - minimum sensitivity: 7.7 E-2 ppm;
 - greatest probable error (GPE): 8.8%.

The TLC method, used to analyse the organic extracts was performed on silica gel, 0.25 mm-thick, TLC plates. The plates were developed in $\text{CHCl}_3:\text{CH}_3\text{COOC}_2\text{H}_5$ (3:1). Sample extracts were overspotted with authentic standards. Radioactive bands were detected using radio-TLC analyser Raytest Rita-6800 and the quantitative analysis was performed using the thin-layer analyser.

The HPLC analysis was performed using a Hewlett Packard 1090 chromatograph equipped with Spherisorb 3 ODS 70 x 10 mm chromatographic column and coupled to UV detector, set at wavelength $\lambda = 254$ nm, and Raytest Ramona 90 radioactivity detector. The chromatographic separation was performed in a linear gradient mode, using the mobile phase consisting of:

- water + 0.4% CH_3COOH as **Solvent A**, and
- CH_3CN + 0.4% CH_3COOH as **Solvent B**.

Gradient elution lasted 40 minutes and the gradient programme was following:

- at 0 min 10% Solvent B;
- at 25 min 100% Solvent B;
- at 40 min 100% Solvent B.

The flow rate was 1 mL/min.

Additional analytical method characterised in the study report was GC-MS, but because nowhere in the study report it was indicated to be used, RMS decided not to provide its characteristic.

Results and their discussion:

The examination of the stability of the test compound performed during Initial Preliminary Test showed that Flufenacet was stable in soil and no degradation products were detected. The same observation was made in the supernatants collected after 48-hours lasting equilibration during the Second Preliminary Test. For that reason at later stages HgCl_2 as sterilising agent was not used. The use of that compound in the Initial Preliminary Test had no influence on the obtained results because in parallel the same experiment without it was performed. Therefore it may be stated that the use of HgCl_2 in initial preliminary test had no impact on the results obtained at that stage as well as on the results of the subsequent stages of the experiment.

The results of the determination of the appropriate soil:solution ratio are presented below in the table B.8.1.2.1.1._CA-2. The reported values represent the averages of the replicate samples. They demonstrated that the highest % of adsorption was obtained for 1:5 soil:solution ratio and that ratio was selected to be used throughout the whole remaining part of the study.

Table B.8.1.2.1.1._CA-2: The results of the determination of the appropriate soil:solution ratio using Stanley Silt loam test soil.

Soil:solution ratio	Initial concentration of Flufenacet [$\mu\text{g/g}$ soil]	Concentration of Flufenacet in solution after 21-hours equilibration [$\mu\text{g/mL}$]	% Flufenacet adsorbed onto soil after 21-hours equilibration
1:5	125	14.4	47.01
1:10	250	17.2	36.36
1:20	500	19.2	26.75
1:50	1250	20.6	34.75

The results of the determination of the appropriate equilibration time for each test soil are presented below in the table B.8.1.2.1.1._CA-3.

Table B.8.1.2.1.1._CA-3: The results of the determination of the appropriate equilibration time for each test soil.

Test soil	Soil:solution ratio	Concentration of Flufenacet in solution [$\mu\text{g/mL}$] and % change/24h interval							Selected optimum equilibration time
		Initial	after 2 hours	after 4 hours	after 8 hours	after 16 hours	After 24 hours	after 48 hours	
Stanley Silt loam	1:5	25	18.0	17.8	17.8	17.5	16.9 6.1	16.6 1.8	24 hours
Hagerstown Clay loam	1:5	25	20.9	18.8	18.5	18.7	18.0 13.9	14.7 18.9	48 hours
Howe Loamy sand	1:5	25	21.2	21.2	20.2	20.7	19.7 7.1	20.2 +2.5	24 hours
Vero Beach Sand	1:5	25	21.6	22.0	21.9	21.9	22.0 +1.9	18.0 18.2	48 hours
Monheim Sandy loam	1:5	25	15.7	15.3	15.2	14.4	14.7 6.4	14.5 1.4	24 hours

The results of the determination of pH and conductivity of supernatants obtained during adsorption and desorption phases of the definitive test are presented below in the table B.8.1.2.1.1._CA-4. In the next table – B.8.1.2.1.1._CA-5 are presented the results of the determination of the distribution of Flufenacet in the test systems with each test soil and recovery at the end of the Definitive Test – determination of Freundlich Adsorption and Desorption isotherms. Finally, in the table B.8.1.2.1.1._CA-6 are presented the results of the Definitive test that were used to plot the Freundlich Adsorption and Desorption isotherms and determine Freundlich sorption isotherm parameters for adsorption and desorption processes.

Table B.8.1.2.1.1_CA-4: The conductivity and pH of the supernatants obtained during adsorption and desorption phases of the definitive test.

Test soil	Nominal initial concentration of Flufenacet the test solution [µg/mL]	Properties of the supernatant obtained during		
		Adsorption phase		Desorption phase
		Conductivity [µmhos]	pH	pH
Stanley Silt loam	21.0	2350	5.9	6.0
	15.8	2380	5.9	6.0
	10.5	2480	5.9	6.0
	2.1	2410	5.9	6.1
	0.04	2240	5.9	5.9
Hagerstown Clay loam	21.0	2420	6.6	7.1
	15.8	2350	6.7	7.0
	10.5	2420	6.7	6.9
	2.1	----	6.8	6.8
	0.04	2210	6.4	6.4
Howe Loamy sand	21.0	2150	5.8	6.0
	15.8	2210	5.8	6.1
	10.5	2210	5.7	6.1
	2.1	----	5.9	6.2
	0.04	2200	5.9	5.8
Vero Beach Sand	21.0	2140	5.8	6.9
	15.8	2190	5.8	7.1
	10.5	2030	6.1	7.0
	2.1	----	6.3	6.8
	0.04	2250	5.9	6.0
Monheim Sandy loam	21.0	2280	6.5	6.8
	15.8	----	6.5	6.8
	10.5	2420	6.5	6.7
	2.1	----	6.6	6.7
	0.04	2370	6.5	6.4

Table B.8.1.2.1.1_CA-5: The distribution of Flufenacet in the test systems.

Test soil	Experimental conditions	Nominal initial concentration of Flufenacet [µg/mL]	Amount of Flufenacet [µg]:				Total Flufenacet recovered [%]
			initial	in supernatant		in soil after desorption	
				adsorption	desorption		
Stanley Silt loam	S:So ratio 1:5; eq. time: 24 h T = 22°C	21.0	104.97	70.06	19.12	11.93	96.29
		15.8	70.92	53.07	14.39	10.06	109.34
		10.5	52.40	34.44	9.18	6.57	95.79
		2.1	10.35	6.01	2.14	1.96	98.15
		0.04	0.20	0.09	0.04	0.07	100.07
Hagerstown Clay loam	S:So ratio 1:5; eq. time: 48 h T = 22°C	21.0	104.97	70.14	16.94	10.40	92.87
		15.8	70.92	51.46	13.55	7.33	102.25
		10.5	52.40	35.93	9.09	5.60	96.59
		2.1	10.35	6.43	1.93	1.32	94.34
		0.04	0.20	0.11	0.04	0.05	98.67
Howe Loamy sand	S:So ratio 1:5; eq. time: 24 h T = 22°C	21.0	104.97	82.84	13.68	5.40	97.09
		15.8	70.92	61.73	10.66	4.22	108.01
		10.5	52.40	40.64	7.35	2.98	97.27
		2.1	10.35	7.66	1.55	0.89	97.72
		0.04	0.20	0.13	0.04	0.03	100.66
Vero Beach Sand	S:So ratio 1:5; eq. time: 48 h T = 22°C	21.0	104.97	89.19	10.87	2.01	96.58
		15.8	70.92	61.42	8.46	1.51	99.13
		10.5	52.40	42.11	5.52	0.94	92.70
		2.1	10.35	8.40	1.18	0.25	95.03
		0.04	0.20	0.17	0.03	0.01	98.80
Monheim Sandy loam	S:So ratio 1:5; eq. time: 24 h T = 22°C	21.0	104.97	57.12	21.38	18.77	96.26
		15.8	70.92	42.28	16.43	16.29	105.75
		10.5	52.40	28.77	10.10	11.23	95.61
		2.1	10.35	5.09	2.23	2.78	97.58
		0.04	0.20	0.08	0.04	0.07	95.00

Table B.8.1.2.1.1_CA-6: The results of the examination of soil sorption of Flufenacet used to construct Freundlich adsorption and desorption isotherms.

Test soil	Nominal initial concentration of Flufenacet [µg/mL]	Results obtained for adsorption phase			Results obtained for desorption phase		
		Concentrations of Flufenacet at equilibrium		% adsorbed onto soil	Concentrations of Flufenacet at equilibrium		% remaining adsorbed onto soil
		in solution – Ce [µg/mL]	in soil – x/m [µg/g]		in solution – Ce [µg/mL]	in soil – x/m [µg/g]	
<i>Stanley Silt loam</i>	0.04	0.02	0.11	55.0	0.01	0.07	35.0
	2.1	1.23	4.34	41.9	0.44	1.96	18.9
	10.5	7.08	17.96	34.3	1.90	6.57	12.5
	15.8	10.76	17.85	25.2	2.94	10.06	14.2
	21.0	14.60	34.91	33.3	4.01	11.93	11.4
<i>Hagerstown Clay loam</i>	0.04	0.02	0.09	45.0	0.01	0.05	25.0
	2.1	1.38	3.92	37.9	0.42	1.32	12.8
	10.5	7.53	16.47	31.3	1.95	5.60	10.7
	15.8	11.15	19.28	27.2	2.95	7.33	10.3
	21.0	14.71	34.83	33.2	3.66	10.40	9.9
<i>Howe Loamy sand</i>	0.04	0.03	0.06	30.0	0.01	0.03	15.0
	2.1	1.57	2.69	26.0	0.33	0.89	8.6
	10.5	8.24	11.77	22.5	1.53	2.98	5.7
	15.8	12.77	9.19	13.0	2.24	4.22	6.0
	21.0	17.50	22.13	21.1	2.89	5.40	5.1
<i>Vero Beach Sand</i>	0.04	0.03	0.03	16.5	0.01	0.01	5.0
	2.1	1.75	1.95	18.8	0.25	0.25	2.4
	10.5	8.78	10.29	19.6	1.17	0.94	1.8
	15.8	13.26	9.50	13.4	1.84	1.51	2.1
	21.0	18.45	15.77	15.0	2.30	2.01	1.9
<i>Monheim Sandy loam</i>	0.04	0.02	0.12	60.0	0.01	0.07	35.0
	2.1	1.04	5.26	50.0	0.46	2.78	26.9
	10.5	5.95	23.63	45.1	2.07	11.23	21.4
	15.8	8.75	28.62	40.4	3.40	16.29	23.0
	21.0	11.91	47.84	45.6	4.52	18.77	17.9

The graphical and numerical results of the experiment – Freundlich adsorption and desorption isotherms and their parameters, are presented below individually for each test soil. On their basis it may be stated that the obtained Freundlich sorption isotherms were of good quality. However, RMS stated that in the study report the way of determination of the Freundlich adsorption constant K_f was not clearly explained, therefore it was difficult to interpret the results. That concerned in particular the values presented in the Table 13 of the study report, in which the K_d values were presented. These were most probably K_f values, but the assumption made by the RMS required verification. The headings of the graphs presenting the isotherms contained the information that they were used for the determination of $1/n$ values, what was confusing. In the body text of the study report were mentioned the K_d values, but referred to as distribution coefficients. Finally, in case of the K_{OC} values it was stated in the study report that they were determined using the OC value calculated using the equation $OC = OM/1.9$. For that reason RMS repeated the analysis using as input data presented above in the table B.8.1.2.1.1_CA-6. The input data and obtained results are presented below the results obtained by the Applicant. Reporting the Applicant's results RMS decided to maintain the format of reporting used in the original study report.

The results obtained by the Applicant:

The graphical results obtained for the experiment with Stanley Silt loam soil are presented on figure B.8.1.2.1.1_CA-2 and the Freundlich isotherm parameters for adsorption and desorption processes obtained in that soil in the table B.8.1.2.1.1_CA-7.

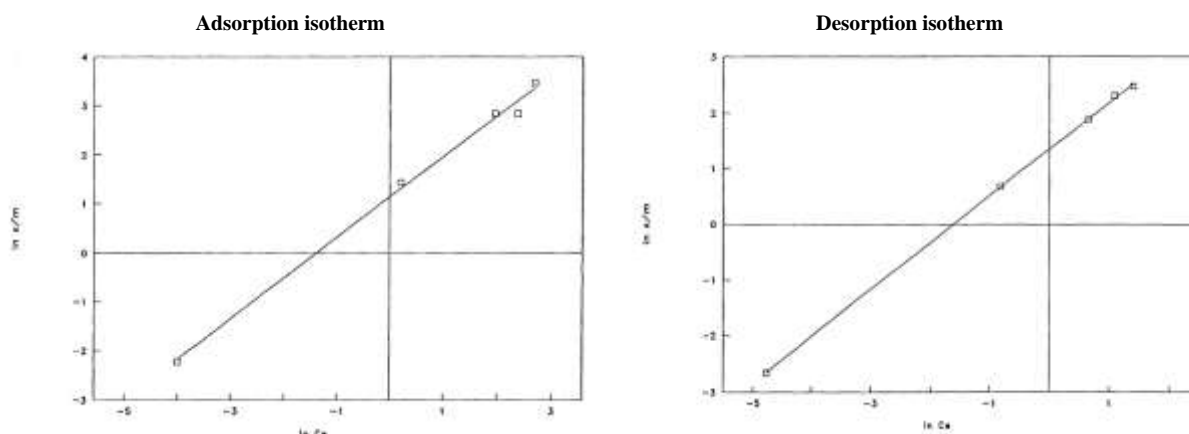


Figure B.8.1.2.1.1_CA-2: The Freundlich adsorption and desorption isotherms obtained for Flufenacet in Stanley Silt loam soil (copied from the study report).

Table B.8.1.2.1.1_CA-7: The parameters of Freundlich adsorption and desorption isotherms for Flufenacet determined in Stanley silt loam soil.

Process	Determined parameter				Correlation coefficient (r)
	K_d [mL/g]	K_{oc} [mL/g]	1/n		
			value	SD	
Adsorption	3.2	213	0.837	0.036	0.9945
Desorption	3.9	254	0.840	0.008	0.9998

The graphical results obtained for the experiment with Hagerstown Clay loam soil are presented on figure B.8.1.2.1.1_CA-3 and the Freundlich isotherm parameters for adsorption and desorption processes obtained in that soil in the table B.8.1.2.1.1_CA-8.

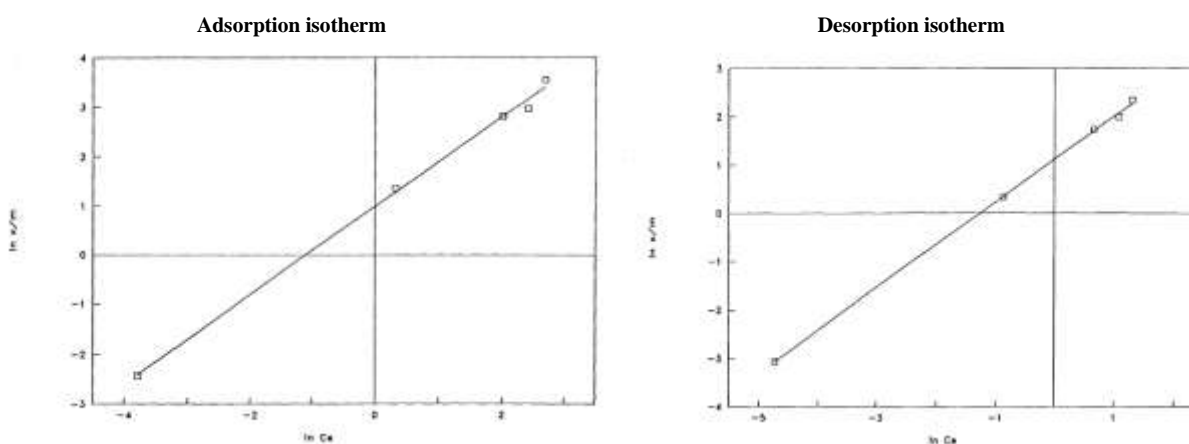
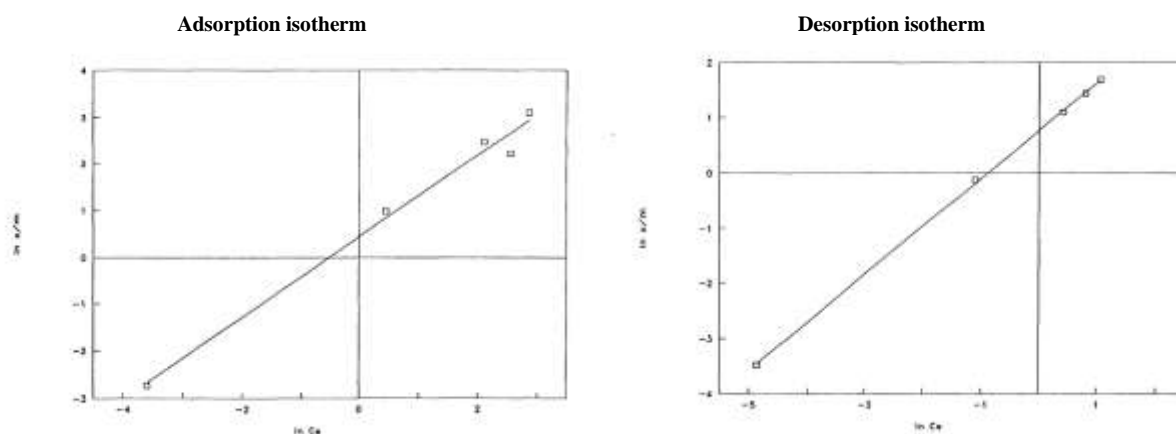


Figure B.8.1.2.1.1_CA-3: The Freundlich adsorption and desorption isotherms obtained for Flufenacet in Hagerstown Clay loam soil (copied from the study report).

Table B.8.1.2.1.1._CA-8: The parameters of Freundlich adsorption and desorption isotherms for Flufenacet determined in Hagerstown Clay loam soil.

Process	Determined parameter				
	$K_d[mL/g]$	$K_{oc}[mL/g]$	$1/n$		Correlation coefficient (<i>r</i>)
			value	SD	
Adsorption	2.7	233	0.899	0.028	0.9971
Desorption	3.1	264	0.884	0.014	0.9993

The graphical results obtained for the experiment with Howe Loamy sand soil are presented on figure B.8.1.2.1.1._CA-4 and the Freundlich isotherm parameters for adsorption and desorption processes obtained in that soil in the table B.8.1.2.1.1._CA-9.

**Figure B.8.1.2.1.1._CA-4:** The Freundlich adsorption and desorption isotherms obtained for Flufenacet in Howe Loamy sand soil (copied from the study report).**Table B.8.1.2.1.1._CA-9:** The parameters of Freundlich adsorption and desorption isotherms for Flufenacet determined in Howe Loamy sand soil.

Process	Determined parameter				
	$K_d[mL/g]$	$K_{oc}[mL/g]$	$1/n$		Correlation coefficient (<i>r</i>)
			value	SD	
Adsorption	1.6	742	0.869	0.057	0.9871
Desorption	2.1	1016	0.866	0.010	0.9996

The graphical results obtained for the experiment with Vero Beach Sand soil are presented on figure B.8.1.2.1.1._CA-5 and the Freundlich isotherm parameters for adsorption and desorption processes obtained in that soil in the table B.8.1.2.1.1._CA-10.

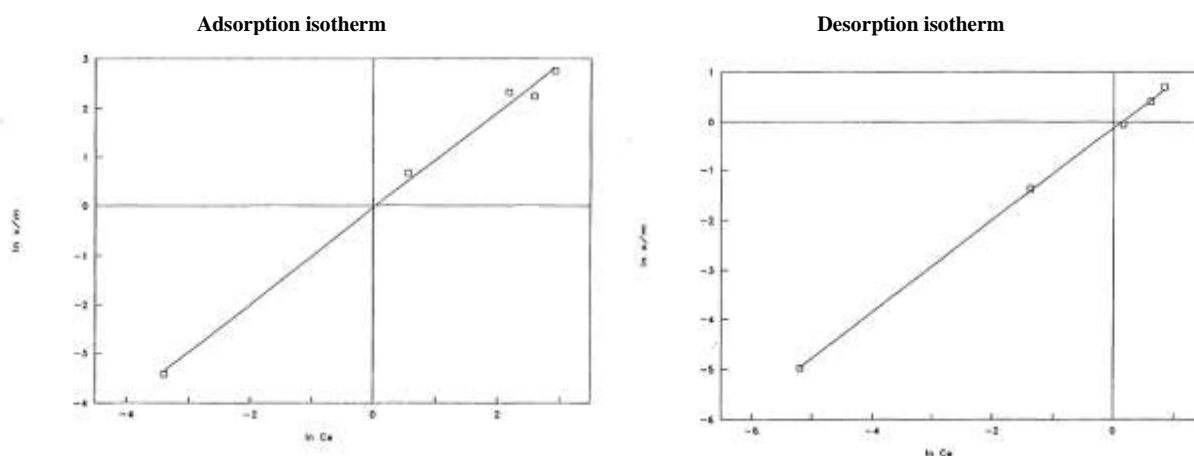


Figure B.8.1.2.1.1._CA-5: The Freundlich adsorption and desorption isotherms obtained for Flufenacet in Vero Beach Sand soil (copied from the study report).

Table B.8.1.2.1.1._CA-10: The parameters of Freundlich adsorption and desorption isotherms for Flufenacet determined in Vero Beach Sand soil.

Process	Determined parameter				
	$K_d[mL/g]$	$K_{oc}[mL/g]$	$1/n$		Correlation coefficient (r)
			value	SD	
Adsorption	1.0	613	0.980	0.043	0.9942
Desorption	0.9	554	0.930	0.013	0.9995

The graphical results obtained for the experiment with Monheim Sandy loam soil are presented on figure B.8.1.2.1.1._CA-6 and the Freundlich isotherm parameters for adsorption and desorption processes obtained in that soil in the table B.8.1.2.1.1._CA-11.

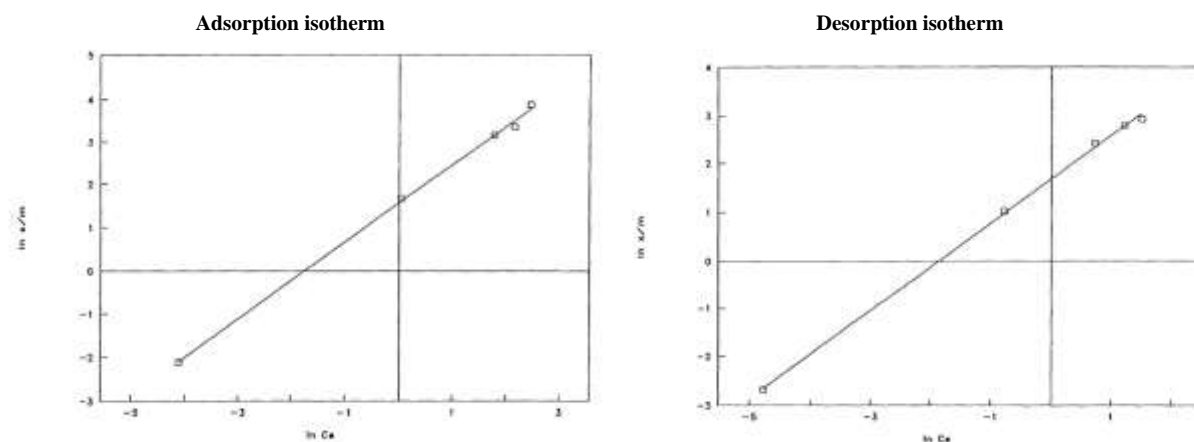


Figure B.8.1.2.1.1._CA-6: The Freundlich adsorption and desorption isotherms obtained for Flufenacet in Monheim Sandy loam soil (copied from the study report).

Table B.8.1.2.1.1_CA-11: The parameters of Freundlich adsorption and desorption isotherms for Flufenacet determined in Monheim Sandy loam soil.

Process	Determined parameter				Correlation coefficient (r)
	K_d [mL/g]	K_{OC} [mL/g]	1/n		
			value	SD	
Adsorption	4.8	354	0.892	0.019	0.9986
Desorption	5.3	395	0.907	0.017	0.9990

The results obtained by the RMS:

Below in the table B.8.1.2.1.1_CA-12 are given the input data used in the repeated determination of Freundlich adsorption and desorption parameters performed by the RMS. To maintain the consistency and comparability with the Applicant's analysis RMS transformed the input data using the natural-logarithm transformation. Therefore the Freundlich adsorption constant was calculated using the following equation:

$$K_f = e^{\ln K}$$

Table B.8.1.2.1.1_CA-12: The input data used in the repeated determination of Freundlich adsorption and desorption isotherms performed by the RMS.

Test soil	Nominal initial concentration of Flufenacet [µg/mL]	Results obtained for adsorption phase				Results obtained for desorption phase			
		Concentrations of Flufenacet at equilibrium		Log-transformed (ln) Concentrations of Flufenacet at equilibrium		Concentrations of Flufenacet at equilibrium		Log-transformed (ln) Concentrations of Flufenacet at equilibrium	
		in solution Ce [µg/mL]	in soil x/m [µg/g]	Ln (Ce)	Ln (x/m)	in solution Ce [µg/mL]	in soil x/m [µg/g]	Ln (Ce)	Ln (x/m)
Stanley Silt loam	0.04	0.02	0.11	-3.912023	-2.207275	0.01	0.07	-4.60517	-2.65926
	2.1	1.23	4.34	0.207014	1.467874	0.44	1.96	-0.820981	0.672944
	10.5	7.08	17.96	1.957274	2.888147	1.90	6.57	0.641854	1.882514
	15.8	10.76	17.85	2.375836	2.882004	2.94	10.06	1.07841	2.308567
	21.0	14.60	34.91	2.68102	3.552773	4.01	11.93	1.388791	2.479056
Hagerstown Clay loam	0.04	0.02	0.09	-3.912023	-2.407946	0.01	0.05	-4.60517	-2.995732
	2.1	1.38	3.92	0.322083	1.366092	0.42	1.32	-0.867501	0.277632
	10.5	7.53	16.47	2.018895	2.801541	1.95	5.60	0.667829	1.722767
	15.8	11.15	19.28	2.411439	2.959068	2.95	7.33	1.081805	1.991976
	21.0	14.71	34.83	2.688528	3.550479	3.66	10.40	1.297463	2.341806
Howe Loamy sand	0.04	0.03	0.06	-3.506558	-2.813411	0.01	0.03	-4.60517	-3.506558
	2.1	1.57	2.69	0.451076	0.989541	0.33	0.89	-1.108663	-0.116534
	10.5	8.24	11.77	2.109	2.465554	1.53	2.98	0.425268	1.091923
	15.8	12.77	9.19	2.547099	2.218116	2.24	4.22	0.806476	1.439835
	21.0	17.50	22.13	2.862201	3.096934	2.89	5.40	1.061257	1.686399
Vero Beach Sand	0.04	0.03	0.03	-3.506558	-3.506558	0.01	0.01	-4.60517	-4.60517
	2.1	1.75	1.95	0.559616	0.667829	0.25	0.25	-1.386294	-1.386294
	10.5	8.78	10.29	2.172476	2.331173	1.17	0.94	0.157004	-0.061875
	15.8	13.26	9.50	2.584752	2.251292	1.84	1.51	0.609766	0.41211
	21.0	18.45	15.77	2.915064	2.758109	2.30	2.01	0.832909	0.698135
Monheim Sandy loam	0.04	0.02	0.12	-3.912023	-2.120264	0.01	0.07	-4.60517	-2.65926
	2.1	1.04	5.26	0.039221	1.660131	0.46	2.78	-0.776529	1.022451
	10.5	5.95	23.63	1.783391	3.162517	2.07	11.23	0.727549	2.418589
	15.8	8.75	28.62	2.169054	3.3562	3.40	16.29	1.223775	2.790551
	21.0	11.91	47.84	2.477378	3.867862	4.52	18.77	1.508512	2.93226

The data were fitted using the CurveExpert Professional 1.0 tool. The linear regression model was applied. The graphical and numerical results are presented below, individually for each test soil. All values were rounded to the two, and in case of 1/n three, digits after the decimal point. The correlation coefficient is reported with four digits after the decimal point

The graphical results obtained for the experiment with Stanley Silt loam soil are presented on figure B.8.1.2.1.1_CA-7 and the Freundlich isotherm parameters for adsorption and desorption processes obtained in that soil in the table B.8.1.2.1.1_CA-13.

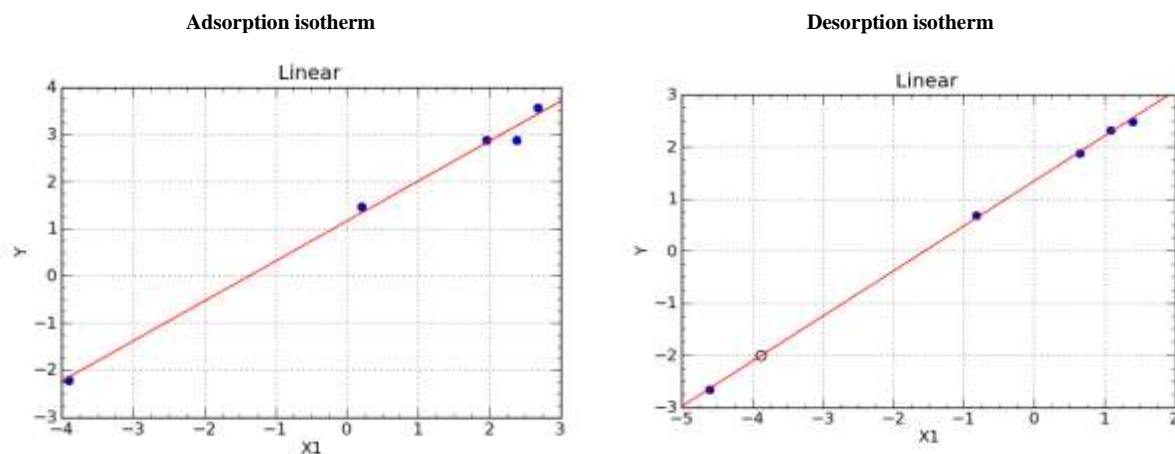


Figure B.8.1.2.1.1_CA-7: The Freundlich adsorption and desorption isotherms obtained for Flufenacet in Stanley Silt loam soil (copied from the study report).

Table B.8.1.2.1.1_CA-13: The parameters of Freundlich adsorption and desorption isotherms for Flufenacet determined in Stanley silt loam soil.

Process	Determined parameter							
	$Ln K_f$		$K_f[mL/g]$	$K_{foc}[mL/g]$	$1/n$		SD	$Correlation coefficient (r)$
	value	SD			value	SD		
Adsorption	1.16	0.0943	3.18	189.28	0.848	0.0226	0.2037	0.9971
Desorption	1.34	0.0226	3.81	226.79	0.864	0.0101	0.0495	0.9998

The graphical results obtained for the experiment with Hagerstown Clay loam soil are presented on figure B.8.1.2.1.1._CA-8 and the Freundlich isotherm parameters for adsorption and desorption processes obtained in that soil in the table B.8.1.2.1.1._CA-14.

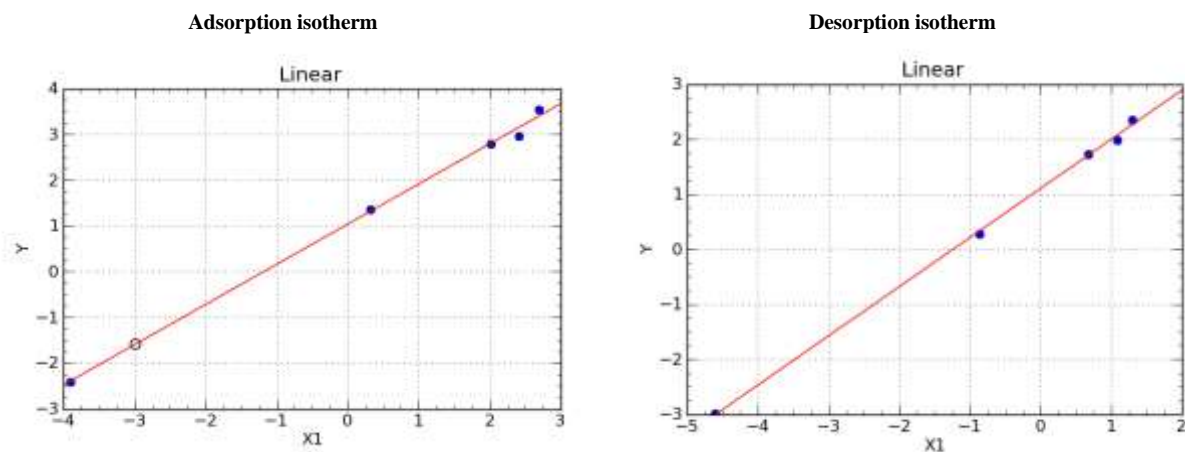


Figure B.8.1.2.1.1._CA-8: The Freundlich adsorption and desorption isotherms obtained for Flufenacet in Hagerstown Clay loam soil (copied from the study report).

Table B.8.1.2.1.1._CA-14: The parameters of Freundlich adsorption and desorption isotherms for Flufenacet determined in Hagerstown Clay loam soil.

Process	Determined parameter						
	$\ln K_f$		$K_f[\text{mL/g}]$	$K_{foc}[\text{mL/g}]$	$1/n$		SD
	value	SD			value	SD	
Adsorption	1.03	0.0678	2.81	219.53	0.878	0.0266	0.1458
Desorption	1.10	0.0331	2.75	214.84	0.893	0.0147	0.0722

The graphical results obtained for the experiment with Howe Loamy sand soil are presented on figure B.8.1.2.1.1._CA-9 and the Freundlich isotherm parameters for adsorption and desorption processes obtained in that soil in the table B.8.1.2.1.1._CA-15.

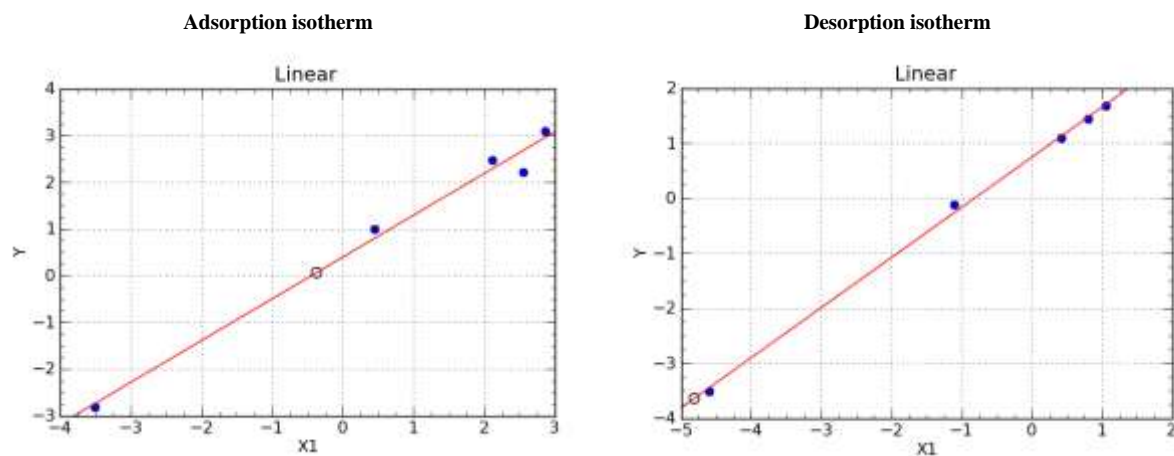


Figure B.8.1.2.1.1._CA-9: The Freundlich adsorption and desorption isotherms obtained for Flufenacet in Howe Loamy sand soil (copied from the study report).

Table B.8.1.2.1.1._CA-15: The parameters of Freundlich adsorption and desorption isotherms for Flufenacet determined in Howe Loamy sand soil.

Process	Determined parameter						
	$\ln K_f$		$K_f [\text{mL/g}]$	$K_{foc} [\text{mL/g}]$	$1/n$		SD
	value	SD			value	SD	
Adsorption	0.39	0.1520	1.48	643.48	0.894	0.0604	0.3177
Desorption	0.74	0.0209	2.10	913.04	0.911	0.0209	0.0984

The graphical results obtained for the experiment with Vero Beach Sand soil are presented on figure B.8.1.2.1.1._CA-10 and the Freundlich isotherm parameters for adsorption and desorption processes obtained in that soil in the table B.8.1.2.1.1._CA-16.

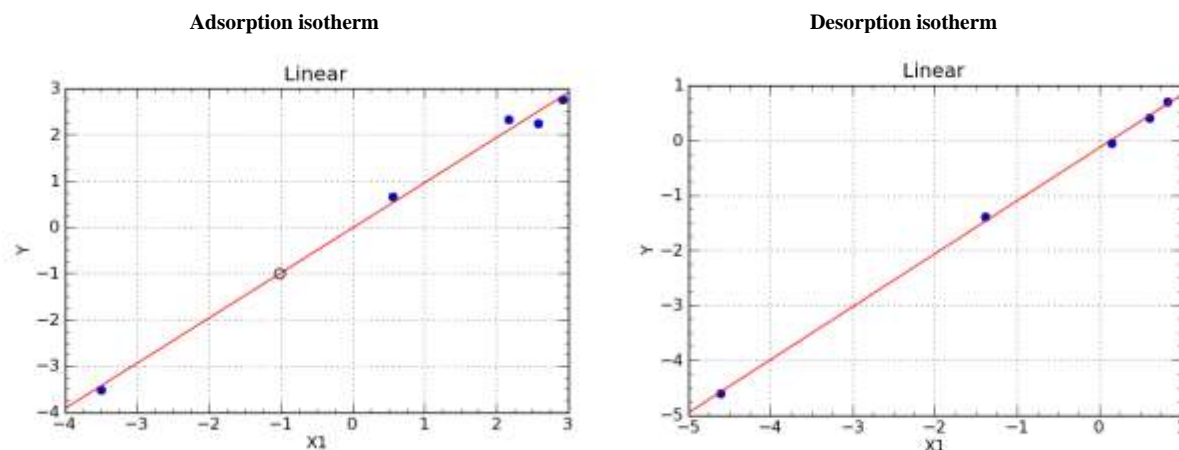


Figure B.8.1.2.1.1._CA-10: The Freundlich adsorption and desorption isotherms obtained for Flufenacet in Vero Beach Sand soil (copied from the study report).

Table B.8.1.2.1.1._CA-16: The parameters of Freundlich adsorption and desorption isotherms for Flufenacet determined in Vero Beach Sand soil.

Process	Determined parameter						
	$\ln K_f$		$K_f [\text{mL/g}]$	$K_{foc} [\text{mL/g}]$	$1/n$		Correlation coefficient (r)
	value	SD			value	SD	
Adsorption	-0.021	0.1059	0.98	576.47	0.975	0.0415	0.9973
Desorption	-0.14	0.0363	0.87	511.76	0.963	0.0165	0.9996

In case of this soil it was demonstrated that level of adsorption was <20%. For that reason the determined Freundlich sorption isotherm parameters, although determined and reported in the table above, should not be used to derive the regulatory endpoints.

The graphical results obtained for the experiment with Monheim Sandy loam soil are presented on figure B.8.1.2.1.1._CA-11 and the Freundlich isotherm parameters for adsorption and desorption processes obtained in that soil in the table B.8.1.2.1.1._CA-17.

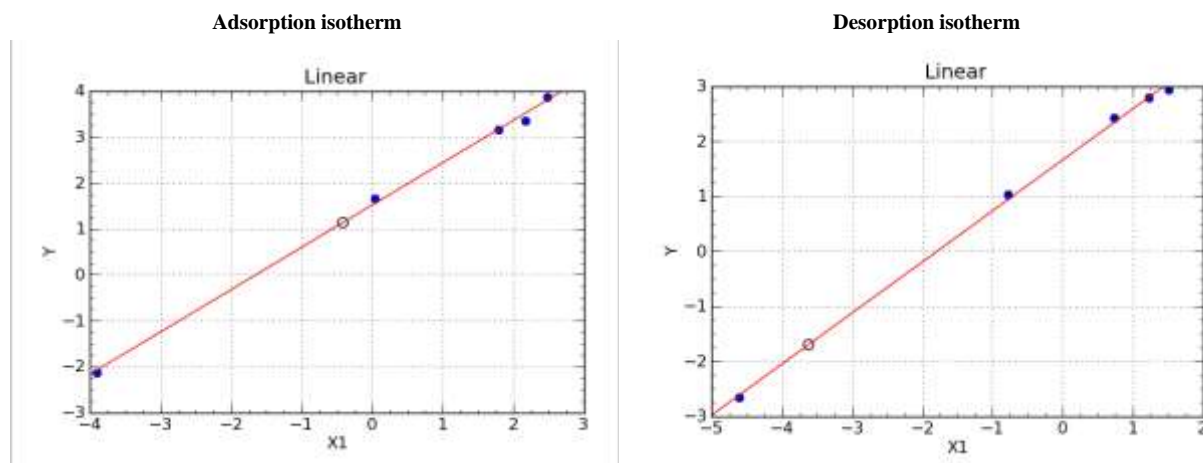


Figure B.8.1.2.1.1._CA-11: The Freundlich adsorption and desorption isotherms obtained for Flufenacet in Monheim Sandy loam soil (copied from the study report).

Table B.8.1.2.1.1._CA-17: The parameters of Freundlich adsorption and desorption isotherms for Flufenacet determined in Monheim Sandy loam soil.

Process	Determined parameter						
	$\ln K_f$		$K_f [mL/g]$	$K_{foc} [mL/g]$	$1/n$		SD
	value	SD			value	SD	
Adsorption	1.51	0.0544	4.55	325.00	0.920	0.0225	0.1190
Desorption	1.66	0.0470	5.25	375.00	0.928	0.0206	0.1037

The final results of the study – Freundlich adsorption parameters for Flufenacet obtained in each test soil, are presented below in the table B.8.1.2.1.1._CA-18. RMS considers these results reliable and possible to be used to derive input parameters for modelling. It shall be noted however, that in case of Vero Beach Sand soil the level of adsorption was lower than the minimum requirement of 20%. Therefore the determined Freundlich adsorption parameters should be considered with care and RMS decided not to include these values into the data set from which the regulatory endpoints are calculated. For that reason those values, being presented in the table B.8.1.2.1.1._CA-18 below, are marked in italics.

Table B.8.1.2.1.1._CA-18: The definitive set of Freundlich adsorption parameters determined for Flufenacet in the study.

Parameter	Test soil				
	Stanley Silt loam	Hagerstown Clay loam	Howe Loamy sand	Vero Beach Sand	Monheim Sandy loam
$K_f [mL/g]$	3.18	2.81	1.48	<i>0.98</i>	4.55
$K_{foc} [mL/g]$	189.28	219.53	643.48	<i>576.47</i>	325.00
$1/n$	0.848	0.878	0.894	<i>0.975</i>	0.920

Study 2:

Report: Hein E.-M., (2012): “[Thiadiazole-5-¹⁴C] FOE 5043 (Flufenacet): Adsorption/Desorption on Five Soils.”; Bayer CropScience AG, BCS-D-EnSa-Testing, 40789 Monheim, Germany; study ID M1312069-2, Report No. EnSa-12-0517; 01 October 2012; study reference number: M-439282-01-1;

Guidelines: The study was performed to comply with the following Guidelines:

- OECD Guideline for the Testing of Chemicals No. 106, Adsorption/Desorption, 2000;
- US EPA OCSPP Fate, Transport and Transformation Test Guidelines, OPPTS 835 1230, Adsorption/Desorption (Batch Equilibrium), 2008;
- Canada PMRA, Guidelines for Registration of Pesticides, Environmental Chemistry and Fate, 1987.

GLP: Yes;

RMS comments: This is a new study, submitted specifically for the purpose of the current assessment. It was evaluated for compliance with the following Guidelines:

- OECD Guideline for the Testing of Chemicals No. 106, Adsorption/Desorption, 2000;
- US EPA OCSPP Fate, Transport and Transformation Test Guidelines, OPPTS 835 1220, Sediment and Soil Adsorption/Desorption Isotherm, 1998;
- US EPA OCSPP Fate, Transport and Transformation Test Guidelines, OPPTS 835 1230, Adsorption/Desorption (Batch Equilibrium), 2008;

The following deviations were stated:

- the soil:solution ratios tested to identify the adequate soil:solution ratio were: 1:1.3, 1:2 and 1:4; the higher soil solution ratios were not tested and the Applicant provided no justification for not additionally examining at least 1:25 ratio recommended by the Guidelines;
- throughout the whole experiment HgCl_2 added to the 0.01M $\text{CaCl}_{2\text{aq}}$ in amount 50 mg/L was used to eliminate the microbial activity of the test soils and in that way grant the stability of the test compound in contact in soil; it shall be noted however that that method of sterilisation is not recommended as potentially influencing the results of the experiment - Hg^{2+} ions may competitively occupy the sorption sites on the surface of the test soil, therefore limiting the extent of the adsorption of the test compound, what in turn may result in underestimation of the adsorption parameters and Freundlich adsorption isotherm constant in particular.

RMS however decided to consider the study valid as in all other aspects it complied with the provisions of the reference Guidelines, at the same time taking into consideration the fact that the adsorption parameters may be underestimated and that the extent of that potential underestimation was not possible to be assessed.

The study is summarised below.

Summary:

The aim of the was to examine the process of the equilibrium sorption – adsorption and desorption, of Flufenacet onto soil. The study was performed using five European test soils. Their characteristic is provided below in the table B.8.1.2.1.1._CA-19. The test soils were sampled from the agriculturally used areas, from the fields covered with grass on which no pesticides were used for 5 years prior to the sampling. They were collected from the 0-20 cm layer using the shovel and transported to the test facility in plastic bags. There they were sieved through 2-mm sieve and stored in a refrigeration room until being used. The storage period was following:

- for Laacher Hof AXXa soil: 63 days;
- for Hoefchen am Hohenseh soil: 18 days;
- for Hanscheider Hof soil: 157 days;
- for Dollendorf II soil: 56 days;
- for Wurmwielse soil: 18 days.

Table B.8.1.2.1.1._CA-19: The characteristic of soils used in the study.

Parameter		Soil				
		<i>Laacher Hof AXXa (AA)</i>	<i>Hoefchen am Hohenseh (HH)</i>	<i>Hanscheider Hof (HN)</i>	<i>Dollendorf II (DD)</i>	<i>Wurmwiess (WW)</i>
Soil origin		Monheim, North Rhine- Westphalia, Germany	Burscheid, North Rhein- Westphalia, Germany	Burscheid, North Rhein- Westphalia, Germany	Blankenheim, North Rhein- Westphalia, Germany	Monheim, North Rhine- Westphalia, Germany
Soil type (USDA)		Loamy sand	Silt loam	Silt loam	Loam	Sandy loam
Particle size distribution	Sand [%]	79	15	31	37	53
	Silt [%]	16	70	54	40	30
	Clay [%]	5	15	15	23	17
Soil pH	in 0.01M CaCl ₂ (1:2)	5.8	6.5	5.3	7.3	5.1
	in water (1:1)	6.2	6.7	5.7	7.5	5.4
	in 1M KCl (1:1)	5.7	6.1	4.9	7.0	4.7
Water holding capacity	maximum, [g H ₂ O/100 g soil]	49.9	55.9	61.3	78.5	61.9
	at 0.1 bar (pF 2.0) [%]	17.2	31.7	36.7	41.1	20.1
	at 0.33 bar (pF 2.5) [%]	12.4	21.9	25.6	34.7	16.5
Organic matter content (OM) [%] ¹⁾		3.79	2.76	4.65	7.59	2.93
Organic carbon content (OC) [%]		2.2	1.6	2.7	4.4	1.7
CEC [meq/100 g]		10.0	11.6	9.6	19.2	9.9
Bulk density [g/cm ³]		1.20	1.11	1.04	0.98	1.08

Footnotes to the table:

- 1) Recalculated by the RMS from organic matter content using the following equation: OM = 1.724 OC (the values are almost identical to those reported by the Applicant, however some inaccuracies related to the rounding procedure were stated);

The test compound used in the experiment was the ¹⁴C-FOE 5043 radiolabelled in C5-thiadiazole position, as shown below on figure B.8.1.2.1.1._CA-12.

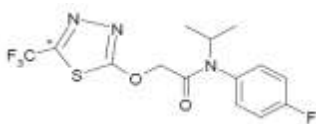


Figure B.8.1.2.1.1._CA-12.: The structural formula of the radiolabelled Flufenacet (FOE 5043) used in the experiment; the asterisk (*) indicates radiolabelling position (copied from the study report).

The specific radioactivity of the test compound used in the experiment was 1.54 MBq/mg and its radiochemical purity, determined using both HPLC and TLC, was > 99%. Also the chemical purity of the test compound, determined using HPLC equipped with UV detector, was > 99%. It was delivered to the test facility as a vacuum-dried solid.

The whole delivered sample was used to prepare a **stock solution** by dissolving it in 17 mL of CH₃OH. The obtained solution had a nominal concentration 2 mg Flufenacet/mL and specific activity 3047 kBq/mL. It was labelled **HO58 SS** and used to prepare all other solutions containing the test compound – [¹⁴C]-Flufenacet, used in the experiment (**Application solutions**). The identity and purity of the test compound in the solution **HO58 SS** was determined using ¹H-NMR and HPLC-MS/MS methods.

The **Application solutions** were prepared as 0.01 M CaCl₂ aq (aqueous) solutions, with or without mercury (II) chloride.

The 0.01 M CaCl₂ aq solutions were prepared as follows:

- the solution of calcium chloride without mercury chloride was prepared by dissolving 2.94 g of CaCl₂ x 2 H₂O in ultrapure water in 2-L volumetric flask – **Aqueous Solution A**;
- the solution of calcium chloride with mercury chloride was prepared by dissolving 2.94 g of CaCl₂ x 2 H₂O and 100 mg of HgCl₂ in ultrapure water in 2-L volumetric flask – **Aqueous solution B**.

The application solutions containing the test item – [^{14}C]-Flufenacet, were prepared in a way characterised below.

Firstly the **Stock solution HS6006 SS1** was prepared by transferring 1.75 mL of the stock solution **HO58 SS** into a glass bottle. Next it was evaporated to dryness under the gentle stream of N_2 and residue redissolved in 350 mL of 0.01 M CaCl_2 aq solution (**Aqueous solution A**) in 15-minutes lasting sonication. The concentration of so prepared solution was determined by LSC – it was 16303.1 Bq/mL, what corresponded to 10.6 μg Flufenacet/mL. That solution was used to prepare a series of the **Application solutions**, varying in concentration of the test item and labelled **Application solution A – E**.

The **Application Solution A** was prepared by diluting the total residual volume of the **Stock solution HS6006 SS1** with 45 mL of **Aqueous solution A**. The obtained solution was analysed for its homogeneity and the radioactivity content by LSC. The determined radioactivity content was 15318 Bq/mL, what corresponded to the concentration of 9.9 mL [^{14}C]-Flufenacet/mL. That solution was used to obtain the final nominal concentration 1.0 mg Flufenacet/mL.

Other **Application solutions – B, C, D and E**, were prepared in a series of dilutions of the **Application Solution A**, in a following way:

- **Application Solution B** by diluting 15 mL of the **Application Solution A** with 35 mL of 0.01 M CaCl_2 aq with HgCl_2 – **Aqueous solution B**, to obtain 50 mL of the solution having a concentration, when determined by LSC, 4446.08 Bq/mL, corresponding to 2.9 mg Flufenacet/mL, and containing 6.447 mmole HgCl_2 . It was used to obtain the final nominal test concentration of 0.3 mg Flufenacet/mL;
- **Application Solution C** by diluting 5 mL of the **Application Solution A** with 45 mL of **Aqueous solution B**, to obtain 50 mL of the solution having a concentration, when determined by LSC, 1482.9 Bq/mL, corresponding to 1.0 mg Flufenacet/mL, and containing 8.289 mmole HgCl_2 . It was used to obtain the final nominal test concentration of 0.1 mg Flufenacet/mL;
- **Application Solution D** by diluting 1.5 mL of the **Application Solution A** with 48.5 mL of **Aqueous solution B**, to obtain 50 mL of the solution having a concentration, when determined by LSC, 453.34 Bq/mL, corresponding to 0.3 mg Flufenacet/mL, and containing 8.934 mmole HgCl_2 . It was used to obtain the final nominal test concentration of 0.03 mg Flufenacet/mL;
- **Application Solution E** by diluting 0.5 mL of the **Application Solution A** with 49.5 mL of **Aqueous solution B**, to obtain 50 mL of the solution having a concentration, when determined by LSC, 150.16 Bq/mL, corresponding to 0.1 mg Flufenacet/mL, and containing 9.118 mmole HgCl_2 . It was used to obtain the final nominal test concentration of 0.01 mg Flufenacet/mL;

The study was carried out using 42-mL Teflon centrifuge tubes with screw cap as test vessels. It consisted of the following experiments:

- **Preliminary tests**, during which were determined:
 - Stability of the test item;
 - Adsorption of the test item onto the surface of the test vessels;
 - Adequate soil:solution ratio;
 - Adequate equilibrium time for adsorption;
 - Adequate equilibrium time for desorption;
 - Mass balance of the test compound – Flufenacet;
- **Definitive test**, consisting of:
 - Determination of Freundlich adsorption isotherm and its parameters – Freundlich adsorption constant $K_{\text{F ads}}$ and corresponding $1/n$ value, in a single-step experiment;
 - Determination of Freundlich desorption isotherm and its parameters – desorption constant $K_{\text{F des}}$ and corresponding $1/n$ value, in a multi-step (three-step) experiment;

All experiments were performed in a walk-in climatic chamber, at constant temperature $T = 20 \pm 2^\circ\text{C}$. The temperature in the experimental chamber was continuously monitored and the results of that monitoring are presented in section “Results and their discussion”, further down the summary.

For agitation (shaking) of the test vessels containing test soil and test solutions the mechanical overhead shaker was used.

The general experimental procedure used in the study, common for all steps, is characterised below.

Its first step was the preparation of the test system. First the designated amounts of each test soil (dry weight) were weighed into centrifuge tubes. Next the appropriate amount of either 0.01 M CaCl_2 aq solution or 0.01 M CaCl_2 aq solution containing 50 mg/L HgCl_2 (184.2 mmole/L), was added. HgCl_2 was used as a sterilising agent, preventing the degradation of the test compound, in all experiments except that aimed on the determination of the appropriate soil:solution ratio. The amount of the solution added into the test vessel containing the test soil was always such, to obtain a total solution volume of 18 mL, taking into account the residual soil moisture.

The so prepared test vessels were sealed and pre-equilibrated for at least 12 hours in the dark by agitation at constant temperature.

After pre-equilibration 2 mL of the adequate **Application solution (A – E)**, characterised above, was added to obtain the final solution volume of 20 mL. All preliminary tests were carried out using the **Application Solution A** – the highest nominal test concentration of 1.0 mg Flufenacet/mL.

The definitive test aimed on the examination of the adsorption was carried out using all five application solutions – **Application solution A – Application solution E**, to cover the concentration range (nominal) of 0.01 – 1.0 mg Flufenacet/mL. The same concentration range was used in examination of the 1st step of desorption. The next desorption steps – 2nd and 3rd, were examined using only one – highest nominal concentration of the test item – 1.0 mg/mL.

After introduction of the test compound the test vessels were closed and the suspensions agitated for the appropriate amount of time. After that period samples were centrifuged and the supernatants decanted. Their aliquots were analysed by LSC, and the supernatants weighed and analysed using radio-HPLC. Additionally in supernatants obtained while examining adsorption in the definitive test, pH was determined.

In definitive tests after decantation of clarified supernatants the fresh 20-mL portions of **Aqueous solution B** were introduced to the test vessels and the procedure repeated to examine the desorption. In case of samples treated with the test compound at nominal concentration 1.0 mg Flufenacet/mL that procedure was repeated three times to examine three-steps desorption.

Finally, to calculate the material balance the soil samples remaining after decantation of supernatants were lyophilised, homogenised and analysed, after combustion, for radioactivity content using LSC.

Because it was demonstrated that the test compound was stable during the experiment, its partition was determined on the basis of its content in the liquid phase and the soil content was not determined.

All test were performed using the duplicate samples.

For the whole experiment the verification of the application rate was performed in a following way: 2 mL of the appropriate **Application solution** were pipetted into 10- mL or 25-mL graduated glass flask and the solution was brought to the volume with CH₃CN/H₂O 1:1. The obtained solution was quantitatively analysed by LSC. The determined radioactivity content was set to 100% AR.

The specific conditions of the performance of each experiment are presented below.

The stability of the test item was examined in the soilless test systems. To the two test vessels 18 mL of the **Aqueous solution B** (containing HgCl₂) were introduced. Next 2 mL of the **Application solution A** were added. The test vessels were sealed and agitated for 96 hours. At pre-defined time points – after 0, 6, 24, 48, 72 and 96 hours the 100-μL aliquots were taken for the LSC analysis. Additionally the samples taken at the following time points: after 0, 24 and 96 hours of equilibration, were analysed by radio-HPLC. In the same experiment was examined the adsorption of the test item – Flufenacet, to the surface of the test vessels. N.b. the samples used in that experiment contained, each, 3.3156 mmol of HgCl₂.

The adequate soil:solution ratio was determined for each test soil by examining the following ratios:

- 1:1.3 – 15 g soil (d. w.) and 20 mL solution;
- 1:2 – 10 g soil (d. w.) and 20 mL solution;
- 1:4 – 5 g soil (d. w.) and 20 mL solution;

That was done in the following way: first the appropriate portions of each test soils were weighed to the test vessels and 18 mL **Aqueous solution A** were added. So prepared test vessels were pre-equilibrated for 24 hours as described above. Next 2 mL of the **Application solution A** were added to each test vessel and they were agitated for 24 hours. After that period the samples were centrifuged for 15 minutes at 5000g, and the 100-μL aliquots of supernatants analysed by LSC.

The soil:solution ratios higher than 1:4 were not tested and the reason for that was not provided. In this test, exclusively, HgCl₂ as sterilising agent was not used.

The adequate adsorption equilibrium time was determined for all test soils. The soil:solution ratio used in this test was 1:4. The test systems were prepared in duplicate for each test soil and pre-equilibrated for 48 hours, as already described. In this test **Aqueous solution B** was used. After pre-equilibration to each sample 2 mL of the **Application solution A** were added. The samples were then agitated for up to 96 hours. At the pre-defined time points – 6, 24, 48, 72 and 96 hours after treatment, samples were centrifuged for 10 minutes at 5000g and 100-μL aliquots of clarified supernatants taken for LSC analysis. After that soil pellets were resuspended and samples returned to the agitating device. The amount of HgCl₂ in each test vessel was 3.3156 mmol.

The adequate desorption equilibrium time was not examined separately, but set to the same value as that determined for the adsorption.

The mass balance of the test item – Flufenacet, was examined in the following way: the samples were prepared in duplicate and pre-equilibrated for the 48-hours in a way described above (4 g test soil, 18 mL of **Aqueous solution B**). The selected soil:solution ratio was 1:4. After pre-equilibration 2 mL of the **Application solution A** were added to each test vessel. After application the samples were equilibrated, by agitating, for 96 hours, then centrifuged for 10 minutes at 5000g and clarified supernatants collected for analysis by LSC (500- μ L aliquots). The amount of collected supernatant for each soil was determined by weighing it.

The soils remaining in the test vessels after decantation of supernatants were extracted by shaking them with four 10-mL portions of $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ 1:1. Each extraction cycle (shaking) lasted 30 minutes. Samples were then centrifuged for 10 min. at 5000g, supernatants decanted and combined, and their total volume determined using the graduated cylinders. The 500- μ L aliquots of each combined extract were analysed by LSC.

The aliquots of aqueous supernatants and soil organic extracts were analysed by radio-HPLC to check the stability of the test item and determine its concentration to establish the mass balance. Aqueous extracts were examined directly and organic extracts after processing. The processing consisted on concentrating of 5-mL aliquots to which 0.1 mL of aqueous solubiliser was added, centrifugation of the concentrated extracts and analysis of the supernatants.

The definitive test aimed on the determination of Freundlich adsorption and desorption isotherms, and Freundlich sorption parameters for both processes was carried out following the procedure presented below on figure B.8.1.2.1.1_CA-13. For examining adsorption and 1st stage of desorption the following initial concentrations of the test item – [^{14}C]-Flufenacet. were used: 0.01 mg/L, 0.03 mg/L, 0.1 mg/L, 0.3 mg/L and 1.0 mg/L.

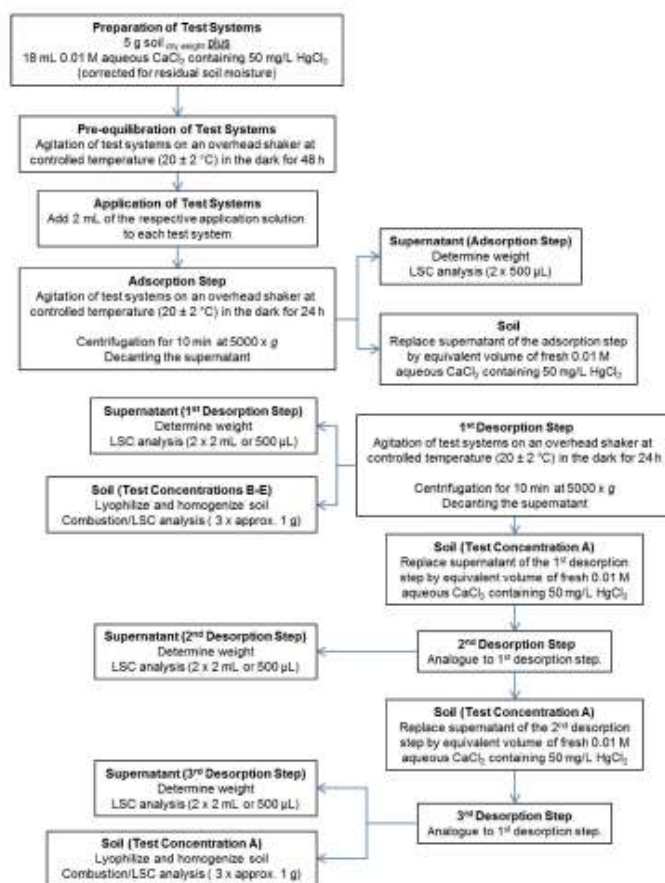


Figure B.8.1.2.1.1_CA-13: The flow chart of the experimental procedure for the definitive test (copied from the study report).

Throughout the definitive tests HgCl_2 was used as soil sterilising agent to prevent degradation of the test item – Flufenacet. As Hg^{2+} ions are known to have strong affinity to the soil organic matter, what might have

influenced the results of the experiment, RMS calculated the amount of HgCl_2 , in mmoles, present in the test systems at each stage of the definitive test. The results are presented below in the table B.8.1.2.1.1._CA-20.

Table B.8.1.2.1.1._CA-20: The amount of HgCl_2 in the test systems at each stage of the definitive test

Nominal concentration of the test item [mg/L]	Amount of HgCl_2 in the sample [mmoles]								
	Adsorption (ads)			Desorption 1 st step (des1)		Desorption 2 nd step (des2)		Desorption 3 rd step (des3)	
	Introduced at pre-equilibration	Introduced with treatment solution	Total	Introduced with solution	Total – (ads + des1)	Introduced with solution	Total – (ads + des1 + des2)	Introduced with solution	Total – (ads + des1 + des2 + des3)
1.0	3.3156	0	3.3156	3.684	6.9996	3.684	10.6836	3.684	14.3676
0.3	3.3156	0.2579	3.5735	3.684	7.2576	----	----	----	----
0.1	3.3156	0.3316	3.6472	3.684	7.3312	----	----	----	----
0.03	3.3156	0.3574	3.6730	3.684	7.3570	----	----	----	----
0.01	3.3156	0.3647	3.6803	3.684	7.3643	----	----	----	----

All liquid samples were analysed for the content of radioactivity using LSC method. The LSC (Liquid Scintillation Counting) analysis was performed using a LS6500 or LKB-Wallac 1219 Spectral counters.

The samples having volume of up to 2000 μL were analysed for the radioactivity content in mini-vials with 2 mL of Quicksafe[®] A solution containing 5% of water. The counting time was 10 min and the background 12 – 16 cpm. The analysis was performed using LS 6500 counter.

Aliquots of application solutions were analysed in maxi-vials using 7 mL of Quicksafe[®] A solution containing 5% of water. The counting time was 10 min and the background 22 – 23 cpm.

The radioactivity in solid samples – soil samples remaining after decantation of liquid phase, was determined after combustion of three 1-g aliquots of dried and homogenised material. The resulting $^{14}\text{CO}_2$ was absorbed in 15 mL of Oxsolve C400 liquid. The counting time was 10 min and the background 17 – 20 cpm and the counting instrument LKB-Wallac 1219 Spectral counter.

The instrumental limit of detection – LOD_i was set to twice maximum instrument background count rate and instrumental limit of quantitation – LOQ_i to three times maximum instrument background count rate. The maximum instrument background count rate was determined to be 0.3 – 0.5 Bq. Therefore for different types of liquid samples the instrumental LOD_i and LOQ_i were as follows:

- samples with scintillation cocktail of 2 mL Quicksafe A + 5% water, $\text{LOD}_i = 0.5$ Bq and $\text{LOQ}_i = 0.8$ Bq;
- samples with scintillation cocktail of 7 mL Quicksafe A + 5% water, $\text{LOD}_i = 0.8$ Bq and $\text{LOQ}_i = 1.2$ Bq;
- samples with scintillation cocktail of 15 mL Oxsolve C400, $\text{LOD}_i = 0.7$ Bq and $\text{LOQ}_i = 1.0$ Bq.

When calculated for different types of analysed samples, the determined LOD and LOQ values for LSC analysis were as presented below in the table B.8.1.2.1.1._CA-21:

Table B.8.1.2.1.1._CA-21: The LOD and LOQ values for different types of samples analysed using LSC.

Type of sample	max. total amount – volume or mass	min. aliquots analysed – volume or mass	LOD (worst case) expressed in:		LOQ (worst case) expressed in:	
			Bq	mass units	Bq	mass units
Supernatant (adsorption)	20 mL	0.5 mL	20	0.65 ng/mL	32	1.04 ng/mL
Supernatant (desorption)	20 mL	0.5 mL	20	0.65 ng/mL	32	1.04 ng/mL
Soil residues	5 g	0.9 g	3	0.34 ng/g	5	0.65 ng/g

The RP-HPLC analysis was performed in a gradient mode. The system consisted of HP 1100 chromatograph equipped with a binary pump, autosampler, on-line degasser, column oven and a Variable Wavelength UV detector set at $\lambda = 254$ nm, coupled with Ramona Star radioactivity detector. The chromatographic separation was performed on Purosphere Star RP 18e 250 mm * 4.6 mm * 5 μm chromatographic column. It worked in the following gradient regime:

- **Mobile phase A:** 985 mL Water + 10 mL HCOOH + 5 mL $\text{NH}_4\text{COOH}_{(\text{aq})}$ (5 mM NH_4COOH /265 mM HCOOH),
- **Mobile phase B:** 985 mL CH_3CN + 10 mL HCOOH + 5 mL $\text{NH}_4\text{COOH}_{(\text{aq})}$ (5 mM NH_4COOH /265 mM HCOOH),
- **Gradient mode:** is presented below in the table B.8.1.2.1.1._CA-22;
- Total run time was 75 minutes.

Table B.8.1.2.1.1._CA-22: The gradient mode used in the analysis.

Time [min.]		0	5	55	60	62	75
Gradient	% A	100	100	5	5	100	100
	% B	0	0	95	95	0	0

The flow rate was set to 1.0 mL/min. The chromatographic column was kept under the ambient temperature. The identification of the test compound – Flufenacet, was carried out by means of the comparison of the retention times. For Flufenacet the retention time R_t was approx. 44.6 min.

The LC-MS analysis was performed as HPLC/MS analysis. It was carried out using HP1000 HPLC system equipped with a Nucleodur Gravity C_{18} chromatographic column (250 * 2 mm, 3 μ m), UV detector followed by the Ramona Star radiodetector and LTQ Orbitrap XL mass spectrometer.

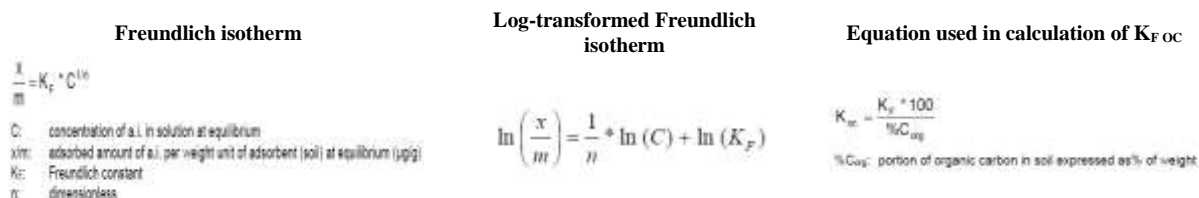
The parameters of chromatographic analysis were following:

- column temperature: 40°C,
- flow rate: 0.2 mL/min,
- elution mode: gradient,
- mobile phase:
 - Solvent A: $H_2O + 0.1\% HCOOH$,
 - Solvent B: $CH_3CN + 0.1\% HCOOH$.
- The gradient programmes used in the analysis is presented below in the table B.8.1.2.1.1._CA-23:

Table B.8.1.2.1.1._CA-23: The gradient mode used in the analysis.

Time [min.]		0	1	25	35
Gradient	% A	95	95	5	5
	% B	5	5	95	95

The calculations of the Freundlich sorption parameters were performed using the equations presented below on figure B.8.1.2.1.1._CA-14.

**Figure B.8.1.2.1.1._CA-14:** The equations used in the calculations of the Freundlich sorption parameters

Results and their discussion:

The characteristic of the test soils used in the study has been presented at the beginning of this summary in table B.8.1.2.1.1._CA-19. It may be stated that the test soils meet the acceptability criteria with regard to their textural characteristic, pH range and OC content range.

The results of the monitoring of the temperature during the experiment are presented below on figure B.8.1.2.1.1._CA-15. On their basis it was stated that the mean $T = 19.5^\circ C$ and its range $18.9 - 20.3^\circ C$. It was therefore within the pre-defined limits of $T = 20 \pm 2^\circ C$. It may be also stated that the temperature was constant within the study period, so all thermodynamic experiments, and in particular that aimed on the determination of the sorption isotherms, returned reliable results.

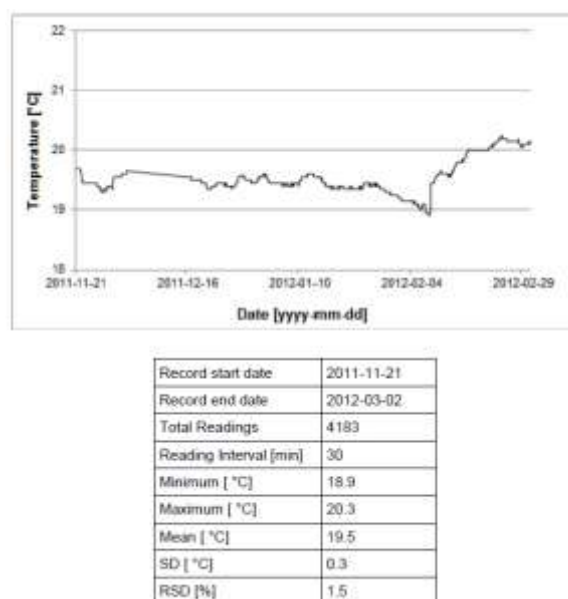


Figure B.8.1.2.1.1_CA-15: The graphical results of the monitoring of the temperature during the study (copied from the study report).

On the basis of the results of the determination of LOD and LOQ for LSC analysis and the results presented in the table B.8.1.2.1.1_CA-20 it was stated that the method was well suited for the analysis of the samples from the lowest treatment concentrations.

The graphical results of the verification of the chromatographic method used in the study – the radio-HPLC, are presented below on figure B.8.1.2.1.1_CA-16. On their basis the instrumental LOD was determined to be 2.5 Bq, equal to 0.3% AR and the LOQ was set to $3 \times \text{LOD} = 0.9\%$ AR.

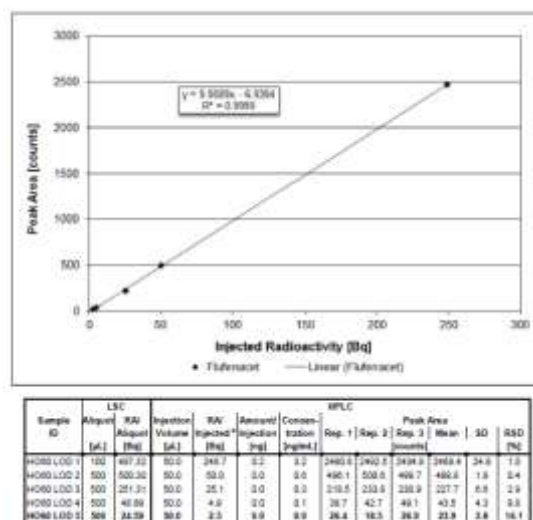


Figure B.8.1.2.1.1_CA-16: The graphical results of the verification of radio-HPLC analytical method used in the study (copied from the study report).

The numerical results of the examination of stability of the test item – Flufenacet in 0.01M CaCl_2 aq solution are presented below in the table B.8.1.2.1.1_CA-24. On their basis it was stated that the compound was stable.

Table B.8.1.2.1.1._CA-24: The results of the examination of the stability of the test item in the test solution.

I) Experimental conditions				
Amount of soil:		Test system without soil		
Amount of test solution in test vessel:		20 mL		
Concentration of the test item:		1.0 mg/L (nominal; highest concentration used in experiment)		
Equilibration time:		0 – 96 h		
II) Results				
Equilibraion time [Hours]	Replicate	Obtained results		
		Total radioactivity in the test vessel [%AR]	Radioactivity identified as Flufenacet	
			% in chromatogram	[% AR]
0	1	95.1	100.0	95.1
	2	96.5	100.0	96.5
6	1	94.3	not examined	
	2	94.9	not examined	
24	1	94.0	100.0	94.0
	2	92.8	100.0	92.8
48	1	94.4	not examined	
	2	95.0	not examined	
72	1	92.6	not examined	
	2	95.6	not examined	
96	1	93.8	99.7	93.5
	2	94.0	99.8	93.8

The results of the determination of the appropriate soil:solution ratio are presented below, in numerical form in the table B.8.1.2.1.1._CA-25 and in graphical form on figure B.8.1.2.1.1._CA-17. The abbreviations used on that graph to denominate test soils were following:

- AX for Laacher Hof AXXa soil;
- HH for Hoefchen am Hohenseh soil;
- HN for Hanscheider Hof soil;
- DD for Dollendorf II soil;
- WW for Wurmwiese soil.

Table B.8.1.2.1.1._CA-25: The numerical results of the determination of the appropriate soil:solution ratio.

Test soil	Soil solution ratio		Amount of Flufenacet remaining in solution [% AR]	Amount of Flufenacet sorbed onto soil [% AR]
	in g soil/mL solution	as ratio		
<i>Laacher Hof AXXa Loamy sand</i>	15/20	1:1.3	23.8	76.2
	10/20	1:2	33.0	67.0
	5/20	1:4	49.9	50.1
<i>Hoefchen am Hohenseh Silt loam</i>	15/20	1:1.3	27.9	72.1
	10/20	1:2	37.5	62.5
	5/20	1:4	55.6	44.4
<i>Hanscheider Hof Silt loam</i>	15/20	1:1.3	17.5	82.5
	10/20	1:2	24.6	62.5
	5/20	1:4	41.4	58.6
<i>Dollendorf II Loam</i>	15/20	1:1.3	13.4	86.6
	10/20	1:2	18.6	81.4
	5/20	1:4	32.5	67.5
<i>Wurmwiese Sandy loam</i>	15/20	1:1.3	29.1	70.9
	10/20	1:2	38.7	61.3
	5/20	1:4	57.8	42.2

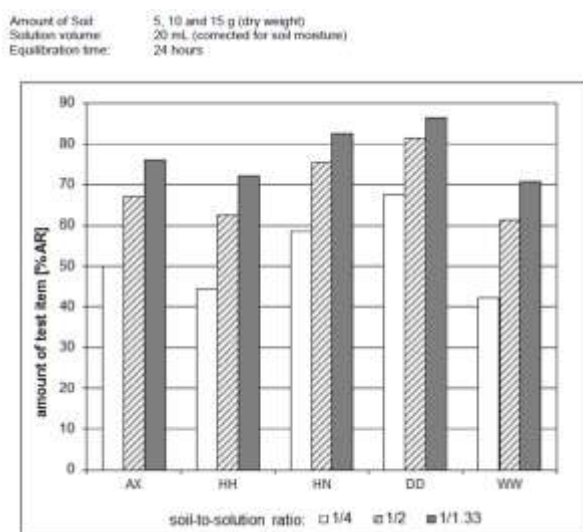


Figure B.8.1.2.1.1_CA-17: The graphical results of the determination of the appropriate soil:solution ratio – amount of Flufenacet adsorbed onto soil (copied from the study report).

On the basis of the obtained results, presented above, the soil:solution ratio 1:4 was selected to be used in further tests.

The results of the determination of the appropriate equilibration time are presented below, in numerical form in the table B.8.1.2.1.1_CA-26 and in graphical form on figure B.8.1.2.1.1_CA-18. The abbreviations used on that graph to denominate test soils were following:

- AX for Laacher Hof AXXa soil;
- HH for Hoefchen am Hohenseh soil;
- HN for Hanscheider Hof soil;
- DD for Dollendorf II soil;
- WW for Wurmwiese soil.

Table B.8.1.2.1.1_CA-26: The numerical results of the determination of the appropriate equilibration time.

Test soil	Replicate	Amount of Flufenacet adsorbed onto soil [% AR] after					
		0 hours	6 hours	24 hours	48 hours	72 hours	96 hours
Laacher Hof AXXa Loamy sand	1	1.8	45.6	49.2	50.2	50.8	50.8
	2	1.8	44.7	45.8	46.7	47.3	47.8
	mean	1.8	45.1	47.5	48.4	49.0	49.3
Hoefchen am Hohenseh Silt loam	1	1.8	39.8	43.1	47.9	50.1	50.7
	2	1.8	40.7	43.3	44.5	46.1	49.2
	mean	1.8	40.3	43.2	46.2	48.1	50.0
Hanscheider Hof Silt loam	1	1.8	53.6	58.9	61.2	62.2	63.1
	2	1.8	53.2	56.6	59.2	60.1	60.7
	mean	1.8	53.4	57.7	60.2	61.1	61.9
Dollendorf II Loam	1	1.8	64.8	68.5	69.7	70.4	70.5
	2	1.8	65.8	68.2	69.4	70.1	69.9
	mean	1.8	65.3	68.3	69.6	70.2	70.2
Wurmwiese Sandy loam	1	1.8	39.2	43.5	44.7	45.0	45.0
	2	1.8	40.4	42.5	43.9	44.5	44.3
	mean	1.8	40.0	43.0	44.3	44.7	44.7

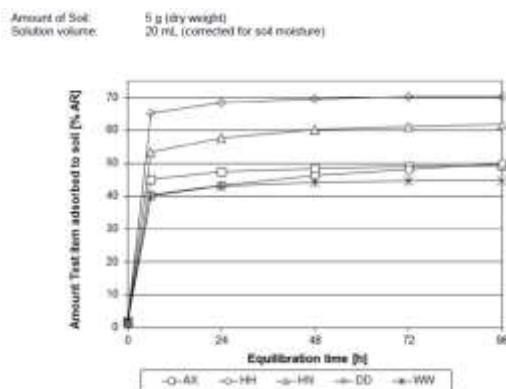


Figure B.8.1.2.1.1_CA-18: The graphical results of the determination of the appropriate equilibration time (copied from the study report).

The results of the determination of the mass balance, performed as one of the preliminary tests for each test soil, are presented below in the table B.8.1.2.1.1_CA-27. In the next table – B.8.1.2.1.1_CA-28 are presented the results of the determination of the mass balance performed for the definitive tests.

Table B.8.1.2.1.1_CA-27: The results of the determination of the mass balance carried out in Preliminary Parental Mass Balance Test.

Test soil	Radioactivity recovered (mean of two replicates) in:						
	<i>CaCl₂ solution</i>		<i>Soil organic extracts</i>		<i>Solid samples (soil)</i>	<i>Total recovered</i>	
	as Total Radioactivity [% AR]	as Flufenacet [% AR]	as Total Radioactivity [% AR]	as Flufenacet [% AR]	as Total Radioactivity [% AR]	as Total Radioactivity [% AR]	as Flufenacet [% AR]
<i>Laacher Hof AXXa Loamy sand</i>	43.3	43.1	58.3	58.3	0.5	102.0	101.4
<i>Hoefchen am Hohenseh Silt loam</i>	41.2	40.8	58.5	58.5	0.7	100.4	99.3
<i>Hanscheider Hof Silt loam</i>	32.3	32.3	67.9	67.9	1.0	101.1	100.2
<i>Dollendorf II Loam</i>	24.7	23.9	76.5	76.1	1.1	102.3	100.0
<i>Wurmweise Sandy loam</i>	47.3	47.3	53.9	53.9	0.7	101.8	101.2

Table B.8.1.2.1.1_CA-28: The results of the determination of the recovery of radioactivity in the definitive test – after adsorption and desorption steps.

Initial (nominal) concentration of Flufenacet	Replicate	Total radioactivity recovery, expressed in [% AR], in experiment with the test soil:				
		<i>Laacher Hof AXXa Loamy sand</i>	<i>Hoefchen am Hohenseh Silt loam</i>	<i>Hanscheider hof Silt loam</i>	<i>Dollendorf II Loam</i>	<i>Wurmweise Sandy loam</i>
1.0 mg/L	1	102.3	98.3	96.3	96.8	97.9
	2	100.7	99.5	99.3	97.5	98.6
0.3 mg/L	1	101.3	97.3	----	97.1	97.5
	2	103.4	98.4	93.5	96.5	98.5
0.1 mg/L	1	102.5	96.2	95.9	97.8	95.5
	2	106.2	96.5	95.7	98.2	97.6
0.03 mg/L	1	105.5	96.1	96.8	99.4	96.5
	2	101.4	96.3	95.9	96.6	97.3
0.01 mg/L	1	96.6	96.5	93.6	97.2	91.0
	2	98.0	98.0	96.5	96.8	102.7
Mean recovery		101.8	97.3	95.9	97.4	97.3

The verification of the application rate of Flufenacet in the definitive test gave the following results:

- for the solution having a nominal concentration **1.0 mg Flufenacet/L** the measured concentration was **0.96 mg Flufenacet/L**;
- for the solution having a nominal concentration **0.3 mg Flufenacet/L** the measured concentration was **0.28 mg Flufenacet/L**;
- for the solution having a nominal concentration **0.1 mg Flufenacet/L** the measured concentration was **0.094 mg Flufenacet/L**;
- for the solution having a nominal concentration **0.03 mg Flufenacet/L** the measured concentration was **0.028 mg Flufenacet/L**;
- for the solution having a nominal concentration **0.01 mg Flufenacet/L** the measured concentration was **0.0095 mg Flufenacet/L**.

The results of the determination of the pH of supernatant after establishing the adsorption equilibrium in the definitive test are given below in the table B.8.1.2.1.1_CA-29. In the next table – B.8.1.2.1.1_CA-30 are presented the analogical results obtained for the desorption phase of the same test.

Table B.8.1.2.1.1_CA-29: The results of the determination of the pH of solution at equilibrium in the adsorption part of the definitive test.

Initial concentration of Flufenacet [mg/L]		Replicate	pH of the solution measured in the test system containing the test soil:				
<i>nominal</i>	<i>measured</i>		<i>Laacher Hof AXXa Loamy sand</i>	<i>Hoefchen am Hohenseh Silt loam</i>	<i>Hanscheider Hof Silt loam</i>	<i>Dollendorf II Loam</i>	<i>Wurmweise Sandy loam</i>
1.0	0.96	1	5.9	6.8	5.4	6.9	5.1
		2	5.8	6.8	5.2	6.9	5.1
0.3	0.28	1	5.8	6.8	----	6.9	5.0
		2	5.8	6.6	5.2	6.9	5.1
0.1	0.094	1	5.8	6.7	5.3	6.9	5.1
		2	5.8	6.8	5.5	6.9	5.1
0.03	0.028	1	5.8	6.8	5.3	6.9	5.1
		2	5.9	6.7	5.4	6.9	5.1
0.01	0.0095	1	5.9	6.7	5.6	6.9	5.2
		2	6.0	6.6	5.6	6.9	5.4
		mean	5.9	6.7	5.4	6.9	5.1

Table B.8.1.2.1.1._CA-29: The results of the determination of the pH of solution at equilibrium in the desorption part of the definitive test.

Desorption step 1 st							
Initial concentration of Flufenacet [mg/L]		Replicate	pH of the solution measured in the test system containing the test soil:				
<i>nominal</i>	<i>measured</i>		<i>Laacher Hof AXXa Loamy sand</i>	<i>Hoefchen am Hohenseh Silt loam</i>	<i>Hanscheider Hof Silt loam</i>	<i>Dollendorf II Loam</i>	<i>Wurmwiese Sandy loam</i>
1.0	0.96	1	5.8	6.8	5.4	7.0	5.1
		2	5.8	6.8	5.2	7.0	5.1
0.3	0.28	1	5.8	6.8	----	7.0	5.1
		2	5.8	6.8	5.3	7.0	5.1
0.1	0.094	1	5.9	6.8	5.4	7.0	5.1
		2	5.9	6.8	5.5	7.0	5.1
0.03	0.028	1	5.9	6.8	5.4	7.0	5.1
		2	5.9	6.8	5.5	7.0	5.2
0.01	0.0095	1	6.0	6.6	5.6	7.0	5.4
		2	6.0	6.6	5.6	7.0	5.6
		mean	5.9	6.8	5.4	7.0	5.2
Desorption step 2 nd							
Initial concentration of Flufenacet [mg/L]		Replicate	pH of the solution measured in the test system containing the test soil:				
<i>nominal</i>	<i>measured</i>		<i>Laacher Hof AXXa Loamy sand</i>	<i>Hoefchen am Hohenseh Silt loam</i>	<i>Hanscheider Hof Silt loam</i>	<i>Dollendorf II Loam</i>	<i>Wurmwiese Sandy loam</i>
1.0	0.96	1	5.6	6.3	5.4	6.9	5.2
		2	5.6	6.3	5.3	7.0	5.2
		mean	5.6	6.3	5.4	7.0	5.2
Desorption step 3 rd							
Initial concentration of Flufenacet [mg/L]		Replicate	pH of the solution measured in the test system containing the test soil:				
<i>nominal</i>	<i>measured</i>		<i>Laacher Hof AXXa Loamy sand</i>	<i>Hoefchen am Hohenseh Silt loam</i>	<i>Hanscheider Hof Silt loam</i>	<i>Dollendorf II Loam</i>	<i>Wurmwiese Sandy loam</i>
1.0	0.96	1	5.8	6.5	5.8	6.9	5.3
		2	5.8	6.5	5.4	7.0	5.3
		mean	5.8	6.5	5.6	7.0	5.3

The results of the definitive phase – the concentrations of the test item – Flufenacet, at equilibrium for adsorption and desorption phases and the determined isotherms, are presented below, individually for each test soil.

a) Results obtained for the test soil Laacher Hof AXXA Loamy sand:

The numerical results obtained for the adsorption phase – concentrations of the test item in soil and solution at equilibrium and the % of the Flufenacet adsorbed onto soil, are presented below in the table B.8.1.2.1.1._CA-30.

Table B.8.1.2.1.1._CA-30: The numerical results of the experiment obtained for the adsorption phase.

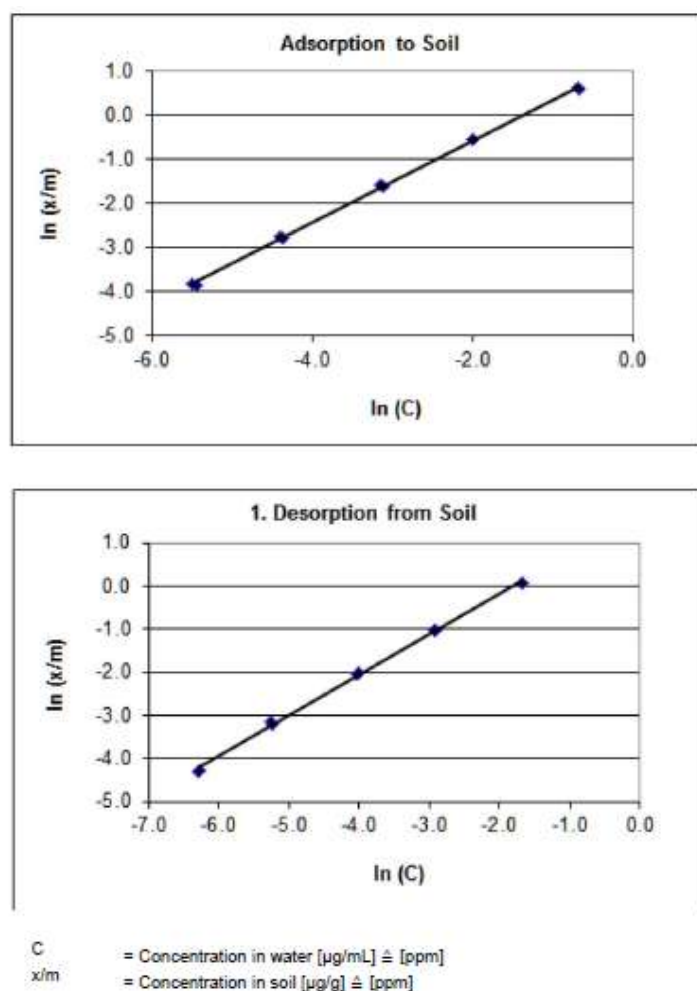
Initial concentration of Flufenacet [mg/L]		Replicate	Concentration of Flufenacet in				Amount adsorbed [% AR]
nominal	measured		Soil		Solution		
			x/m [µg/g]	Ln (x/m)	Ce [µg/mL]	Ln (Ce)	
1.0	0.96	1	1.824	0.60	0.507	-0.68	47.3
		2	1.804	0.59	0.512	-0.67	46.8
		mean	1.814	----	0.510	----	47.1
0.3	0.28	1	0.579	-0.55	0.135	-2.00	51.8
		2	0.575	-0.55	0.136	-2.00	51.5
		mean	0.577	----	0.135	----	51.6
0.1	0.094	1	0.204	-1.59	0.043	-3.15	54.3
		2	0.197	-1.63	0.045	-3.11	52.4
		mean	0.201	----	0.044	----	53.3
0.03	0.028	1	0.063	-2.76	0.012	-4.39	56.1
		2	0.062	-2.79	0.013	-4.36	54.6
		mean	0.062	----	0.013	----	55.3
0.01	0.0095	1	0.022	-3.83	0.004	-5.49	56.7
		2	0.021	-3.87	0.004	-5.45	54.8
		mean	0.021	----	0.004	----	55.8

The numerical results obtained for the desorption phase – concentration of the test item in soil and solution at equilibrium and the % of Flufenacet remaining adsorbed are presented below in the table B.8.1.2.1.1._CA-31.

Table B.8.1.2.1.1._CA-31: The numerical results of the experiment obtained for the desorption phase.

Desorption step 1 st							
Initial concentration of Flufenacet [mg/L]		Replicate	Concentration of Flufenacet in				Amount remaining adsorbed [% AR]
nominal	measured		Soil		Solution		
			x/m [µg/g]	Ln (x/m)	Ce [µg/mL]	Ln (Ce)	
1.0	0.96	1	1.085	0.08	0.185	-1.69	28.1
		2	1.066	0.06	0.185	-1.69	27.7
		mean	1.075	----	0.185	----	27.9
0.3	0.28	1	0.363	-1.01	0.054	-2.92	32.5
		2	0.362	-1.02	0.053	-2.93	32.4
		mean	0.362	----	0.054	----	32.5
0.1	0.094	1	0.132	-2.02	0.018	-4.02	35.2
		2	0.126	-2.07	0.018	-4.04	33.6
		mean	0.129	----	0.018	----	34.4
0.03	0.028	1	0.043	-3.16	0.005	-5.26	37.7
		2	0.040	-3.12	0.005	-5.24	35.8
		mean	0.041	----	0.005	----	36.8
0.01	0.0095	1	0.014	-4.26	0.002	-6.27	36.9
		2	0.014	-4.30	0.002	-6.30	35.5
		mean	0.014	----	0.002	----	36.2
Desorption step 2 nd							
Initial concentration of Flufenacet [mg/L]		Replicate	Concentration of Flufenacet in				Amount remaining adsorbed [% AR]
nominal	measured		Soil		Solution		
			x/m [µg/g]	Ln (x/m)	Ce [µg/mL]	Ln (Ce)	
1.0	0.96	1	0.680	-0.39	0.101	-2.29	17.6
		2	0.668	-0.40	0.099	-2.31	17.4
Desorption step 3 rd							
Initial concentration of Flufenacet [mg/L]		Replicate	Concentration of Flufenacet in				Amount remaining adsorbed [% AR]
nominal	measured		Soil		Solution		
			x/m [µg/g]	Ln (x/m)	Ce [µg/mL]	Ln (Ce)	
1.0	0.96	1	0.451	-0.80	0.057	-2.86	11.7
		2	0.451	-0.80	0.054	-1.91	11.7

The graphical results of the experiment – Freundlich adsorption and desorption isotherms are presented below on figure B.8.1.2.1.1._CA-19. The numerical results – Freundlich adsorption and desorption parameters, are presented in the table B.8.1.2.1.1._CA-32.



Evaluation of linear regression according to Freundlich:

		Adsorption	Desorption
Regression	R^2	0.9991	0.9988
Slope	$1/n$	0.9285	0.9440
Interception	$\ln K_F$	1.2684	1.7192

Figure B.8.1.2.1.1._CA-19: The Freundlich adsorption and desorption isotherms obtained for Flufenacet in the experiment (copied from the study report).

Table B.8.1.2.1.1._CA-32: The parameters of Freundlich adsorption and desorption isotherms for Flufenacet.

Process	Determined parameter			
	K_F [mL/g]	K_{Foc} [mL/g]	$1/n$	R^2
Adsorption	3.555	161.6	0.928	0.9991
Desorption	5.580	253.6	0.944	0.9988

b) Results obtained for the test soil Hoefchen am Hohenseh Silt loam:

The numerical results obtained for the adsorption phase – concentrations of the test item in soil and solution at equilibrium and the % of the Flufenacet adsorbed onto soil, are presented below in the table B.8.1.2.1.1._CA-33.

Table B.8.1.2.1.1._CA-33: The numerical results of the experiment obtained for the adsorption phase.

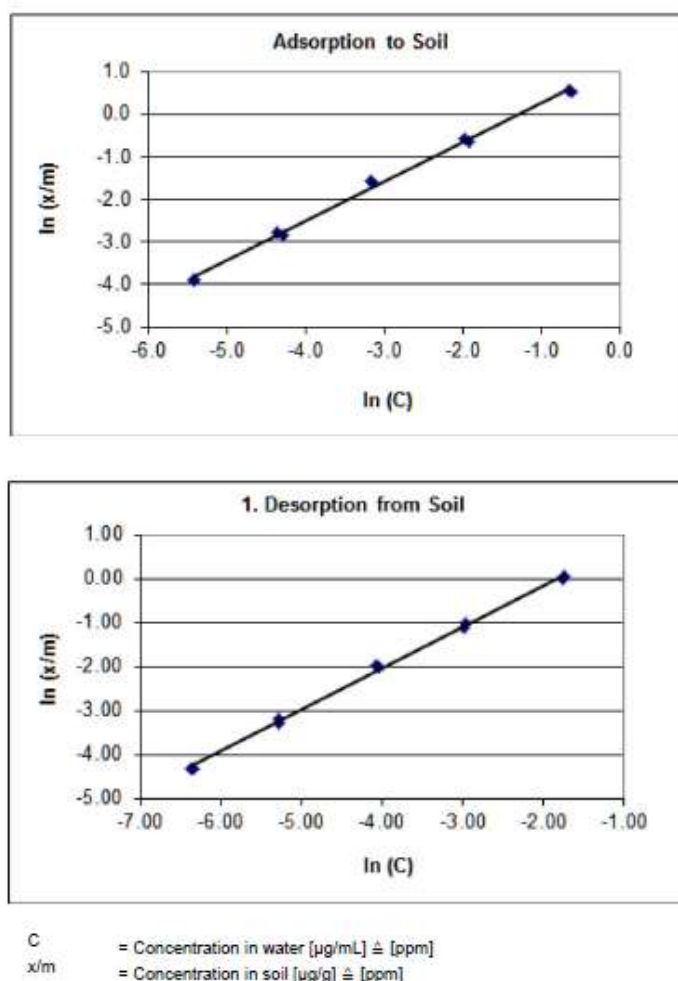
Initial concentration of Flufenacet [mg/L]		Replicate	Concentration of Flufenacet in				Amount adsorbed [% AR]
nominal	measured		Soil		Solution		
			x/m [µg/g]	Ln (x/m)	Ce [µg/mL]	Ln (Ce)	
1.0	0.96	1	1.740	0.55	0.528	-1.75	45.2
		2	1.674	0.52	0.545	-1.77	43.5
		mean	1.707	----	0.536	----	44.3
0.3	0.28	1	0.529	-0.64	0.147	-2.98	47.3
		2	0.565	-0.57	0.138	-2.96	50.6
		mean	0.547	----	0.143	----	49.0
0.1	0.094	1	0.207	-1.57	0.042	-4.08	55.1
		2	0.203	-1.59	0.043	-4.05	54.0
		mean	0.205	----	0.043	----	54.6
0.03	0.028	1	0.058	-2.85	0.014	-5.28	51.3
		2	0.061	-2.79	0.013	-5.27	54.3
		mean	0.060	----	0.013	----	52.8
0.01	0.0095	1	0.020	-3.90	0.004	-6.38	52.9
		2	0.020	-3.89	0.004	-6.33	53.3
		mean	0.020	----	0.004	----	53.1

The numerical results obtained for the desorption phase – concentration of the test item in soil and solution at equilibrium and the % of Flufenacet remaining adsorbed are presented below in the table B.8.1.2.1.1._CA-34.

Table B.8.1.2.1.1._CA-34: The numerical results of the experiment obtained for the desorption phase.

Desorption step 1 st							
Initial concentration of Flufenacet [mg/L]		Replicate	Concentration of Flufenacet in				Amount remaining adsorbed [% AR]
nominal	measured		Soil		Solution		
			x/m [µg/g]	Ln (x/m)	Ce [µg/mL]	Ln (Ce)	
1.0	0.96	1	1.044	0.04	0.174	-1.75	27.1
		2	0.992	-0.01	0.171	-1.77	25.7
		mean	1.018	----	0.172	----	26.4
0.3	0.28	1	0.326	-1.12	0.051	-2.98	29.2
		2	0.358	-1.03	0.052	-2.96	32.1
		mean	0.342	----	0.051	----	30.6
0.1	0.094	1	0.140	-1.97	0.017	-4.08	37.1
		2	0.133	-2.02	0.017	-4.05	35.4
		mean	0.136	----	0.017	----	36.3
0.03	0.028	1	0.037	-3.28	0.005	-5.28	33.3
		2	0.041	-3.20	0.005	-5.27	36.2
		mean	0.039	----	0.005	----	34.8
0.01	0.0095	1	0.013	-4.31	0.002	-6.38	35.1
		2	0.013	-4.33	0.002	-6.33	34.6
		mean	0.013	----	0.002	----	34.9
Desorption step 2 nd							
Initial concentration of Flufenacet [mg/L]		Replicate	Concentration of Flufenacet in				Amount remaining adsorbed [% AR]
nominal	measured		Soil		Solution		
			x/m [µg/g]	Ln (x/m)	Ce [µg/mL]	Ln (Ce)	
1.0	0.96	1	0.679	-0.39	0.091	-2.40	17.6
		2	0.625	-0.47	0.092	-2.39	16.2
Desorption step 3 rd							
Initial concentration of Flufenacet [mg/L]		Replicate	Concentration of Flufenacet in				Amount remaining adsorbed [% AR]
nominal	measured		Soil		Solution		
			x/m [µg/g]	Ln (x/m)	Ce [µg/mL]	Ln (Ce)	
1.0	0.96	1	0.474	-0.75	0.051	-2.97	12.3
		2	0.417	-0.87	0.052	-2.96	10.8

The graphical results of the experiment – Freundlich adsorption and desorption isotherms are presented below on figure B.8.1.2.1.1._CA-20. The numerical results – Freundlich adsorption and desorption parameters, are presented in the table B.8.1.2.1.1._CA-35.



Evaluation of linear regression according to Freundlich:

		Adsorption	Desorption
Regression	R^2	0.9965	0.9980
Slope	$1/n$	0.9262	0.9426
Interception	$\ln K_F$	1.1879	1.7293

Figure B.8.1.2.1.1._CA-20: The Freundlich adsorption and desorption isotherms obtained for Flufenacet in the experiment (copied from the study report).

Table B.8.1.2.1.1._CA-35: The parameters of Freundlich adsorption and desorption isotherms for Flufenacet.

Process	Determined parameter			
	$K_F[\text{mL/g}]$	$K_{F,OC}[\text{mL/g}]$	$1/n$	R^2
Adsorption	3.280	205.0	0.926	0.9965
Desorption	5.637	352.3	0.943	0.9980

c) Results obtained for the test soil Hanscheider Hof Silt loam:

The numerical results obtained for the adsorption phase – concentrations of the test item in soil and solution at equilibrium and the % of the Flufenacet adsorbed onto soil, are presented below in the table B.8.1.2.1.1._CA-36.

Table B.8.1.2.1.1._CA-36: The numerical results of the experiment obtained for the adsorption phase.

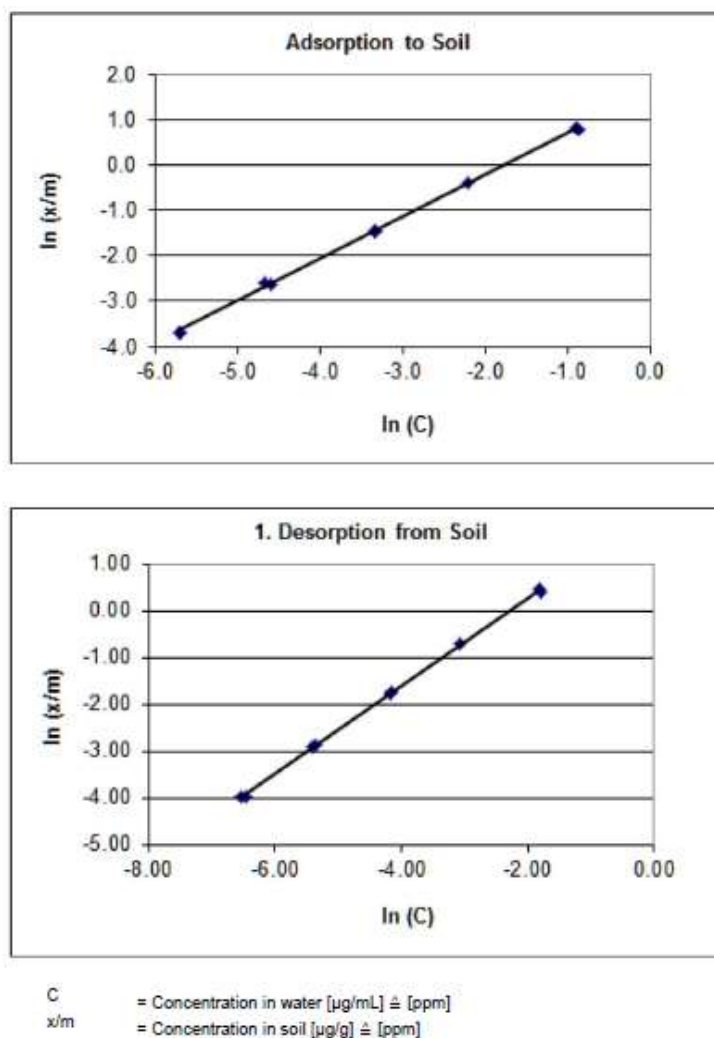
Initial concentration of Flufenacet [mg/L]		Replicate	Concentration of Flufenacet in				Amount adsorbed [% AR]
nominal	measured		Soil		Solution		
			x/m [µg/g]	Ln (x/m)	Ce [µg/mL]	Ln (Ce)	
1.0	0.96	1	2.226	0.80	0.407	-0.90	57.8
		2	2.176	0.78	0.420	-0.87	56.4
		mean	2.199	----	0.413	----	57.1
0.3	0.28	1	----	----	----	----	----
		2	0.680	-0.39	0.109	-2.21	60.8
		mean	0.680	----	0.109	----	60.8
0.1	0.094	1	0.235	-1.45	0.035	-3.35	62.5
		2	0.231	-1.47	0.036	-3.32	61.4
		mean	0.233	----	0.036	----	62.0
0.03	0.028	1	0.072	-2.62	0.010	-4.60	64.3
		2	0.075	-2.59	0.009	-4.66	66.5
		mean	0.074	----	0.010	----	65.4
0.01	0.0095	1	0.025	-3.70	0.003	-5.69	64.6
		2	0.025	-3.69	0.003	-5.71	65.3
		mean	0.025	----	0.003	----	64.9

The numerical results obtained for the desorption phase – concentration of the test item in soil and solution at equilibrium and the % of Flufenacet remaining adsorbed are presented below in the table B.8.1.2.1.1._CA-37.

Table B.8.1.2.1.1._CA-37: The numerical results of the experiment obtained for the desorption phase.

Desorption step 1 st							
Initial concentration of Flufenacet [mg/L]		Replicate	Concentration of Flufenacet in				Amount remaining adsorbed [% AR]
nominal	measured		Soil		Solution		
			x/m [µg/g]	Ln (x/m)	Ce [µg/mL]	Ln (Ce)	
1.0	0.96	1	1.569	0.45	0.164	-1.81	40.5
		2	1.508	0.41	0.166	-1.80	39.1
		mean	1.539	----	0.165	----	39.8
0.3	0.28	1	----	----	----	----	----
		2	0.495	-0.70	0.046	-3.08	44.3
		mean	0.495	----	0.046	----	44.3
0.1	0.094	1	0.173	-1.76	0.016	-4.16	45.9
		2	0.169	-1.78	0.015	-4.18	45.1
		mean	0.171	----	0.015	----	45.5
0.03	0.028	1	0.054	-2.91	0.004	-5.40	48.3
		2	0.056	-2.88	0.005	-5.36	49.8
		mean	0.055	----	0.005	----	49.1
0.01	0.0095	1	0.019	-3.97	0.001	-6.55	49.5
		2	0.019	-3.98	0.002	-6.46	48.9
		mean	0.019	----	0.001	----	49.2
Desorption step 2 nd							
Initial concentration of Flufenacet [mg/L]		Replicate	Concentration of Flufenacet in				Amount remaining adsorbed [% AR]
nominal	measured		Soil		Solution		
			x/m [µg/g]	Ln (x/m)	Ce [µg/mL]	Ln (Ce)	
1.0	0.96	1	1.167	0.15	0.100	-2.30	30.1
		2	1.098	0.09	0.103	-2.28	28.5
Desorption step 3 rd							
Initial concentration of Flufenacet [mg/L]		Replicate	Concentration of Flufenacet in				Amount remaining adsorbed [% AR]
nominal	measured		Soil		Solution		
			x/m [µg/g]	Ln (x/m)	Ce [µg/mL]	Ln (Ce)	
1.0	0.96	1	0.888	-0.12	0.070	-2.66	22.9
		2	0.829	-0.19	0.067	-2.70	21.5

The graphical results of the experiment – Freundlich adsorption and desorption isotherms are presented below on figure B.8.1.2.1.1_CA-21. The numerical results – Freundlich adsorption and desorption parameters, are presented in the table B.8.1.2.1.1_CA-38.



Evaluation of linear regression according to Freundlich:

		Adsorption	Desorption
Regression	R^2	0.9992	0.9996
Slope	$1/n$	0.9265	0.9374
Interception	$\ln K_F$	1.6295	2.1387

Figure B.8.1.2.1.1_CA-21: The Freundlich adsorption and desorption isotherms obtained for Flufenacet in the experiment (copied from the study report).

Table B.8.1.2.1.1_CA-38: The parameters of Freundlich adsorption and desorption isotherms for Flufenacet.

Process	Determined parameter			
	K_F [mL/g]	K_{FOC} [mL/g]	$1/n$	R^2
Adsorption	5.101	188.9	0.926	0.9992
Desorption	8.488	314.4	0.937	0.9996

d) Results obtained for the test soil Dollendorf II Loam:

The numerical results obtained for the adsorption phase – concentrations of the test item in soil and solution at equilibrium and the % of the Flufenacet adsorbed onto soil, are presented below in the table B.8.1.2.1.1._CA-39.

Table B.8.1.2.1.1._CA-39: The numerical results of the experiment obtained for the adsorption phase.

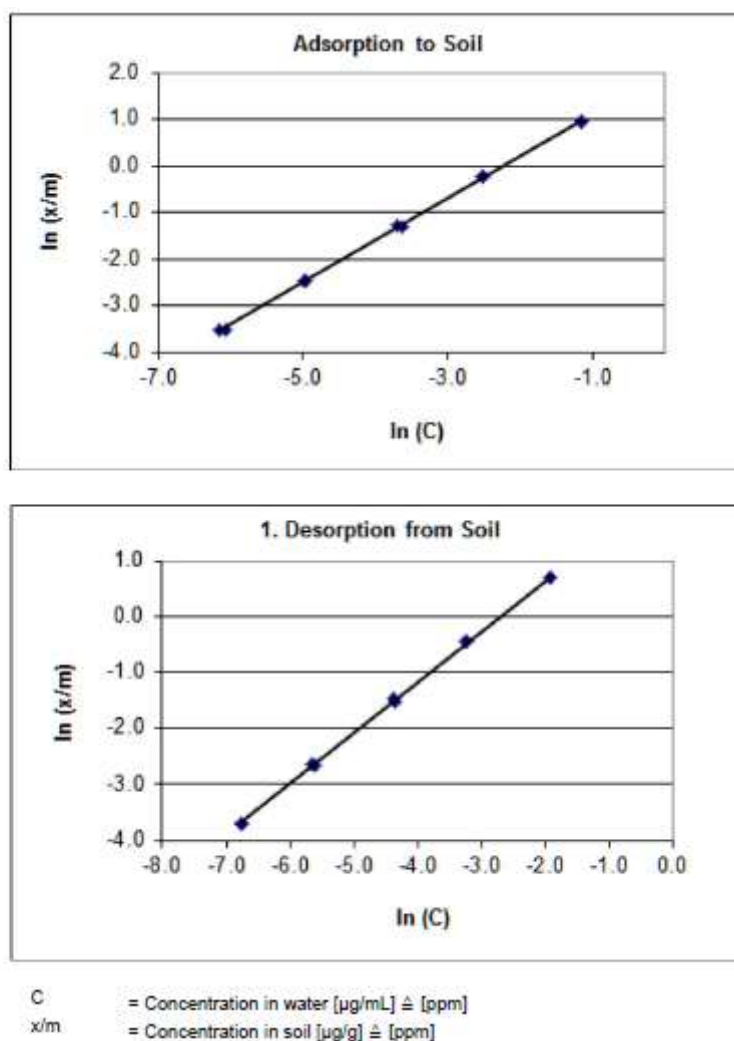
Initial concentration of Flufenacet [mg/L]		Replicate	Concentration of Flufenacet in				Amount adsorbed [% AR]
nominal	measured		Soil		Solution		
			x/m [µg/g]	Ln (x/m)	Ce [µg/mL]	Ln (Ce)	
1.0	0.96	1	2.601	0.96	0.313	-1.16	67.5
		2	2.577	0.95	0.319	-1.14	66.9
		mean	2.589	----	0.316	----	67.2
0.3	0.28	1	0.797	-0.23	0.080	-2.53	71.4
		2	0.791	-0.23	0.082	-2.51	70.8
		mean	0.794	----	0.081	----	71.1
0.1	0.094	1	0.277	-1.28	0.025	-3.70	73.7
		2	0.270	-1.31	0.026	-3.63	71.9
		mean	0.274	----	0.026	----	72.8
0.03	0.028	1	0.085	-2.46	0.007	-4.98	75.6
		2	0.085	-2.47	0.007	-4.96	75.2
		mean	0.085	----	0.007	----	75.4
0.01	0.0095	1	0.029	-3.54	0.002	-6.07	75.8
		2	0.030	-3.52	0.002	-6.16	77.9
		mean	0.029	----	0.002	----	76.9

The numerical results obtained for the desorption phase – concentration of the test item in soil and solution at equilibrium and the % of Flufenacet remaining adsorbed are presented below in the table B.8.1.2.1.1._CA-40.

Table B.8.1.2.1.1._CA-40: The numerical results of the experiment obtained for the desorption phase.

Desorption step 1 st							
Initial concentration of Flufenacet [mg/L]		Replicate	Concentration of Flufenacet in				Amount remaining adsorbed [% AR]
nominal	measured		Soil		Solution		
			x/m [µg/g]	Ln (x/m)	Ce [µg/mL]	Ln (Ce)	
1.0	0.96	1	2.103	0.70	0.147	-1.92	52.2
		2	1.990	0.69	0.147	-1.92	51.7
		mean	2.002	----	0.147	----	51.9
0.3	0.28	1	0.637	-0.45	0.040	-3.22	57.1
		2	0.635	-0.45	0.039	-3.25	56.8
		mean	0.636	----	0.039	----	56.9
0.1	0.094	1	0.227	-1.48	0.012	-4.39	60.5
		2	0.218	-1.52	0.013	-4.35	58.2
		mean	0.223	----	0.013	----	59.4
0.03	0.028	1	0.071	-2.64	0.003	-5.67	63.3
		2	0.070	-2.66	0.004	-5.62	62.3
		mean	0.071	----	0.004	----	62.8
0.01	0.0095	1	0.024	-3.72	0.001	-6.76	63.6
		2	0.025	-3.68	0.001	-6.77	65.8
		mean	0.025	----	0.001	----	64.7
Desorption step 2 nd							
Initial concentration of Flufenacet [mg/L]		Replicate	Concentration of Flufenacet in				Amount remaining adsorbed [% AR]
nominal	measured		Soil		Solution		
			x/m [µg/g]	Ln (x/m)	Ce [µg/mL]	Ln (Ce)	
1.0	0.96	1	1.587	0.46	0.107	-2.24	41.1
		2	1.566	0.45	0.106	-2.24	40.7
Desorption step 3 rd							
Initial concentration of Flufenacet [mg/L]		Replicate	Concentration of Flufenacet in				Amount remaining adsorbed [% AR]
nominal	measured		Soil		Solution		
			x/m [µg/g]	Ln (x/m)	Ce [µg/mL]	Ln (Ce)	
1.0	0.96	1	1.276	0.24	0.078	-2.55	33.0
		2	1.252	0.23	0.078	-2.55	32.6

The graphical results of the experiment – Freundlich adsorption and desorption isotherms are presented below on figure B.8.1.2.1.1_CA-22. The numerical results – Freundlich adsorption and desorption parameters, are presented in the table B.8.1.2.1.1_CA-41.



Evaluation of linear regression according to Freundlich:

		Adsorption	Desorption
Regression	R^2	0.9994	0.9996
Slope	$1/n$	0.9033	0.9081
Interception	$\ln K_F$	2.0142	2.4601

Figure B.8.1.2.1.1_CA-22: The Freundlich adsorption and desorption isotherms obtained for Flufenacet in the experiment (copied from the study report).

Table B.8.1.2.1.1_CA-41: The parameters of Freundlich adsorption and desorption isotherms for Flufenacet.

Process	Determined parameter			
	K_F [mL/g]	$K_{F\ oc}$ [mL/g]	$1/n$	R^2
Adsorption	7.495	178.5	0.903	0.9994
Desorption	11.707	278.7	0.908	0.9996

e) Results obtained for the test soil Wurmwiess Sandy loam:

The numerical results obtained for the adsorption phase – concentrations of the test item in soil and solution at equilibrium and the % of the Flufenacet adsorbed onto soil, are presented below in the table B.8.1.2.1.1._CA-42.

Table B.8.1.2.1.1._CA-42: The numerical results of the experiment obtained for the adsorption phase.

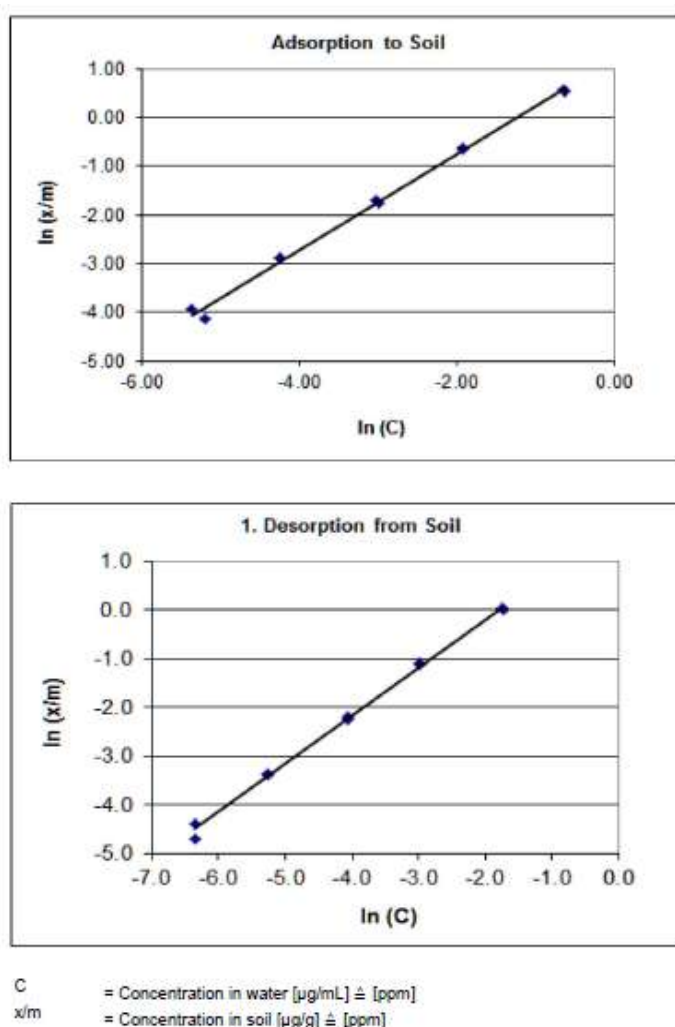
Initial concentration of Flufenacet [mg/L]		Replicate	Concentration of Flufenacet in				Amount adsorbed [% AR]
nominal	measured		Soil		Solution		
			x/m [µg/g]	Ln (x/m)	Ce [µg/mL]	Ln (Ce)	
1.0	0.96	1	1.734	0.55	0.530	-0.64	45.0
		2	1.700	0.53	0.538	-0.62	44.1
		mean	1.717	----	0.534	----	44.6
0.3	0.28	1	0.532	-0.63	0.146	-1.92	47.6
		2	0.525	-0.64	0.148	-1.91	47.0
		mean	0.529	----	0.147	----	47.3
0.1	0.094	1	0.180	-1.71	0.049	-3.02	48.0
		2	0.174	-1.75	0.050	-2.99	46.4
		mean	0.177	----	0.050	----	47.2
0.03	0.028	1	0.055	-2.89	0.014	-4.24	49.0
		2	0.055	-2.90	0.014	-4.24	48.7
		mean	0.055	----	0.014	----	48.9
0.01	0.0095	1	0.019	-3.94	0.005	-5.36	50.9
		2	0.016	-4.13	0.006	-5.20	42.0
		mean	0.018	----	0.005	----	46.4

The numerical results obtained for the desorption phase – concentration of the test item in soil and solution at equilibrium and the % of Flufenacet remaining adsorbed are presented below in the table B.8.1.2.1.1._CA-43.

Table B.8.1.2.1.1._CA-43: The numerical results of the experiment obtained for the desorption phase.

Desorption step 1 st							
Initial concentration of Flufenacet [mg/L]		Replicate	Concentration of Flufenacet in				Amount remaining adsorbed [% AR]
nominal	measured		Soil		Solution		
			x/m [µg/g]	Ln (x/m)	Ce [µg/mL]	Ln (Ce)	
1.0	0.96	1	1.035	0.03	0.175	-1.74	26.9
		2	0.987	-0.01	0.178	-1.73	25.6
		mean	1.011	----	0.176	----	26.3
0.3	0.28	1	0.331	-1.11	0.050	-2.99	29.6
		2	0.323	-1.13	0.051	-2.98	28.9
		mean	0.327	----	0.050	----	29.3
0.1	0.094	1	0.112	-2.19	0.017	-4.07	29.8
		2	0.105	-2.25	0.017	-4.06	28.0
		mean	0.109	----	0.017	----	28.9
0.03	0.028	1	0.034	-3.37	0.005	-5.25	30.5
		2	0.034	-3.37	0.005	-5.27	30.5
		mean	0.034	----	0.005	----	30.5
0.01	0.0095	1	0.012	-4.39	0.002	-6.35	32.6
		2	0.009	-4.71	0.002	-6.34	23.5
		mean	0.011	----	0.002	----	28.1
Desorption step 2 nd							
Initial concentration of Flufenacet [mg/L]		Replicate	Concentration of Flufenacet in				Amount remaining adsorbed [% AR]
nominal	measured		Soil		Solution		
			x/m [µg/g]	Ln (x/m)	Ce [µg/mL]	Ln (Ce)	
1.0	0.96	1	0.656	-0.42	0.095	-2.36	17.0
		2	0.609	-0.50	0.095	-2.36	15.8
Desorption step 3 rd							
Initial concentration of Flufenacet [mg/L]		Replicate	Concentration of Flufenacet in				Amount remaining adsorbed [% AR]
nominal	measured		Soil		Solution		
			x/m [µg/g]	Ln (x/m)	Ce [µg/mL]	Ln (Ce)	
1.0	0.96	1	0.434	-0.84	0.056	-2.89	11.2
		2	0.388	-0.95	0.055	-2.90	10.1

The graphical results of the experiment – Freundlich adsorption and desorption isotherms are presented below on figure B.8.1.2.1.1_CA-23. The numerical results – Freundlich adsorption and desorption parameters, are presented in the table B.8.1.2.1.1_CA-44.



Evaluation of linear regression according to Freundlich:

		Adsorption	Desorption
Regression	R^2	0.9966	0.9967
Slope	$1/n$	0.9797	0.9886
Interception	$\ln K_F$	1.1995	1.7818

Figure B.8.1.2.1.1_CA-23: The Freundlich adsorption and desorption isotherms obtained for Flufenacet in the experiment (copied from the study report).

Table B.8.1.2.1.1_CA-44: The parameters of Freundlich adsorption and desorption isotherms for Flufenacet.

Process	Determined parameter			
	K_F [mL/g]	$K_{F oc}$ [mL/g]	$1/n$	R^2
Adsorption	3.391	195.2	0.980	0.9966
Desorption	5.490	349.4	0.989	0.9967

Final conclusion of the study:

The final results of the study – Freundlich adsorption parameters for Flufenacet obtained in each test soil, are presented below in the table B.8.1.2.1.1._CA-45. RMS considers these results reliable and possible to be used to derive input parameters for modelling.

In case of the desorption the results should be considered with care because the use of HgCl_2 as sterilising agent might have a considerable impact on them – the competitive sorption of mercury ions could possibly caused the higher desorption of the test compound.

Table B.8.1.2.1.1._CA-45: The definitive set of Freundlich adsorption parameters determined for Flufenacet in the study.

Parameter	Test soil				
	Laacher Hof AXXa Loamy sand	Hoefchen am Hohensch Silt loam	Hanscheider Hof Silt loam	Dollendorf II Loam	Wurmweise Sandy loam
$K_f [\text{mL/g}]$	3.555	3.280	5.101	7.495	3.319
$K_{foc} [\text{mL/g}]$	161.6	205.0	188.9	178.5	195.2
$1/n$	0.928	0.926	0.926	0.903	0.980

Study 3:

Report: Stupp H. P. (2010): “[Phenyl-UL-¹⁴C] Flufenacet: Adsorption on Two Japanese Soils.”; Bayer CropScience AG – Development, Environmental Safety Metabolism/ADME and Environmental Fate, Alfred-Nobel-Str. 50, D-40789 Monheim am Rhein, Germany (performing laboratory) for Bayer CropScience K. K, 6-5 Marunouchi 1-chome, Chiyoda-ku, 100-8262 Tokyo, Japan; Study No. M1311954-4; Bayer Report No. MEF-10/534; 04. 08. 2010; study reference number: M-3875732-01-1;

Guidelines: The study was performed to comply with the following Guidelines:

- Japanese MAFF New Test Guidelines for Supporting Registration of Pesticides, 12 Nousan 8147;
- OECD Guideline for the Testing of Chemicals No. 106, Adsorption/Desorption, 2000;

GLP: Yes;

RMS comments: This is a new study, submitted specifically for the purpose of the current assessment. It was evaluated for compliance with the following Guidelines:

- OECD Guideline for the Testing of Chemicals No. 106, Adsorption/Desorption, 2000;
- US EPA OCSPF Fate, Transport and Transformation Test Guidelines, OPPTS 835 1220, Sediment and Soil Adsorption/Desorption Isotherm, 1998;
- US EPA OCSPF Fate, Transport and Transformation Test Guidelines, OPPTS 835 1230, Adsorption/Desorption (Batch Equilibrium), 2008;

The following deviations were stated:

- Of the two test soils used in the study one – Ushiku Sandy loam soil, was of volcanic ash origin and as such not representative for the EU conditions. Also in case of that soil the history of the pesticide use on the collection site is not precise, what makes impossible to state whether Flufenacet or any plant protection product belonging to the same chemical group was used during 5 years prior to sampling.
- Test soils used in experiment were not freshly sampled, but stored after pre-processing (sieving and air-drying) for 19 months before being used. Additionally in case of Kamikawa Loam soil the date of sampling was not provided what makes impossible to estimate exact time elapsing between sampling and the beginning of storage period.
- Very atypical was soil solution ratio used in the definitive test – 3:20 when expressed in g soil:mL solution or 1:6.6667 when expressed as unitless ratio (the second ratio calculated by the RMS). Applicant however declared in the study report that that ratio was 1:7, substantially rounding the value representing the relative amount of solution in the test system. That however had only minimal influence on the obtained results.

RMS never the less decided to consider the study valid as in all other aspects it complied with the provisions of the reference Guidelines.

The study is summarised below.

Summary:

The aim of the study was to investigate soil sorption of Flufenacet onto two Japanese soils in line with the requirements of the Japanese MAFF New Test Guidelines for Supporting Registration of Pesticides. The experiment was performed according to the provisions of the OECD 106 Guideline. The test soils used in the experiment were Sandy loam soil of the volcanic ash origin (OECD type 2) and Loam soil of the alluvial origin (OECD type 4), representative for agriculturally used areas in Japan. Their brief characteristic is provided below in the table B.8.1.2.1.1_CA-46. It shall be noted that one of the test soils – Sandy loam soil, due to its origin cannot be considered representative for the EU. The test soils were collected from the top 30-cm layer using shovel, air-dried to sieve conditions, sieved through 2-mm sieve, placed in the plastic bag and transferred to the test laboratory. There they were stored for about 19 months at T = 5⁰C until being used. The Ushiku test soil was collected from turf field and Kamikawa test soil from paddy field. In case of the Ushiku soil it was stated, with regard to pesticide use history of the collection site, that it received conventional application, not explaining the meaning of the expression. For Kamikawa test soil it was stated that on the collection site no pesticides were used for 5 years prior to the sampling.

Table B.8.1.2.1.1._CA-46: The characteristic of soils used in the study.

Parameter	Soil	
	<i>Ushiku</i>	<i>Kamikawa</i>
Soil geographical origin	Ushiku, prefecture Ibaraki, Japan	Kamikawa, island of Hokkaido, Japan
Soil series	Volcanic ash (OECD type 2)	Alluvial soil (OECD type 4)
Soil type – USDA	Sandy loam	Loam
Particle size distribution	Sand (50 µm – 2 mm) [%]	49
	Silt (2 – 50 µm) [%]	32
	Clay (< 2 µm) [%]	19
Soil pH	in CaCl ₂	4.9
	in water	5.3
	in KCl	4.4
Organic carbon content (OC) [%] ²⁾	4.3	2.1
Organic matter content (OM) [%]	7.4	3.6
Cation Exchange Capacity – CEC [mEq/100g]	15.9	12.2
Water holding capacity at 0.33 bar [% moisture]	41.9	36.5
Bulk density (disturbed) [g/cm ³]	0.78	0.97

Footnotes to the table:

1) As provided in the study report; recalculated from OM using the following equation: OC = OM/1.724.

The test compound used in the experiment was the ¹⁴C-FOE 5043 radiolabelled uniformly in phenyl ring, as shown below on figure B.8.1.2.1.1._CA-24.

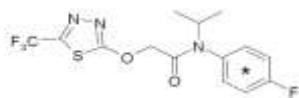


Figure B.8.1.2.1.1._CA-24: The structural formula of the radiolabelled Flufenacet (FOE 5043) used in the experiment; the asterisk (*) indicates radiolabelling position (copied from the study report).

The specific radioactivity of the test compound used in the experiment was 6.11 MBq/mg (165.14 µCi/mg) and its radiochemical purity, determined using both HPLC and TLC, was > 99%. Also the chemical purity of the test compound, determined using HPLC equipped with UV detector, was > 99%.

The whole delivered sample was used to prepare a **stock solution**, by dissolving it in 5.5 mL of CH₃CN. The obtained solution had a nominal concentration 1 mg Flufenacet/mL and specific activity 6.132 MBq/mL. It was labelled **KR05SS** and used to prepare all other solutions containing the test compound – [¹⁴C]-Flufenacet, used in the experiment (**Application solutions**). The identity and purity of the test compound in the solution **KR05SS** was determined using ¹H-NMR and HPLC-MS/MS methods.

The **Application solutions** were prepared as aqueous solutions in 0.01 M CaCl₂ aq.

The 0.01 M CaCl₂ aq solution was prepared by dissolving 2.94 g of CaCl₂ x 2 H₂O in Milli-Q water in 2-L volumetric flask.

Five application solutions, labelled **Application solution A1 – E** and having concentrations of [¹⁴C]-Flufenacet in range 0.1 mg/L – 10.0 mg/L, were prepared.

To prepare the **Application Solution A1** 0.2 mL of the solution **KR05SS** was transferred into 20-mL volumetric flask and the solvent gently evaporated. The residue was re-dissolved in 20 mL of 0.01 M CaCl₂ aq and the so prepared solution was sonicated for 15 minutes to grant proper dissolution of the test item. The concentration of the so prepared **Application solution A1** was 10 mg/L. It was labelled **KR05APP-A1**.

To prepare the **Application Solution B** 0.06 mL of the solution **KR05SS** was transferred into 20-mL volumetric flask and the solvent gently evaporated. The residue was re-dissolved in 20 mL of 0.01 M CaCl₂ aq and the so prepared solution was sonicated for 15 minutes to grant proper dissolution of the test item. The concentration of the so prepared **Application solution B** was 3.0 mg/L. It was labelled **KR05APP-B**.

To prepare **Application Solution C** 2.0 mL of the solution **KR05APP-A1** was transferred into 20-mL volumetric flask and diluted to 20 mL with 0.01 M CaCl_2 aq. The concentration of the so prepared **Application solution C** was 1.0 mg/L. It was labelled **KR05APP-C**.

To prepare **Application Solution D** 2.0 mL of the solution **KR05APP-B** was transferred into 20-mL volumetric flask and diluted to 20 mL with 0.01 M CaCl_2 aq. The concentration of the so prepared **Application solution D** was 0.3 mg/L. It was labelled **KR05APP-D**.

To prepare **Application Solution E** 2.0 mL of the solution **KR05APP-C** was transferred into 20-mL volumetric flask and diluted to 20 mL with 0.01 M CaCl_2 aq. The concentration of the so prepared **Application solution E** was 0.1 mg/L. It was labelled **KR05APP-E**.

The study was carried out using 43-mL Teflon centrifuge tubes with screw caps as test vessels. Additionally, in the test examining the adsorption of the test item onto the surface of the test vessels the glass vessels were used as well.

The study consisted of the following experiments:

- **Preliminary tests**, during which were determined:
 - Stability of the test item;
 - Adsorption of the test item onto the surface of the test vessels;
 - Adequate soil:solution ratio;
 - Adequate equilibrium time for adsorption;
 - Mass balance of the test compound – Flufenacet;
- **Definitive test**, consisting of:
 - Determination of Freundlich adsorption isotherm and its parameters – Freundlich adsorption constant $K_{F\text{ ads}}$ and corresponding $1/n$ value, in a single-step experiment;

All experiments were performed in a walk-in climatic chamber, at constant temperature $T = 25 \pm 2^\circ\text{C}$. The temperature in the experimental chamber was continuously monitored and the results of that monitoring are presented in section “Results and their discussion”, further down the summary.

For agitation (shaking) of the test vessels containing test soil and test solutions the mechanical overhead shaker, set to 30 rpm, was used.

The test aimed on the examination of the stability of the test item and adsorption of the test item onto the surface of the test vessels was performed in the systems without soil. It was carried out using Teflon or glass test vessels containing 20 mL of the **Application solution A1** and lasted 48 hours.

All experiments with soil started with the pre-equilibration of the test systems. To do that firstly the designated amounts of each test soil (dry weight) were weighed into centrifuge tubes. Next, the appropriate amount of 0.01 M CaCl_2 aq solution was added. The volume of the added liquid was always such, to obtain a total solution volume of 18 mL, taking into account the residual soil moisture.

The so prepared test vessels were sealed and pre-equilibrated for at least 24 hours in the dark by agitation at constant temperature $T = 25^\circ\text{C}$.

After pre-equilibration 2 mL of the adequate **Application solution (A1 – E)**, characterised above, was added to obtain the final solution volume of 20 mL. All preliminary tests were carried out using the **Application Solution A1** – that having the highest nominal test concentration of 1.0 mg Flufenacet/mL.

The definitive test aimed on the examination of the adsorption was carried out using all five application solutions – **Application solution A1 – Application solution E**, to cover the concentration range (nominal) of 0.01 – 1.0 mg Flufenacet/mL.

After introduction of the test compound the test vessels were closed and the suspensions agitated for the appropriate amount of time. After that period samples were centrifuged and the supernatants decanted. Their aliquots were analysed by LSC and HPLC. Additionally the pH of the supernatants was measured.

The remaining soil samples were freeze-dried and analysed, after combustion, by LSC. That was done to calculate the mass balance.

In case of the preliminary test, aimed on the determination of Parental Mass Balance, the soil samples remaining after decantation of supernatant were also analysed (extracted and obtained organic extracts analysed by LSC and HPLC) for the content of the test compound.

All test were performed using the duplicate samples.

The specific conditions of the performance of each experiment are presented below.

The adequate soil:solution ratio was determined for both test soils by examining the following ratios:

- 1:4 – 5 g soil (d. w.) and 20 mL solution;
- 1:7 – 3 g soil (d. w.) and 20 mL solution;
- 1:20 – 1 g soil (d. w.) and 20 mL solution;

That was done in the following way: firstly the appropriate portions of each test soils were weighed to the test vessels and 18 mL 0.01 M CaCl_2 _{aq} solution were added. So prepared test vessels were pre-equilibrated for 24 hours as described above. Next 2 mL of the **Application solution A1** were added to each test vessel, vessels were sealed and agitated for 24 hours. After that period the samples were centrifuged for 10 minutes at 4000 rpm, supernatants decanted and their three 500- μL aliquots analysed by LSC.

The adequate adsorption equilibrium time was determined for all test soils. The soil:solution ratio used in this test was 1:7. The test systems were prepared in duplicate for each test soil and pre-equilibrated for 24 hours, as already described. After pre-equilibration to each sample 2 mL of the **Application solution A1** were added. The samples were then agitated for up to 48 hours. At the pre-defined time points – 6, 24 and 48 hours after treatment samples were centrifuged for 10 minutes at 4000 rpm and 500- μL aliquots of clarified supernatants taken for LSC analysis.

The mass balance of the test item – Flufenacet, was examined in the following way: the samples were prepared in duplicate and pre-equilibrated for the 48-hours in a way described above (3 g test soil, 18 mL of 0.01M CaCl_2 _{aq} solution). The selected soil:solution ratio was 1:7. After pre-equilibration 2 mL of the **Application solution A1** were added to each test vessel. After application the samples were equilibrated, by agitating, for 48 hours, then centrifuged for 10 minutes at 4000 rpm and clarified supernatants collected for analysis by LSC (50- μL aliquots) and HPLC.

The soils remaining in the test vessels after decantation of supernatants were extracted by shaking them with three 10-mL portions of $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ 80:20 v/v. After each extraction cycle samples were centrifuged, supernatants decanted and combined, and their total volume determined. Three 250- μL aliquots of each combined extract were analysed by LSC. Extracts were also analysed by HPLC.

The definitive test aimed on the determination of Freundlich adsorption isotherm and Freundlich sorption parameters was carried out following the the procedure preseneted below on figure B.8.1.2.1.1._CA-24. For examining it the following initial (nominal) concentrations of the test item – [^{14}C]-Flufenacet, were used: 0.01 mg/L, 0.03 mg/L, 0.1 mg/L, 0.3 mg/L and 1.0 mg/L.

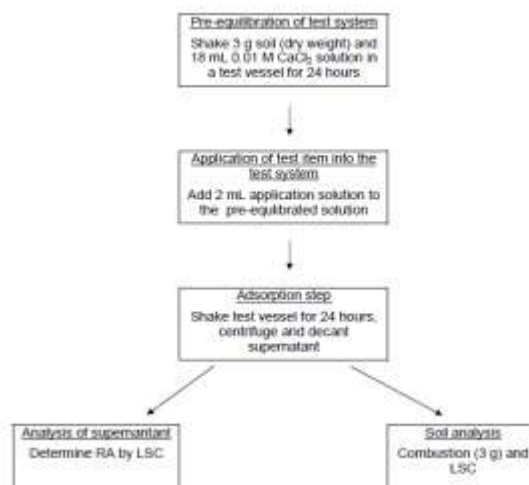


Figure B.8.1.2.1.1._CA-24: The flow chart of the experimental procedure for the definitive test (copied from the study report).

All liquid samples were analysed for the content of radioactivity using LSC method. The LSC (Liquid Scintillation Counting) analysis was performed using a LS6000LL/LS6500 or LKB-Wallac 1219 Spectral counters.

The samples having a volume up to 500 µL were analysed for the radioactivity content in mini-vials with 2 mL of Quicksafe® A solution containing 5% of water. The counting time was 10 min and the background 13 – 15 cpm. The analysis was performed using LS6000LL/LS6500 counter.

The radioactivity in solid samples – soil samples remaining after decantation of liquid phase, was determined after combustion of dried material. The resulting $^{14}\text{CO}_2$ was absorbed in 15 mL of Oxysolve C400 liquid. The counting time was 10 min and the background 18 – 20 cpm and the counting instrument LKB-Wallac 1219 Spectral counter.

The instrumental limit of detection – LOD_i was set to twice maximum instrument background count rate and instrumental limit of quantitation – LOQ_i to three times maximum instrument background count rate. The maximum instrument background count rate was determined to be 0.3 Bq. As a result the instrumental $\text{LOD}_i = 0.6 \text{ Bq}$ and $\text{LOQ}_i = 1.8 \text{ Bq}$.

The RP-HPLC analysis was performed in a gradient mode. The system consisted of Agilent 1200 Series chromatograph workstation equipped with a UV detector set at $\lambda = 254 \text{ nm}$, coupled with Ramona Star radioactivity detector. The chromatographic separation was performed on LiChrospher100 RP 18e 250 mm * 4.6 mm * 5 µm chromatographic column. It worked in the following gradient regime:

- **Mobile phase A:** water + 0.1% HCOOH,
- **Mobile phase B:** CH_3CN + 0.1% HCOOH,
- **Gradient mode:** is presented below in the table B.8.1.2.1.1._CA-47;
- Total run time was 66 minutes.

Table B.8.1.2.1.1._CA-47: The gradient mode used in the analysis.

Time [min.]		0	5	60	65	66
Gradient	% A	100	100	0	0	100
	% B	0	0	100	100	0

The flow rate was set to 1.5 mL/min. The chromatographic column was kept under the constant temperature $T = 40^\circ\text{C}$. The identification of the test compound – Flufenacet, was carried out by means of the comparison of the retention times. For Flufenacet the retention time R_t was approx. 44 min.

The LC-MS analysis was performed as HPLC/MS analysis. It was carried out using Agilent HP1100 HPLC system equipped with a Nucleodur Gravity C_{18} chromatographic column (250 * 2 mm, 3 µm), UV detector followed by the Ramona Star radiodetector and LTQ Orbitrap XL mass spectrometer.

The parameters of chromatographic analysis were following:

- column temperature: 40°C ,
- flow rate: 0.2 mL/min,
- elution mode: gradient,
- mobile phase:
 - Solvent A: H_2O + 0.1% HCOOH,
 - Solvent B: CH_3CN + 0.1% HCOOH.
- The gradient programmes used in the analysis is presented below in the table B.8.1.2.1.1._CA-48:

Table B.8.1.2.1.1._CA-48: The gradient mode used in the analysis.

Time [min.]		0	1	25	35
Gradient	% A	95	95	5	5
	% B	5	5	95	95

The calculations of the Freundlich sorption parameters were performed using the equations presented below on figure B.8.1.2.1.1._CA-25.

Freundlich isotherm	Log-transformed Freundlich isotherm	Equation used in calculation of $K_{F\text{OC}}$
$\frac{x}{m} = K_F \cdot C^{1/n}$ <p> C: concentration of a.i. in solution at equilibrium x/m: adsorbed amount of a.i. per weight unit of adsorbent (soil) at equilibrium ($\mu\text{g/g}$) K_F: Freundlich constant n: dimensionless </p>	$\ln\left(\frac{x}{m}\right) = \frac{1}{n} \cdot \ln(C) + \ln(K_F)$	$K_{oc} = \frac{K_F \cdot 100}{\%C_{oc}}$ <p>$\%C_{oc}$: portion of organic carbon in soil expressed as% of weight</p>

Figure B.8.1.2.1.1._CA-25: The equations used in the calculations of the Freundlich sorption parameters.

Results and their discussion:

The characteristic of the test soils used in the study has been presented at the beginning of this summary in table B.8.1.2.1.1._CA-46. It may be stated that the test soils meet the acceptability criteria with regard to their textural characteristic, pH range and OC content range. However, one of the test soils – Ushiku Sandy loam soil, was of the volcanic origin. For that reason the results obtained for that soil, although partly presented in this summary (due to the fact that the results for both test soils were presented together) cannot be considered acceptable, because they are not representative for the EU conditions.

The results of the monitoring of the temperature during the experiment are presented below on figure B.8.1.2.1.1._CA-26. On their basis it was stated that the mean $T = 25.21^{\circ}\text{C}$ and its range $25.00 - 25.55^{\circ}\text{C}$. It was therefore within the pre-defined limits of $T = 25 \pm 2^{\circ}\text{C}$. It may be also stated that the temperature was constant within the study period, so all thermodynamic experiments, and in particular that aimed on the determination of the sorption isotherms, returned reliable results.

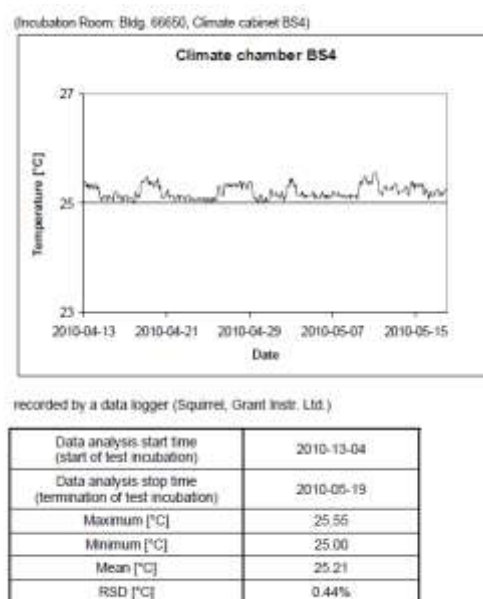


Figure B.8.1.2.1.1._CA-26: The graphical results of the monitoring of the temperature during the study (copied from the study report).

On the basis of the results of the determination of LOD and LOQ for LSC analysis it was stated that the method was well suited for the analysis of the samples from the lowest treatment concentrations.

The LOD and LOQ for the radio-HPLC method were determined to be $\text{LOD} = 0.2\% \text{ AR}$ and $\text{LOQ} = 3 \cdot \text{LOD} = 0.6\% \text{ AR}$.

The results of the examination of the test item – Flufenacet, in the test solution and its adsorption onto the surface of the test vessels are presented below in the table B.8.1.2.1.1._CA-49. On their basis it was stated that Flufenacet was stable in the test system and it did not adsorb onto the test vessels.

Table B.8.1.2.1.1._CA-49: The results of the examination of the stability of the test item in the test solution.

I) Experimental conditions				
Amount of soil:		Test system without soil		
Amount of test solution in test vessel:		20 mL		
Concentration of the test item:		1.0 mg/L (nominal; highest concentration used in experiment)		
Equilibration time:		0 – 48 h		
II) Results				
Equilibraion time [Hours]	Type of the test vessel	Obtained results		
		Total radioactivity in the test vessel [%AR]	Radioactivity identified as Flufenacet	
	% in chromatogram		[% AR]	
0	Teflon	100.0	100.0	
	Glass	103.4	103.4	
24	Teflon	103.2	103.2	
	Glass	105.5	105.5	
48	Teflon	98.0	100.0	
	Glass	102.0	100.0	

The results of the determination of the appropriate soil:solution ratio are presented below, in numerical form in the table B.8.1.2.1.1._CA-50 and in graphical form on figure B.8.1.2.1.1._CA-27. The abbreviations used on the figure stand for: U – Ushiku soil, K – Kamikawa soil.

Table B.8.1.2.1.1._CA-50: The numerical results of the determination of the appropriate soil:solution ratio.

Test soil	Soil solution ratio		Amount of Flufenacet remaining in solution [% AR]	Amount of Flufenacet sorbed onto soil [% AR]
	in g soil/mL solution	as ratio		
Ushiku	1/20	1:20	82.9	17.1
	3/20	1:7	51.1	49.0
	5/20	1:4	36.6	63.4
Kamikawa	1/20	1:20	77.8	22.2
	3/20	1:7	48.1	51.9
	5/20	1:4	33.7	66.3

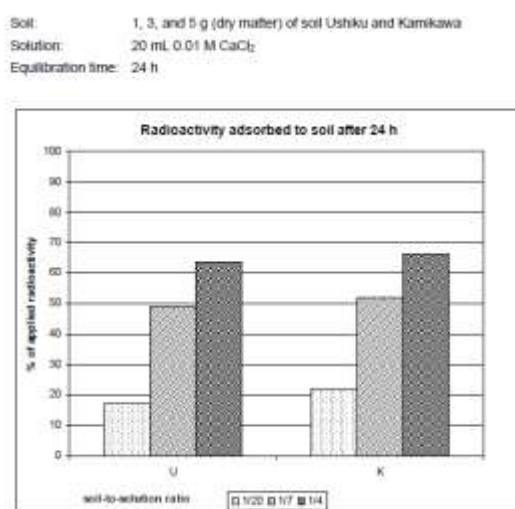


Figure B.8.1.2.1.1._CA-27: The graphical results of the determination of the appropriate soil:solution ratio – amount of Flufenacet adsorbed onto soil (copied from the study report).

On the basis of the presented above obtained results, the soil:solution ratio 1:7 (3:20) was selected to be used in further tests.

The results of the determination of the appropriate equilibration time are presented below, in numerical form in the table B.8.1.2.1.1._CA-51 and in graphical form on figure B.8.1.2.1.1._CA-28. The abbreviations used on that graph to denominate test soils were following:

- U for Ushiku Sandy loam soil;
- K for Kamikawa Loam soil.

Table B.8.1.2.1.1._CA-51: The numerical results of the determination of the appropriate equilibration time.

Test soil	Replicate	Amount of Flufenacet [% AR] after equilibration time:							
		0 hours		6 hours		24 hours		48 hours	
		in supernatant	adsorbed onto soil	in supernatant	adsorbed onto soil	in supernatant	adsorbed onto soil	in supernatant	adsorbed onto soil
<i>Ushiku Sandy loam</i>	1	78.7	21.3	50.2	49.8	44.2	55.8	41.4	58.6
	2	76.6	23.4	50.5	49.5	44.6	55.4	40.1	59.9
	mean	77.7	22.3	50.3	49.7	44.4	55.6	40.7	59.3
<i>Kamikawa Loam</i>	1	66.6	33.4	44.6	55.4	41.4	58.6	38.5	61.5
	2	65.8	34.2	43.3	56.7	41.5	58.5	38.7	61.3
	mean	66.2	33.8	44.0	56.0	41.5	58.5	38.6	61.4

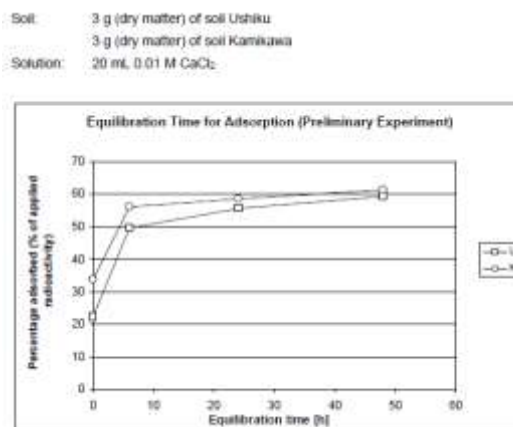


Figure B.8.1.2.1.1._CA-28: The graphical results of the determination of the appropriate equilibration time (copied from the study report).

The results of the determination of the mass balance, performed as one of the preliminary tests for each test soil, are presented below in the table B.8.1.2.1.1._CA-52. In the next table – B.8.1.2.1.1._CA-53 are presented the results of the determination of the mass balance performed for the definitive tests.

Table B.8.1.2.1.1._CA-52: The results of the determination of the mass balance carried out in Preliminary Parental Mass Balance Test.

Test soil	Radioactivity recovered (mean of two replicates) in:					
	<i>CaCl₂ solution</i>		<i>Soil organic extracts</i>		<i>Total recovered</i>	
	as Total Radioactivity [% AR]	as Flufenacet [% AR]	as Total Radioactivity [% AR]	as Flufenacet [% AR]	as Total Radioactivity [% AR]	as Flufenacet [% AR]
<i>Ushiku Sandy loam</i>	37.3	37.3	66.5	66.5	103.8	103.8
<i>Kamikawa Loam</i>	37.5	37.5	67.3	67.3	104.8	104.8

Table B.8.1.2.1.1._CA-53: The results of the determination of the recovery of radioactivity in the definitive test – after adsorption and desorption steps.

Initial (nominal) concentration of Flufenacet	Total radioactivity recovery, expressed in [% AR], in experiment with the test soil:	
	<i>Ushiku Sandy loam soil</i>	<i>Kamikawa Loam soil</i>
1.0	96.5	94.1
0.3	99.3	98.9
0.1	99.0	98.4
0.03	98.8	96.7
0.01	96.5	96.2
Mean recovery (with SD)	98.0 (1.3)	96.9 (1.7)

The verification of the application rate of Flufenacet in the definitive test gave the following results:

- for the solution having a nominal concentration **1.0 mg Flufenacet/L** the measured concentration was **1.000 mg Flufenacet/L**;
- for the solution having a nominal concentration **0.3 mg Flufenacet/L** the measured concentration was **0.292 mg Flufenacet/L**;
- for the solution having a nominal concentration **0.1 mg Flufenacet/L** the measured concentration was **0.087 mg Flufenacet/L**;
- for the solution having a nominal concentration **0.03 mg Flufenacet/L** the measured concentration was **0.029 mg Flufenacet/L**;
- for the solution having a nominal concentration **0.01 mg Flufenacet/L** the measured concentration was **0.009 mg Flufenacet/L**.

The results of the determination of the pH of supernatant after establishing the adsorption equilibrium in the definitive test is given below in the table B.8.1.2.1.1._CA-54.

Table B.8.1.2.1.1._CA-54: The results of the determination of the pH of solution at equilibrium in the adsorption part of the definitive test.

Initial concentration of Flufenacet [mg/L]		Replicate	pH of the solution measured in the test system containing the test soil:		
<i>nominal</i>	<i>measured</i>		<i>Ushiku Sandy loam soil</i>	<i>Kamikawa Loam soil</i>	<i>Control without soil</i>
1.0	1.000	1	6.06	5.41	8.03
		2	----	----	----
0.3	0.292	1	6.04	5.45	8.07
		2	----	----	----
0.1	0.087	1	6.04	5.45	8.11
		2	----	----	----
0.03	0.029	1	5.94	5.39	8.13
		2	----	----	----
0.01	0.009	1	6.06	5.44	8.13
		2	----	----	----

The results of the definitive test are presented below. The numerical results obtained for the adsorption phase – concentrations of the test item in soil and solution at equilibrium and the % of the Flufenacet adsorbed onto soil, are presented below, individually for each test soil, in the table B.8.1.2.1.1._CA-55 for Ushiku soil and in the table B.8.1.2.1.1._CA-56 for Kamikawa soil.

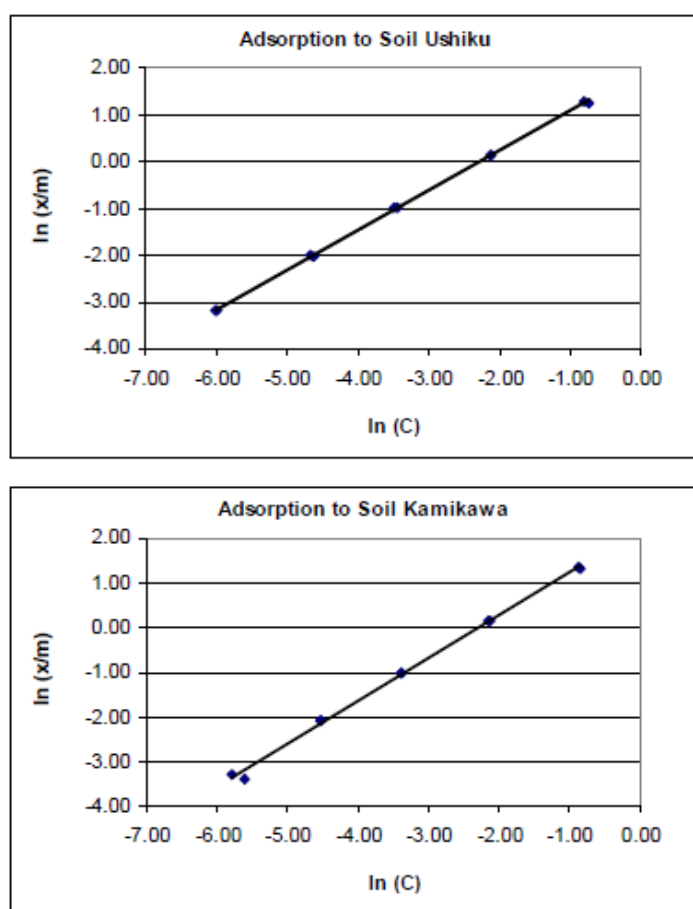
Table B.8.1.2.1.1._CA-55: The numerical results of the experiment obtained for the adsorption phase in experiment with Ushiku soil.

Initial concentration of Flufenacet [mg/L]		Replicate	Concentration of Flufenacet in				Amount adsorbed [% AR]
nominal	measured		Soil		Solution		
			x/m [µg/g]	Ln (x/m)	Ce [µg/mL]	Ln (Ce)	
1.0	1.000	1	3.466	1.24	0.480	-0.73	52.0
		2	3.651	1.30	0.452	-0.79	54.8
		mean	3.559	----	0.466	----	53.4
0.3	0.292	1	1.145	0.14	0.120	-2.12	58.9
		2	1.154	0.14	0.118	-2.13	59.4
		mean	1.149	----	0.119	----	59.1
0.1	0.087	1	0.376	-0.98	0.031	-3.48	64.8
		2	0.369	-1.00	0.032	-3.45	63.6
		mean	0.373	----	0.031	----	64.2
0.03	0.028	1	0.132	-2.02	0.010	-4.64	67.2
		2	0.135	-2.01	0.009	-4.68	68.5
		mean	0.133	----	0.009	----	67.8
0.01	0.009	1	0.042	-3.18	0.002	-6.00	71.6
		2	0.042	-3.17	0.002	-6.02	72.1
		mean	0.042	----	0.002	----	71.8

Table B.8.1.2.1.1._CA-56: The numerical results of the experiment obtained for the adsorption phase in experiment with Kamikawa soil.

Initial concentration of Flufenacet [mg/L]		Replicate	Concentration of Flufenacet in				Amount adsorbed [% AR]
nominal	measured		Soil		Solution		
			x/m [µg/g]	Ln (x/m)	Ce [µg/mL]	Ln (Ce)	
1.0	1.000	1	3.860	1.35	0.421	-0.87	57.9
		2	3.795	1.33	0.430	-0.84	56.9
		mean	3.827	----	0.426	----	57.4
0.3	0.292	1	1.152	0.14	0.119	-2.13	59.3
		2	1.162	0.15	0.117	-2.14	59.8
		mean	1.157	----	0.118	----	59.5
0.1	0.087	1	0.356	-1.03	0.034	-3.39	61.4
		2	0.357	-1.03	0.034	-3.39	61.5
		mean	0.357	----	0.034	----	61.4
0.03	0.028	1	0.125	-2.08	0.011	-4.54	63.7
		2	0.125	-2.08	0.011	-4.54	63.8
		mean	0.125	----	0.011	----	63.8
0.01	0.009	1	0.037	-3.28	0.003	-5.78	64.6
		2	0.033	-3.40	0.004	-5.60	57.5
		mean	0.035	----	0.003	----	61.1

The graphical results of the experiment – Freundlich adsorption isotherms for Flufenacet in Ushiku and Kamikawa soils are presented below on figure B.8.1.2.1.1._CA-29. The numerical results – Freundlich adsorption parameters for Flufenacet in Kamikawa soil are presented in the table B.8.1.2.1.1._CA-57. The values obtained in Ushiku soil are presented for completeness. RMS however decided to mark them in italics in order to indicate that they will not be used in the subsequent assessment because of the very limited utility. That is due to the fact that Ushiku soil is of volcanic origin, therefore not representative for the EU agriculturally used areas.



C: Concentration in water in $\mu\text{g/mL}$ (ppm)
 x/m: Concentration in soil in $\mu\text{g/g}$ (ppm)

Evaluation of linear regression according to FREUNDLICH:

Soil		Ushiku	Kamikawa
Regression	R^2	0.9996	0.9973
Slope	$1/n$	0.8479	0.9583
Interception	$\ln K_F$	1.9338	2.1923

Figure B.8.1.2.1.1_CA-29: The Freundlich adsorption isotherms obtained for Flufenacet in Ushiku and Kamikawa test soils (copied from the study report).

Table B.8.1.2.1.1_CA-57: The parameters of Freundlich adsorption isotherms for Flufenacet obtained in the experiment.

Test soil	Determined parameter			
	$K_F[\text{mL/g}]$	$K_{F\text{ oc}}[\text{mL/g}]$	$1/n$	R^2
Ushiku Sandy loam soil	6.916	160.8	0.848	0.9996
Kamikawa Loam soil	8.956	426.5	0.958	0.9984

Study 4:

Report: Christensen K. P., Yen P. Y., (1994): “FOE 5043 – determination of the Adsorption and Desorption Properties in Canadian Soils.”; Springborn Laboratories Inc., Environmental Sciences Division, 790 Main Street, Wareham, Massachusetts 02571-1075, USA (performing laboratory) for Miles Inc., Agriculture Division, Research and Development Department, P. O. Box 4913, Kansas City, Missouri 64120, USA; Springborn Laboratories Report No #94-5-5256; Miles Inc. Study No. F3182103, Miles Inc. Report No. 106578, ; Bayer Report No. MR 106578; 12 September 1994; study reference number: M-002186-01-1;

Guidelines: The study was performed to comply with the following Guidelines:

- Canadian Guidelines T-1-255 # 6.2, B-1 Adsorption/Desorption Measurements.

GLP: Yes;

RMS comments: The study had been evaluated for the previous authorisation of Flufenacet in the EU, by its inclusion into the Annex I of the Directive 91/414/EEC. Its summary can be found under the point B.7.2.1.1, in section B.7 of the Annex B to the Monograph prepared by the RMS – France, for Flufenacet. For the present authorisation in the EU the study was evaluated for its compliance with OECD Guideline for the Testing of Chemicals 106 – Adsorption-Desorption Using a Batch Equilibrium Method. Additionally the study was checked for its validity against the US EPA Fate, Transport and Transformation Test Guideline OPPTS 835.1220 – Sediment and Soil Adsorption/Desorption Isotherm. and SETAC Guidance Document “Procedures for Assessing the Environmental Fate and Ecotoxicity of Pesticides.” It was stated that the study generally complied with the provisions of the three evoked Guidance documents. However, in the study report in section reporting the protocol deviations it was stated, as a first deviation listed, that although the study was declared to be carried out in constant temperature $T = 20 \pm 2^{\circ}\text{C}$, the temperature actually recorded during the whole study duration ranged from 15.9°C to 22.9°C . That deviation was considered by the study director to have an insignificant influence on the obtained results, but it shall be indicated that the 5°C -difference in temperature recorded during the equilibrium test aimed on the determination of the time necessary for reaching the equilibrium state may have a significant impact on the results. As a result, the RMS – Poland is of the opinion that although study generally complies with the provisions of the relevant Guidelines, it cannot be considered acceptable for the scientific reason – because of high uncertainty of the determined thermodynamical parameters, in particular Freundlich isotherm constant, due to the reported fluctuations of the temperature during the experiment. The issue is discussed in details in the brief summary provided below. Finally, it shall be stated that, because of the stated lack of reliability of the adsorption parameters determined in the study, the results of this study will not be included into the List of End Points nor used to derive the input parameters for the model GW and SW exposure assessment for Flufenacet.

Summary:

The aim of the study was to investigate soil sorption of Flufenacet onto two Canadian soils in line with the requirements of the Canadian Guideline T-1-255 #6.2, B. The test soils used in the experiment were Loam and Silt loam originating from Ontario, Canada. Their brief characteristic is provided below in the table B.8.1.2.1.1._CA-58.

Table B.8.1.2.1.1._CA-58: The characteristic of soils used in the study.

Parameter		Soil	
		Loam	Silt loam
Soil origin		Harriston, Ontario, Canada	St. George, Ontario, Canada
Soil type ¹⁾		Loam	Silt loam
Particle size distribution	Sand (50 µm – 2 mm) [%]	42	20
	Silt (2 – 50 µm) [%]	50	56
	Clay (< 2 µm) [%]	8	24
pH (measurement medium not defined)		7.1	7.3
Organic carbon content (OC) [%] ²⁾		4.3	2.8
Organic matter content (OM) [%]		7.3	4.7
Cation Exchange Capacity – CEC [mEq/100g]		14.6	17.1
Water holding capacity	at ½ bar [g H ₂ O/100 g soil]	32.2	27.1
	at 15 bar [g H ₂ O/100 g soil]	21.0	20.1
Bulk density (disturbed) [g/cm ³]		0.91	0.96

Footnotes to the table:

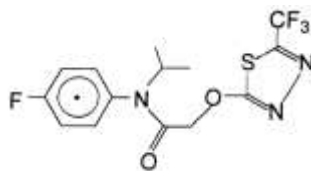
1) As declared in the study report;

2) As provided in the study report; recalculated from OM using the following equation: OC = OM/1.7.

The test soils were representative for the agricultural regions in which Flufenacet was intended to be used. They were collected from the pasture/hayfield sites in Ontario, on which no pesticides were used for 5 years prior to the sampling. Soil samples were taken from the top 15-cm layer and placed in plastic bags shipped directly to the test facility. There they were stored refrigerated until being used.

At the beginning of the experiment the test soils were sieved through 2-mm sieve to remove skeletal elements – rocks and large plant parts, and their portions were sent to the laboratory performing characterisation of soil properties. The determination of the soil moisture content was performed in the test facility at the beginning of each stage of the testing of soil equilibrium sorption of Flufenacet.

The test compound was [¹⁴C]-Flufenacet radiolabelled uniformly in fluorophenyl ring. Its declared radiochemical purity was 98.98 – 99.1% and specific activity 66.5 mCi/mmol. The structural formula is presented below on figure B.8.1.2.1.1._CA-30.

**Figure B.8.1.2.1.1._CA-30:** The structural formula of the test compound. The radiolabelling position is indicated by the asterisk (*) (copied from the study report).

Also the non-radiolabelled Flufenacet was used in the experiment. It had the chemical purity of 99.6%.

The characterised above radiolabelled test compound was used to prepare the **Stock solution** in acetonitrile, having a concentration 0.0867 mg Flufenacet/mL and radiochemical purity of 99.9%. That solution was used to prepare two **secondary stock solutions**, both containing radiolabelled and non-radiolabelled test compound.

The first of them, **fortification secondary stock solution** had concentration of the test item 14.9 mg/mL. The second, **additional secondary stock solution** was prepared by diluting the **fortification secondary stock solution** 100 times (to the concentration of the test item 0.149 mg/mL) with acetone.

The test solutions were prepared by diluting the appropriate amounts of the **Stock solutions** with 0.01 M CaCl₂ or ASTM type II water.

The examination of the soil equilibrium soil sorption of Flufenacet consisted of the following tests:

- **Screening test**, in which were determined the approximate distribution coefficients (K_d) for Flufenacet in each soil and established the soil:solution ratio optimal to provide ~50% of the applied amount of Flufenacet in the liquid phase;
- **Equilibrium test** aimed on the determination of the time necessary for reaching the equilibrium between the adsorbed and dissolved test item;
- **Isotherm determination**, in which the adsorption and desorption isotherms were determined.

The concentrations of the test compound – Flufenacet, were determined only in liquid phase by LSC and HPLC analysis. The amounts remaining in the adsorbent – soil, were calculated as a difference between the initial amount in the test system and that determined in the liquid phase at the end of each test.

The preliminary experiments showed that Flufenacet was stable in the system and did not adsorb to the test vessels. The optimum soil:solution ratio was determined to be 1:5 and the optimum equilibration time – 24 hours for Loam soil and 48 hours for Silt loam soil.

The Freundlich sorption isotherms were determined using the following initial concentrations of the test item: 0.21 mg/L, 1.0 mg/L, 5.1 mg/L and 14.2 mg/L.

In Loam soil the % of the test compound adsorbed after equilibration ranged from 46.0% to 51.9%. The three-cycle desorption resulted in desorption of the 81.1% of Flufenacet adsorbed onto soil.

In Silt loam soil the % of the test compound adsorbed after equilibration was 36.6 – 54.0%. The three-cycle desorption resulted in approx. 90.7% of the adsorbed Flufenacet being desorbed.

For each test soil the Freundlich adsorption isotherm and Freundlich desorption isotherm were determined.

Characterising the protocol deviations the Study director stated that:

- the testing was intended to be performed at $T = 20 \pm 2^{\circ}\text{C}$, in line with the recommendations of the relevant Guidelines;
- actually, the temperature during the whole testing fluctuated from $T = 15.9^{\circ}\text{C}$ to $T = 22.9^{\circ}\text{C}$, so the difference between the lowest and highest value recorded during the study was 7°C ;
- in case of the screening test the measured temperature was in range $15.9 - 22.8^{\circ}\text{C}$ (the difference 6.9°C);
- in case of the equilibrium test the measured temperature range was $17.9 - 22.9^{\circ}\text{C}$ (the difference 5.0°C);
- in case of the determination of adsorption and desorption isotherms for Flufenacet in Loam soil the measured temperature was in range $17.1 - 21.5^{\circ}\text{C}$ (the difference 4.4°C);
- in case of the determination of adsorption and desorption isotherms for Flufenacet in Silt loam the range of the measured temperature was $17.5 - 21.7^{\circ}\text{C}$ (the difference 4.2°C);
- additionally, although it was declared that the temperature records would be collected daily during the experiment, on one day it was not;
- the problems described above were attributed to the equipment malfunctioning;
- at the same time it was stated that although the overall range was relatively large, as well as that measured in the screening test, in later stages it was $\leq 1^{\circ}\text{C}$;
- as a final conclusion it was stated that “*in this case, the slight difference in temperature probably did not significantly affect the results.*”.

It shall be indicated that in the study report the detailed data on the temperature recorded during the study were not provided. As a result it is very difficult to verify some of the statements, in particular the penultimate one.

RMS does not fully agree with the final conclusion: the 4°C -difference cannot be considered a “*slight difference in temperature*”, in particular in case when the thermodynamic constants are determined, and such is the Freundlich adsorption constant. It shall be also pointed out that the significant difference in temperature recorded in the screening test might already have compromised the results, as the test was performed using the solution containing the test item. It shall be indicated that the whole experiment is based on the determination of the distribution at equilibrium of the compound in liquid and solid phases. The test item is organic compound of limited solubility in aqueous solutions ($S_{\text{aq}} = 56 \text{ mg/L}$ at $T = 20^{\circ}\text{C}$), so the temperature may be a driving factor in the experiment, especially in case it rises. Finally, aqueous solubility of the organic compound in function of time may not be linear, therefore it may be very difficult to predict how that influenced the results. Last but not least, lack of data presenting the changes of the temperature during the experiment makes it impossible to assess how the fluctuations reported above influenced the results.

All that taken into account RMS is of the opinion that due to the deviations reported above the obtained results, and in particular the determined Freundlich sorption parameters bear to significant level of uncertainty to be considered reliable.

As a result, RMS decided not to present them in the summary, include them in the List of End Points nor to use them to derive the input parameters for Flufenacet to be used in model GW and SW exposure assessment (calculation of the PEC values).

Additionally the data on the soil sorption of Flufenacet at equilibrium were provided in three open-source publications summarised below as **Studies 5-7**. It shall be indicated that two of them have already been summarised in this Renewal Assessment Report as they covered also the issue of degradation of Flufenacet in soil examined under laboratory conditions and its dissipation in soil under field conditions.

Study 5:

Report: Gupta S., Gajbhiye V. T., Agnihotri N. P. (2001): “Adsorption-Desorption, Persistence and Leaching Behavior of Flufenacet in Alluvial Soil of India.”; Division of Agricultural Chemicals, Indian Agricultural Research Institute, New Delhi 110 012, India; published study - published in: “Bulletin of Environmental Contamination and Toxicology”, vol. 66, 2001, pp 9-16.

Guidelines: : None declared as this is an open-source study, therefore not submitted for the regulatory purposes.

GLP: no, not applicable – peer-reviewed scientific paper

RMS comments: The paper presents the results of the examination of soil equilibrium sorption (determination of Freundlich sorption isotherms), mobility in soil profile (column leaching experiment) and persistence in aerobic and anaerobic soil, for Flufenacet. The experiments were performed using one test soil. Although in the paper it was not indicated that the experiments were performed in line with any relevant guidelines, it can be stated that the study protocol generally complied with the OECD 307 guideline for soil persistence, OECD 106 Guideline for examining batch sorption and OECD 312 for column leaching. The level of details was sufficient to evaluate the study for its validity. The study may be considered valid, and therefore is summarised below, in this section of the Assessment Report for its part examining the soil sorption (adsorption and desorption) of Flufenacet in soil under laboratory conditions. However, RMS is of the opinion that the results it provides may be regarded only as supplementary and confirmatory to the endpoints provided by the regulatory studies submitted by the Applicant, and should not be used as a source of regulatory endpoints.

Summary:

The Editor has not provided the abstract for that publication. However the paper contained the introduction, clearly outlining the aims and scope of the research activity described in it, which may be considered a summary of the study. Due to the copyright restrictions, RMS could not present it here and the readers are kindly asked to consult the relevant document. Instead, below is presented the extended summary prepared by the RMS.

Extended summary prepared by RMS:

The aim of the study was to examine the mobility and persistence of Flufenacet in soil. The test soil used in the experiment was an agricultural soil, of the type of inceptisol, having the following physicochemical properties:

- **particle size distribution:** 64.7% sand, 15.6% silt and 19.7% clay;
- **soil texture class:** Sandy loam;
- **pH:** 7.1;
- **OC:** 0.34%;
- **Moisture content at FC (field capacity):** 20%.

The soil used in the experiment was freshly sampled from the top 15-cm layer of the fields of Indian Agricultural Research Institute in New Delhi, India. It was then air-dried and sieved through 2-mm mesh screen before being used.

The test compound was analytical grade Flufenacet, having a purity of > 99.5%, provided by M/s Bayer India Ltd. It was applied to the test soil in form of aqueous solution in 0.01 N (0.005 M) CaCl_2 aq, prepared from the stock solution of Flufenacet in acetone, having a concentration of 0.5 mg/mL.

The aliquot of this solution was transferred into the glass tube and left at $T = 25 \pm 2^\circ\text{C}$ to evaporate acetone. The residue was reconstituted in 0.01N (0.005 M) CaCl_2 aq. That solution was used as a treatment solution in the experiment examining batch sorption of Flufenacet.

As a first step was performed a preliminary experiment aimed on the determination of appropriate equilibration time. It was performed in glass tubes containing 10 g soil and 20 mL solution – 0.01N (0.005 M)

CaCl₂ _{aq} spiked with 0.5 mg Flufenacet. That gave the soil:solution ratio 1:2. In the paper it was not determined on what basis that ratio was selected. The so prepared samples were equilibrated for 1, 2, 4, 6 and 24 hours by shaking on horizontal shaker. After that time samples were removed, centrifuged and clear supernatants analysed for the content of the test compound – Flufenacet. It was stated that the maximum sorption occurred during the first four hours. Therefore the 4-hours equilibration time was selected as optimum for further examination.

The main test – the examination of the adsorption of Flufenacet onto soil at equilibrium in order to determine the parameters of Freundlich adsorption isotherm sorption was carried out in glass tubes containing the test soil and 0.01N CaCl₂ _{aq} solution in ratio 1:2 (10 g soil: 20 mL solution). The test compound – Flufenacet was introduced into the system in the solution. Its initial concentrations were: 0.1 mg/L, 0.5 mg/L, 1 mg/L, 2 mg/L, 5 mg/L, 10 mg/L 20 mg/L and 30 mg/L. The equilibration time was 4 hours and the temperature $T = 25 \pm 2^{\circ}\text{C}$. Samples were prepared in duplicate. After equilibration samples were centrifuged for 10 min at 2000 rpm, clarified supernatants decanted, their 10-mL aliquots diluted with saturated NaCl aqueous solution and extracted with 3 30-mL portions of CH₂Cl₂. Organic extracts were collected, combined and dried by passing through anhydrous Na₂SO₄. The combined organic extract was then evaporated to dryness, reconstituted in n-hexane and analysed by GC-ECD.

The desorption isotherm was determined in a separate study using one concentration of the test compound – 30 mg Flufenacet/L (highest concentration tested in the experiment on adsorption). The soil:solution ratio was 1:2 and the samples containing the test compound were equilibrated for 4 hours. After that time samples were centrifuged, supernatant decanted and a fresh 20-mL portion of a blank 0.01N (0.005 M) CaCl₂ _{aq} solution added. The samples were equilibrated for another 4 hours and then centrifuged and the clarified supernatants collected and processed in the same way as described for the adsorption phase. The procedure was repeated five times to obtain the data for five-step desorption process.

All samples were analysed using GC-ECD technique on Helwett Packard 5890 Gas Chromatograph equipped with ⁶³Ni electron capture detector. The separation was performed on megabore HP-1 capillary GC column, 10-metres long, 0.53-mm of internal diameter and having 2.65 µm-thick film. The GC oven was programmed at initial temperature of $T = 160^{\circ}\text{C}$ lasting for 9 minutes, then increasing at rate $30^{\circ}\text{C}/\text{min}$ to $T = 260^{\circ}\text{C}$, held at that level for 3 minutes. The carrier gas was N₂ administered at a rate 15 mL/min.

For Flufenacet the $R_t = 7.4$ min. The LOQ = 0.005 µg/g for both soil and aqueous matrices.

The numerical results of the examination of adsorption at equilibrium are presented below in the table B.8.1.2.1.1._CA-59. Analysing these results RMS stated that in case of the concentration of Flufenacet adsorbed probably the units were wrongly reported - µg/mL instead of µg/g.

Table B.8.1.2.1.1._CA-59: The numerical results of the examination of adsorption at equilibrium.

Initial concentration of Flufenacet in solution [µg/mL]	Concentration of Flufenacet at equilibrium:		Distribution coefficient - K_d
	In solution – C_e [µg/mL]	In soil (adsorbed) – C_s [µg/mL]	
0.1	0.06	0.09	1.57
0.5	0.24	0.51	2.11
1.0	0.42	1.15	2.72
2.0	0.88	3.91	4.43
5.0	2.29	5.43	2.38
10.0	4.86	10.29	2.12
20.0	9.84	20.33	2.07
30.0	16.66	26.69	1.60

To determine the Freundlich adsorption isotherm the presented above concentrations at equilibrium were logarithmically transformed using Log₁₀-transformation and then fitted to the equation representing the linearised form of Freundlich isotherm:

$$\text{Log } C_s = \text{Log } K + 1/n \text{ Log } C_e$$

The determined parameters were following:

- $\text{Log } K = 0.3545$
- $1/n = 0.988$
- $r = 0.99$

When recalculated Freundlich adsorption constant $K_{f \text{ ads}} = 2.26$ mL/g. The calculated $K_{f \text{ OC}} = 664.71$ mL/g, indicating strong sorption of the test compound to the test soil.

The calculated change of the free energy of adsorption $\Delta G = -3.317$ Kcal/mol, indicating that the process of the adsorption was spontaneous and that its nature was physisorption.

RMS comments:

The study protocol indicates that it was in line with the provisions of the OECD 106 Guideline. However, the fact that the test soil was a non-EU soil that was not well characterised and the problems revealed during the analysis of the data lead to the conclusion that the adsorption parameters determined in it cannot be used to derive the EU regulatory endpoints. The results may be therefore considered solely as indicative.

Study 6:

Report: Gajbhiye V. T., Gupta S. (2001): “Adsorption-desorption behaviour of flufenacet in five different soils of India.”; Division of Agricultural Chemicals, Indian Agricultural Research Institute, New Delhi 110 012, India; published study - published in: “Pest Management Science”, vol 57, 2001, pp 633 – 639.

Guidelines: : None declared as this is an open-source study, therefore not submitted for the regulatory purposes.

GLP: no, not applicable – peer-reviewed scientific paper.

RMS comments: The paper presents the results of the examination of soil equilibrium sorption (determination of Freundlich adsorption and desorption isotherms) for Flufenacet. The experiment was performed using five test soils. Although in the paper it was not indicated that the experiments were performed in line with any relevant guidelines, it can be stated that the study protocol generally complied OECD 106 Guideline. The level of details was sufficient to evaluate the study for its validity. The study may be considered valid, and therefore is summarised below. However, RMS is of the opinion that the results it provides may be regarded only as supplementary and confirmatory to the endpoints provided by the regulatory studies submitted by the Applicant, and should not be used as a source of regulatory endpoints.

Summary:

The paper contains an abstract, outlining the aims of the experiment and its key results, which was made available on-line. However, due to the copyright restrictions RMS could not present it here and the readers are kindly asked to consult the relevant document. Instead, below is presented the extended summary prepared by the RMS. For the same reason RMS could not present the graphical results of the experiment and in particular the determined adsorption isotherms.

Extended summary prepared by RMS:

The aim of the study was to examine the sorption (adsorption and desorption) of Flufenacet in soil at equilibrium by determining the parameters of the adsorption and desorption isotherms. Also examined was the mechanism of the adsorption and its correlation with key soil properties, such as soil pH, soil OC/OM content and soil clay content. The whole experiment was performed at ambient temperature, most probably at $T = 25^{\circ}\text{C}$ (the indicator for that was the declared temperature for which the change of free Gibbs energy – ΔG , was determined).

The experiment was carried out on five Indian agricultural soils, coming from different geographic and climatic regions of the country. Their characteristic provided below in the table B.8.1.2.1.1._CA-60. The soils were sampled from the top 0-15 cm layer (plough layer) from the agriculturally used fields on which Flufenacet was not used prior to the sampling. The soils were air-dried, ground and passed through 2-mm sieve before being used. They were characterised for their physicochemical properties using the methodology in line with that described by Day P. R. in “*Methods of Analysis*” Part I, ed. by Black CA, 1965 on pp. 545 – 567, and by Jackson M. L. in “*Soil Chemical Analysis*”, Prentice Hall of India Pvt Ltd, New Delhi, 1973.

Table B.8.1.2.1.1_CA-60: The characteristic of soils used in the study.

Parameter		Soil				
		<i>Delhi</i>	<i>Ranchi</i>	<i>Nagpur</i>	<i>Kerala</i>	<i>Assam</i>
Soil origin		Northern plains, India	Eastern plateau, India	Deccan plateau, India	Western ghats, India	Assam plains, India
Climate type		Semi-arid with cold winter	Subhumid	Semi-arid with mild winter	Coastal	Humid
Soil type		Inceptisol	Ultisol	Vertisol	Alfisol	Oxisol
Soil textural type (reported in the study)		Sandy loam	Sandy loam	Clayley	Loam	Loamy sand
Soil textural type – USDA (determined by RMS)		Loamy sand	Sandy clay loam	Clay	Sandy clay loam	Silt loam
Particle size distribution	Sand [%]	77.5	60.0	40.0	50.0	45.8
	Silt [%]	17.5	8.8	16.3	25.0	51.7
	Clay [%]	5.0	31.2	43.7	25.0	2.5
Soil pH (medium not determined)		7.69	5.54	8.35	4.45	6.87
Organic matter content (OM) [%]		0.864	0.072	0.688	0.786	0.553
Organic carbon content (OC) [%]		0.501	0.042	0.399	0.456	0.321
CEC [meq/100 g]		6.95	3.86	13.69	20.20	14.00

The test compound was analytical grade Flufenacet, having a purity of > 99.5%, provided by M/s Bayer India Ltd. It was used to prepare the stock solutions in acetone, first having a concentration 1000 mg Flufenacet/L and the second, diluted, having a concentration of 100 mg Flufenacet/L.

All experiments were performed using aqueous solutions of Flufenacet – in 0.01M CaCl_2 aq. The aqueous stock solution of Flufenacet, having a concentration of 30 mg/L was prepared from the diluted acetone stock solution, having a concentration of 100 mg Flufenacet/L. To do that the appropriate aliquot of the diluted acetone stock solution was transferred to the volumetric flask and left to evaporate acetone. The residue was reconstituted in 0.01M CaCl_2 aq. In order to grant proper dissolution of the test compound the flask was shaken for 2 hours on mechanical shaker. That solution was used to prepare other treatment solutions used in the experiment examining batch sorption of Flufenacet.

As a first step was performed a preliminary experiment aimed on the determination of appropriate equilibration time. It was performed in 50-mL glass-joint test tubes containing 10 g soil and 20 mL solution – 0.01M CaCl_2 aq containing 10 mg/L Flufenacet. That gave the soil:solution ratio 1:2. In the paper it was not determined on what basis that ratio was selected. The so prepared samples were equilibrated for 1, 2, 4, 6, 12 and 24 hours by shaking on a mechanical shaker. At designated time points (listed above) samples were removed, centrifuged and clear supernatants analysed for the content of the test compound – Flufenacet. It was stated that the maximum sorption occurred during first 2-4 hours, depending on the test soil. Therefore the 4-hours equilibration time was selected as optimum for further examination.

The main test – the examination of the adsorption of Flufenacet onto soil at equilibrium in order to determine the parameters of Freundlich adsorption isotherm was carried out in glass tubes containing the test soil and 0.01M CaCl_2 aq solution in ratio 1:2 (10 g soil: 20 mL solution). The test compound – Flufenacet was introduced into the system in the solution. Its initial concentrations were: 0.0 mg/L, 0.1 mg/L, 0.5 mg/L, 1 mg/L, 2 mg/L, 5 mg/L, 10 mg/L 20 mg/L and 30 mg/L. The equilibration time was 4 hours at room temperature. Samples were prepared in duplicate. After equilibration samples were centrifuged for 10 min at 2000 rpm, clarified supernatants decanted and their 5-mL aliquots diluted with 5 mL of saturated NaCl aqueous solution, then extracted with three 20-mL portions of CH_2Cl_2 . Organic extract was collected, combined and dried by passing through anhydrous Na_2SO_4 . It was then evaporated to dryness, reconstituted in n-hexane and analysed by GC-ECD.

The desorption isotherm was determined in a separate study using one concentration of the test compound – 30 mg Flufenacet/L (highest concentration tested in the experiment on adsorption). The soil:solution ratio was 1:2 and the samples containing the test compound were equilibrated for 4 hours. After that time samples were centrifuged, supernatant decanted and a fresh 20-mL portion of a blank 0.01M CaCl_2 aq solution added. The samples were equilibrated for another 4 hours and then centrifuged and the clarified supernatants collected and processed in the same way as described for the adsorption phase. The procedure was repeated five times to obtain the data for five-step desorption process.

All samples were analysed using GC-ECD technique on Helwett Packard 5890 Gas Chromatograph equipped with ^{63}Ni electron capture detector. The separation was performed on megabore HP-1 capillary GC column, 10-metres long, 0.53-mm of internal diameter and having 2.65 μm -thick film. The GC oven was programmed at initial temperature of $T = 160^\circ\text{C}$ lasting for 9 minutes, then increasing at rate $30^\circ\text{C}/\text{min}$ to $T = 260^\circ\text{C}$, held at that level for 3 minutes. The carrier gas was N_2 administered at a rate 15 mL/min. For Flufenacet the $R_t = 7.4$ min.

The numerical results of the experiment presenting the concentrations of Flufenacet in solution and that adsorbed onto soil were not provided. Instead in the paper were presented the results of the determination of the distribution coefficients for Flufenacet in each test soil and for each initial concentration in solution. They are presented below in the table B.8.1.2.1.1._CA-61.

Table B.8.1.2.1.1._CA-61: The adsorption distribution coefficients – K_d , determined for Flufenacet in each test soil.

Initial (nominal) concentration of Flufenacet [mg/L]	The K_d [mL/g] values determined for Flufenacet in the test soil:				
	<i>Delhi</i> (Loamy sand)	<i>Ranchi</i> (Sandy clay loam)	<i>Nagpur</i> (Clay)	<i>Kerala</i> (Sandy clay loam)	<i>Assam</i> (Silt loam)
0.1	1.57	2.44	0.99	5.69	0.90
0.5	2.11	2.88	2.98	2.76	0.88
1.0	2.72	4.05	3.54	4.89	0.74
2.0	2.52	6.58	3.62	2.88	0.53
5.0	2.38	5.76	3.89	4.76	0.68
10.0	2.12	4.70	3.87	5.24	0.58
20.0	2.07	3.21	3.84	5.21	1.08
30.0	1.60	2.74	3.57	4.73	0.77
<i>average K_d</i>	<i>2.14</i>	<i>4.05</i>	<i>3.29</i>	<i>4.52</i>	<i>0.77</i>

In the paper there were presented the adsorption isotherms determined in each soil for the not transformed equilibrium concentrations of Flufenacet in soil and solution (they are not presented here due to the copyright restrictions; to see them the readers are kindly asked to refer to the original paper). In case of the four isotherms – those obtained in Delhi Loamy sand soil, Ranchi Sandy clay loam soil, Nagpur Clay soil and Kerala Sandy clay loam soil, the shape of the isotherms complied with the model Freundlich sorption isotherm (Linear or Type I isotherm, in the paper named “C” type isotherm). In case however of Assam soil, the isotherm acquired a different shape – sigmoidal (Type V isotherm), therefore more appropriate model describing adsorption in that soil seems to be BET isotherm.

The concentrations at equilibrium, for both adsorption and desorption, were logarithmically transformed (Log_{10} -transformation) in order to determine Freundlich sorption isotherms in their linearised form and Freundlich sorption parameter for adsorption and desorption processes. The resulting linear regression equations and corresponding correlation coefficients are presented below in the table B.8.1.2.1.1._CA-62. In case of Assam soil the regression equations and corresponding correlation coefficients are given in italics, because the shape of the adsorption isotherm indicate that they may not well comply with the Freundlich model.

Table B.8.1.2.1.1._CA-62: The regression equation for linearised Freundlich adsorption and desorption isotherms obtained for Flufenacet in each test soil.

Test soil	Isotherms determined for the process of:			
	<i>Adsorption</i>		<i>Desorption</i>	
	Regression equation	Correlation coefficient r	Regression equation	Correlation coefficient r
<i>Delhi (Loamy sand)</i>	$\text{Log}(C_s) = 0.3230 + 0.9963 \text{ Log}(C_e)$	0.99	$\text{Log}(C_s) = 1.2954 + 0.1205 \text{ Log}(C_e)$	0.94
<i>Ranchi (Sandy clay loam)</i>	$\text{Log}(C_s) = 0.5588 + 0.9812 \text{ Log}(C_e)$	0.98	$\text{Log}(C_s) = 0.8086 + 0.4358 \text{ Log}(C_e)$	0.91
<i>Nagpur (Clay)</i>	$\text{Log}(C_s) = 0.5056 + 1.2213 \text{ Log}(C_e)$	0.99	$\text{Log}(C_s) = 1.1621 + 0.4430 \text{ Log}(C_e)$	0.85
<i>Kerala (Sandy clay loam)</i>	$\text{Log}(C_s) = 0.6429 + 1.0151 \text{ Log}(C_e)$	0.99	$\text{Log}(C_s) = 1.5380 + 0.0856 \text{ Log}(C_e)$	0.97
<i>Assam (Silt loam)</i>	$\text{Log}(C_s) = -0.1206 + 0.985 \text{ Log}(C_e)$	0.99	$\text{Log}(C_s) = 0.6015 + 0.4395 \text{ Log}(C_e)$	0.96

The determined parameters of the Freundlich adsorption isotherm, including the change in free Gibbs energy - ΔG in function of the organic matter content, are presented below in the table B.8.1.2.1.1._CA-63. RMS decided not to present the parameters of the Freundlich desorption isotherm as from the paper it was not clear how that isotherm was experimentally determined. RMS decided not to present the results obtained in Assam Silt loam soil.

Table B.8.1.2.1.1._CA-63: The determined Freundlich adsorption parameters for Flufenacet in each test soil

Test soil	OM content [%]	Freundlich isotherm parameters				Thermodynamic effect - ΔG_{OM}
		K_F [mL/g]	K_{FOM} [mL/g]	K_{FOC} [mL/g]	1/n	
<i>Delhi</i> (Loamy sand)	0.864	2.10	243.06	419.16	0.996	-3.27
<i>Ranchi</i> (Sandy clay loam)	0.072	3.62	5027.78	8619.05	0.981	-5.08
<i>Nagpur</i> (Clay)	0.688	3.20	465.12	802.00	1.221	-3.66
<i>Kerala</i> (Sandy clay loam)	0.786	4.39	558.52	962.72	1.015	-3.77

Additionally for the adsorption process the effect of different physico-chemical soil properties – soil pH, OM content and clay content, on the phenomenon was determined. That was done by calculating the multiple regression equation between soil properties and the Freundlich adsorption constant – K_F . The calculated equation was following:

$$K_F = 4.27 + 1.3248 (\% \text{ OM}) + 0.0644 (\% \text{ clay}) - 0.5511 \text{pH}$$

with correlation coefficient $r = 0.95$.

The results of the examination of the multi-step desorption using a single, highest, concentration are presented below in the table B.8.1.2.1.1._CA-64.

Table B.8.1.2.1.1._CA-64: The results of the determination of multi-step desorption.

Test soil	Flufenacet adsorbed at equilibrium [mg/kg soil]	% of initially adsorbed flufenacet desorbed at:				
		Step 1	Step 2	Step 3	Step 4	Step 5
<i>Delhi</i> (Loamy sand)	26.69	4.20	1.13	9.90	8.40	8.30
<i>Ranchi</i> (Sandy clay loam)	24.92	16.40	13.70	7.60	4.50	2.60
<i>Nagpur</i> (Clay)	41.00	7.34	7.15	6.70	3.86	3.24
<i>Kerala</i> (Sandy clay loam)	42.18	3.40	2.10	1.73	1.26	0.86
<i>Assam</i> (Silt loam)	16.62	5.16	13.50	9.70	6.40	3.20

Conclusions drawn from the study were following:

- Flufenacet was moderately to strongly adsorbed to all test soils;
- The adsorption was only partly reversible and the release by desorption was expected to be slow;
- The process was spontaneous and its mechanism was predominantly a physisorption;
- It was strongly and positively correlated with soil organic matter content, while the correlation with soil pH was negative;
- The influence of the soil clay content on the adsorption of Flufenacet onto the test soils did not play a significant role;
- At the same time it was stated that none of the soil properties individually were highly correlated with the process, but the high correlation was observed for the combination of all three of them;
- At least in four of five test soils the adsorption was in good agreement with the assumed model – Freundlich isotherm.

RMS comments:

The study protocol indicates that it was in line with the provisions of the OECD 106 Guideline. However, the fact that the test soil was a non-EU soils and some stated limitations of the study itself and the reporting of its results (e. g. concentrations at equilibrium for the adsorption phase not reported) lead to the conclusion that the adsorption parameters determined in it cannot be used to derive the EU regulatory endpoints. The results may be

therefore considered solely as indicative. It is worth noting that the study confirms the observation made in the previously summarised study that the adsorption is spontaneous and predominantly is physical in its nature.

Study 7:

Report: Rouchaud J.^{a)}, Neus O.^{a)}, Eelen H.^{b)}, Bulcke R.^{b)} (2001): “Persistence, Mobility and Adsorption of the Herbicide Flufenacet in the Soil of Winter Wheat Crops.”; Laboratory of Phytopharmacy, Université Catholique de Louvain, B-1348 Louvain-la-Neuve, Belgium (a) and Weed Research Center, Universiteit Ghent, B-9000 Gent, Belgium; published study - published in: “The Bulletin of Environmental Contamination and Toxicology”, vol 67, 2001, pp 609 – 616.

Guidelines: None declared as this is an open-source study, therefore not submitted for the regulatory purposes.

GLP: no, not applicable – peer-reviewed scientific paper;

RMS comments: The paper presents the results of the examination of persistence of Flufenacet in soil under realistic – field conditions. The compound was performed on four trial sites located in Belgium, on which winter cereals (winter wheat) were grown. The test compound – Flufenacet was applied to the soil as post-emergent pesticide, in autumn, at application rate 240 g/ha. examined for two fortification levels. Although in the paper it was not indicated that the part of the experiment aimed on the determination of adsorption parameters was performed line with any relevant guidelines, it can be stated that the study protocol generally seems to comply with the provisions of the OECD 106 Guideline. However only the final results of the examination – Freundlich isotherm adsorption parameters were reported. For that reason, although the level of detail enabled the evaluation of the study for its validity (the study may be considered valid, and therefore is summarised below), RMS is of the opinion that the results it provides may be regarded only as supplementary and confirmatory to the endpoints provided by the regulatory studies submitted by the Applicant and should not be used as a source of regulatory endpoints.

Summary:

The paper contains an abstract, outlining the aims of the experiment and its key results, which was made available on-line. However, due to the copyright restrictions RMS could not present it here and the readers are kindly asked to consult the relevant document. Instead, below is presented the extended summary prepared by the RMS.

Extended summary prepared by RMS:

The aim of the study was to examine the persistence and mobility of Flufenacet in soil under realistic – field conditions and on cropped field. The experiment was performed on four trial sites in Belgium: Melle, Zingem and Zevekote, located 40 km apart, and Cortil-Noirmont, 100 km-distant from Melle. The characteristic of each trial site, as provided in the paper, is given below in the table B.8.1.2.1.1._CA-65.

Table B.8.1.2.1.1._CA-65: The brief characteristic of the trial sites.

Parameter		Trial site			
		Melle	Zingem	Zevekote	Cortil-Noirmont
Soil type		Sandy loam	Loamy sand	Clay loam	Silt loam
Particle size distribution	Sand [%]	55	79	19	11
	Silt [%]	38	11	45	75
	Clay [%]	7	10	36	14
pH value		7.0	6.4	6.6	6.7
Organic matter content (OM) [%]		1.51	1.60	2.12	1.2

The organic fertilization of soil on the trial sites was following:

- on Melle trial site no organic fertilizer was used on the year when the experiment started – 1999; before that year the trial site was fertilized every second year at spring with 40 tonnes/ha of either cow slurry or cow manure;

- on Zevekote trial site no organic fertilizer was used on the year when the experiment began – 1999; before that date the trial site was fertilized every second year, in September with 40 tonnes/ha of pig slurry or 40 tonnes/ha of cow manure;
- on Zingem trial site on the year when the experiment started – 1999, the soil was fertilized with cow manure applied at rate 40 tonnes/ha in October; in the preceding years the test field was fertilized every second year with either 40 tonnes/ha of cow manure or 40 tonnes/ha of pig slurry;
- on Cortil-Noirmont on the year when the experiment started soil was organically fertilized by incorporation of the leftovers of the preceding crop (sugar beet leaves) into the soil; in preceding years the test fields were fertilized by applying onto them 40 tonnes/ha of the cow manure every fourth year.

At the beginning of the experiment – in November 1999, test fields were tilled to prepare a seed bed and winter wheat was sown. On each test field four 6 x 10 metres plot were located at random, onto which the test substance – Flufenacet, was applied. It was applied to the soil surface of the test fields at rate 240 g/ha on the following dates:

- Melle trial site: on 25th November 1999;
- Zingem trial site: on 25th November 1999;
- Zevekote trial site: on 26th November 1999;
- Cortil-Noirmont: on 26th November 1999.

Additionally at trial sites Melle and Zingem the test compound was applied to the previously untreated plots at the same application rate in early spring of the following year : on 17th March 2000 at Melle and 4th April 2000 at Zingem.

One day before the autumn application of the test compound – Flufenacet onto the soil on each of the trial sites, from each test field soil samples were taken from the 0-10 cm layer. The sampled soils were used in the experiment aimed on the examination of the soil sorption of Flufenacet. This was a supplementary experiment aimed on the identification of the factors other than climatic conditions, such as bioavailability of the test compound, that possibly influenced the rate of degradation of Flufenacet under realistic – field conditions.

The equilibrium sorption was examined in the test system with soil solution ratio 1:2 (100 g soil and 200 mL 0.01M CaCl₂ _{aq} solution containing the appropriate amount of Flufenacet). The selected equilibration time was 24 hours. The experiments were performed in the dark at constant temperature T = 20°C. The test compound – Flufenacet was administered in form of the aqueous solutions in 0.01M CaCl₂. The initial concentrations of the test item selected for the experiment were: 20, 50, 100 and 200 µg/kg water (solution?).

After equilibration the test vessels were centrifuged for 10 minutes at 3500 rpm and the liquid – clear supernatant, and solid – remaining soil, phases analysed separately for the content of Flufenacet. The analytical procedure has already been described in the summary of the same study (**Study 10**) provided under the point B.8.1.1.2.2.1._CA of this renewal assessment report. The determined parameters of the Freundlich adsorption isotherm for Flufenacet in each test soil are presented below in the table B.1.2.1.1._CA-66.

Table B.8.1.2.1.1._CA-66: The parameters of the Freundlich adsorption isotherm determined for Flufenacet in each test soil.

Test soil	Freundlich adsorption isotherm parameters		
	K _F [mL/g]	1/n	K _{F OC} [mL/g]
<i>Melle (Sandy loam)</i>	16	0.89	1802
<i>Zingem (Loamy sand)</i>	43	0.91	4602
<i>Zevekote (Clay loam)</i>	15	0.93	1231
<i>Cortil-Noirmont (Silt loam)</i>	9	0.94	1257

RMS comments:

The study protocol indicates that it was in line with the provisions of the OECD 106 Guideline. However, due to the deficiencies displayed by the study protocol – the description of the experiment was very brief, as well as the fact that the examination of the adsorption was only a supplementary experiment carried out with aim to explain what are the possible mechanisms influencing the rate of degradation of Flufenacet in soil under realistic – field conditions, RMS is of the opinion that that the adsorption parameters determined in it cannot be used to derive the EU regulatory endpoints.

Summary: the sorption of Flufenacet onto soil at equilibrium

The Applicant submitted four studies examining the sorption of Flufenacet onto soil at equilibrium – two “existing” studies, evaluated for the previous authorisation of Flufenacet in the EU, and two new studies. Their evaluation carried out for the purpose of the present assessment showed that one “existing” study cannot be considered acceptable because the equilibrium sorption was examined at variable temperature (the differences were up to 7°C).

Three remaining studies were considered acceptable, although the determined Freundlich adsorption isotherm parameters cannot be considered reliable for all test soils (those obtained in two of twelve test soils had to be rejected because one of them was found not representative and the other had too low OC content to consider the adsorption parameters fully reliable). The reliable results are presented below in the table B.8.1.2.1.1._CA-67. On their basis it can be stated that Flufenacet displays medium to low mobility in soil. It was also stated that the adsorption of Flufenacet onto soil is not a pH-dependent process.

Table B.8.1.2.1.1._CA-67: The final results of the determination of the adsorption of Flufenacet onto soil at equilibrium – the reliable parameters of the Freundlich adsorption isotherm.

Soil name	Soil properties			Adsorption distribution coefficients		Freundlich adsorption isotherm parameters			
	Soil type (USDA)	pH	OC [%]	K_d [mL/g]	$K_{d\text{OC}}$ [mL/g]	K_f [mL/g]	$K_{f\text{OC}}$ [mL/g]	1/n	R^2
Stanley (307)	Silt loam	5.9	1.68	----	----	3.18	189.28	0.848	0.9971
Hagerstown (318)	Clay loam	6.4	1.28	----	----	2.81	219.53	0.878	0.9986
Howe (395)	Loamy sand	6.4	0.23	----	----	1.48	643.48	0.894	0.9932
Monheim (3253)	Sandy loam	6.4	1.4	----	----	4.55	325.00	0.920	0.9991
Laacher Hof AXXa (AA)	Loamy sand	5.8	2.2	----	----	3.555	161.6	0.928	0.9991
Hoefchen am Hohenseh (HH)	Silt loam	6.5	1.6	----	----	3.280	205.0	0.926	0.9965
Hanscheider Hof (HN)	Silt loam	5.3	2.7	----	----	5.101	188.9	0.926	0.9992
Dollendorf II (DD)	Loam	7.3	4.4	----	----	7.495	178.5	0.903	0.9994
Wurmwielse (WW)	Sandy loam	5.1	1.7	----	----	3.391	195.2	0.980	0.9966
Kamikawa	Loam	4.9	2.1	----	----	8.956	426.5	0.958	0.9984
Geomean (n = 10)						3.89	245.9	----	----
Arithmetic mean (n = 10)						----	----	0.916	----
pH dependence						No		----	

The additional pieces of information on the soil sorption of Flufenacet at equilibrium were provided by three open-literature scientific papers. The key results obtained in them are presented below in the table B.8.1.2.1.1._CA-68. The values reported below may be considered as indicative and should not be used to derive the regulatory endpoints characterising soil sorption of Flufenacet.

Table B.8.1.2.1.1._CA-67: The results of the determination of the adsorption of Flufenacet onto soil at equilibrium obtained in the open-source literature scientific papers.

Study	Soil name	Soil properties			Freundlich adsorption isotherm parameters			
		Soil type	pH	OC [%]	K_f [mL/g]	$K_{f\text{OC}}$ [mL/g]	1/n	r
Gupta, Gajbhiye & Agnihotri; 2001	Inceptisol	Sandy loam	7.1	0.34	2.26	664.71	0.988	0.99
Gajbhiye & Gupta; 2001	Delhi	Loamy sand	7.69	0.501	2.10	419.16	0.996	0.99
	Ranchi	Sandy clay loam	5.54	0.042	3.62	8619.05	0.981	0.98
	Nagpur	Clay	8.35	0.399	3.20	802.00	1.221	0.99
	Kerala	Sandy clay loam	4.45	0.456	4.39	962.72	1.015	0.99
Rouchaud, Neus, Eelen, Bulcke; 2001	Melle	Sandy loam	7.0	1.51 ¹⁾	16	1802	0.89	----
	Zingem	Loamy sand	6.4	1.60 ¹⁾	43	4602	0.91	----
	Zevekote	Clay loam	6.6	2.1 ¹⁾	15	1231	0.93	----
	Cortil-Noirmont	Silt loam	6.7	1.2 ¹⁾	9	1257	0.94	----

Footnotes to the table:

1) OM content reported, no values for OC content

In the studies by [Gupta, Gajbhiye and Agnihotri; 2001] and [Gajbhiye and Gupta; 2001] for adsorption of Flufenacet onto test soil the value of the free Gibbs energy of adsorption – ΔG , was determined. It was in range $\Delta G = (-3.27) - (-5.08)$ [Kcal/mol], indicating that adsorption of Flufenacet onto soil was a spontaneous process and mechanistically it was predominantly physisorption. It was also demonstrated, in the study by [Gupta, Gajbhiye and Agnihotri; 2001], that the soil sorption of Flufenacet was strongly positively correlated with soil OC/OM content. As the results obtained in these two studies are in line with those obtained in reliable regulatory studies, that conclusion may be considered to be a general conclusion with regard to the adsorption of Flufenacet onto soil.

Additionally all results of the examination of the adsorption of Flufenacet onto soil at equilibrium considered relevant for the regulatory purpose are presented below in format recommended for reporting the EU end points.

Soil adsorption active substance (Regulation (EU) N° 283/2013, Annex Part A, point 7.1.3.1.1 and Regulation (EU) N° 284/2013, Annex Part A, point 9.1.2.1)

Parent							
Soil Type	OC %	Soil pH ^{a)}	K _d (mL/g)	K _{doc} (mL/g)	K _F (mL/g)	K _{Foc} (mL/g)	1/n
Silt loam	1.68	5.9 ¹⁾			3.18	189.28	0.848
Clay loam	1.28	6.4 ¹⁾			2.81	219.53	0.878
Loamy sand	0.23	6.4 ¹⁾			1.48	643.48	0.894
Sandy loam	1.4	6.4 ¹⁾			4.55	325.00	0.920
Loamy sand	2.2	5.8 ²⁾			3.555	161.6	0.928
Silt loam	1.6	6.5 ²⁾			3.280	205.0	0.926
Silt loam	2.7	5.3 ²⁾			5.101	188.9	0.926
Loam	4.4	7.3 ²⁾			7.495	178.5	0.903
Sandy loam	1.7	5.1 ²⁾			3.391	195.2	0.980
Loam	2.1	4.9 ³⁾			8.956	426.5	0.958
Geometric mean (if not pH dependent)*					3.89	245.9	
Arithmetic mean (if not pH dependent)							0.916
pH dependence, <i>Yes or No</i>			No				

^{a)} Measured in: medium not specified for values marked 1), 0.01M CaCl₂ for values marked 2) and CaCl₂ for values marked 3);

* Only relevant after implementation of the published EFSA guidance.

B.8.1.2.1.2. – Adsorption and desorption of the metabolites

The Applicant submitted four study reports presenting the results of the examination of the equilibrium sorption of the degradation products of Flufenacet onto soil. Of them one is existing study, evaluated for the previous authorisation of the active substance in Europe and the remaining three are the new studies, submitted to address the issue of the soil sorption of three degradation products not previously identified as major soil and/or aquatic degradation products. They are summarised below as **Studies 1-4**. Additionally the already summarised in its part related to the degradation in soil under aerobic soil study on the long-term of FOE Sulfonic acid provides the data that may be used to estimate the approximate parameters of the Freundlich sorption isotherm for that compound. The RMS decided to present these data in the study summary as **Study 5**. However, in RMS's opinion these results should be considered as conformatory only and not to be used to derive the regulatory endpoints. Finally, for FOE Methylsulfide – the major aquatic degradation product of Flufenacet RMS determined the adsorption constant using QSAR method. The results are presented in the short report under the heading **Study 6**.

The repeated open literature search did not result in identification of any publications examining the adsorption of the degradation products of Flufenacet.

The examination of fate and behaviour of Flufenacet in aquatic environment (aerobic water/sediment system studies) resulted in identification of an additional degradation product not found in soil – FOE Methylsulfide. As for that degradation products no study examining its sorptive behaviour was submitted by the Applicant, RMS decided to estimate its adsorption parameters – the would be adsorption constant K_{OC} , using QSAR methods. The calculations are briefly characterised under this data point as **Study 6**, while the full report of QSAR estimation, performed using EPISuite tool, is provided in the Appendix 3 to this Assessment Report.

Study 1:

Report: Blumhorst M. R., Yen P. Y., Marlow V. A. (1994): "Soil Adsorption/Desorption of FOE 5043 Degradates: FOE Sulfonic acid, FOE Methyl Sulfoxide, FOE Oxalate, FOE Alcohol and Thiadone."; EPL Bio-analytical Services, Inc. (EPL-BAS), P. O. Box 109, 395N. Memorial Parkway, Harristown IL 62537, USA (performing laboratory) for Miles Inc., Agriculture Division, Research and Development Department, P. O. Box 4913, Kansas City, MO 64120- 0013, USA; EPL-BAS study No. 122S19, study report (Miles) No. MR 106598; 26 September 1994; study reference number: M-002185-01-1;

Guidelines: The study was performed to comply with the following Guidelines:

- US. EPA Guidelines for Pesticide Registration, Subdivision N, Section 163-1, Adsorption/Desorption.

GLP: Yes;

RMS comments: The study had been evaluated for the previous authorisation of Flufenacet in the EU, by its inclusion into the Annex I of the Directive 91/414/EEC. Its summary can be found under the point B.7.2.1.1, in section B.7 of the Annex B to the Monograph prepared by the RMS – France, for Flufenacet. For the present authorisation in the EU the study was evaluated for its compliance with OECD Guideline for the Testing of Chemicals 106 – Adsorption-Desorption Using a Batch Equilibrium Method. Additionally the study was checked for its validity against the US EPA Fate, Transport and Transformation Test Guidelines OPPTS 835.1230 – Adsorption/Desorption (Batch Equilibrium) and OPPTS 835.1220 – Sediment and Soil Adsorption/Desorption Isotherm as well as SETAC Guidance Document "Procedures for Assessing the Environmental Fate and Ecotoxicity of Pesticides.". Also consulted was the Guideline which was declared in the study report to be a reference document – US EPA Guideline 163-1 for determining the adsorption/desorption of chemicals. The following deviations from the main Guideline – OECD 106, were stated:

- The pH of the test soils, measured in water, was too narrow, being in range 5.8 – 6.6, and therefore not covering at all the range for alkaline soils and narrowly that for acidic soils. Taking into account however the sorptive properties of the test compounds it may be stated that it will not have a significant influence on the conclusions of the study. That is because all degradation products, which are n.b. rather strong organic acids, are weakly sorbed onto soil and the would-be pH-dependence of the adsorption would probably not significantly alter the Freundlich adsorption constants.

- Of the four test soils one – Vero Beach Sand soil displayed lower than recommended OC content – 0.27%. It shall be indicated however that in light of the provisions of the Guideline declared as a reference for this study – US. EPA Guidelines for Pesticide Registration, Subdivision N, Section 163-1, Adsorption/Desorption, that test soil was selected correctly.
- The definitive experiment – the determination of Freundlich sorption isotherms and Freundlich parameters for adsorption and desorption processes, was carried out using only four concentrations of the test items, while OECD 106 Guideline recommends to use for that purpose five. However such solution was in line with the recommendations of the evoked US EPA Guidelines and SETAC Guidelines, therefore it may be considered acceptable.
- The amount of the test items sorbed onto soil during the preliminary tests was lower than the recommended 20% in case of either some test soils – the problem observed for FOE Methyl Sulfoxide, FOE Alcohol and FOE Thiadone, or all soils – as stated for FOE Sulfonic acid and FOE Oxalate. For that reason the soil solution ratio used in the experiment was 3:10, corresponding to 1:3.333. In such cases the best solution, recommended by OECD 106 Guideline, would be to use 1:1 soil:solution ratio. However, due to the fact that the compounds displayed consistently low adsorption onto soil, that deviation had, in RMS's opinion, not very significant impact on the outcome of the study.

In general, despite the problems listed above, RMS found the study acceptable, and possible to be used for the regulatory purposes. The study is summarised below.

Summary:

The aim of the study was to examine soil sorption – adsorption and desorption, and determine Freundlich sorption isotherm parameters Freundlich adsorption/desorption constants and corresponding $1/n$ values, for five degradation products of Flufenacet – FOE Sulfonic acid, FOE Methyl Sulfoxide, FOE Oxalate, FOE Alcohol and FOE Thiadone. The experiment was carried out on four test soils, characterised below in the table B.8.1.2.1.2_CA-1.

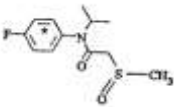
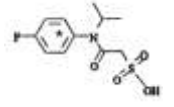
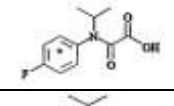
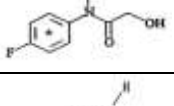
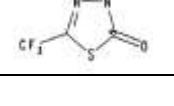
Table B.8.1.2.1.2_CA-1: The characteristic of soils used in the study.

Parameter		Soil			
		<i>Winder (396)</i>	<i>Shipshe (411)</i>	<i>Drummer (413)</i>	<i>Oska-Martin (414)</i>
Soil origin		Vero Beach, FL, USA	Howe, IN, USA	Champaign, IL, USA	Stilwell, KS, USA
Soil textural class (USDA)		Sand	Sandy loam	Silty clay loam	Silty clay
Particle size distribution	Sand [%]	92.5	68.5	11.1	3.1
	Silt [%]	1.3	17.6	54.1	47.1
	Clay [%]	6.3	13.9	34.8	49.8
Soil pH (in water)		5.8	6.3	6.6	6.0
Organic matter content (OM) [%]		0.5	1.3	3.7	2.1
Organic carbon content (OC) [%]		0.27	0.75	2.13	1.21
CEC [meq/100 g]		3.3	7.9	22.4	29.3
Moisture content @ $\frac{1}{3}$ bar [%]		5.0	8.3	24.8	28.1

No information concerning the sampling procedures of the test soils was provided in the study report.

The study was performed using the test compounds in radiolabelled and non-radiolabelled form (technical-grade test items). The characteristic of the radiolabelled test compounds is provided below in the table B.8.1.2.1.2_CA-2. The structural formulas reported in the table are copied from the study report and the radiolabelling position is indicated with an asterisk (*). Below that table are provided the key parameters characterising their non-radiolabelled (technical-grade) equivalents. The structural formulas of the test items are not provided as they would be identical to those presented in the preceding table.

Table B.8.1.2.1.2._CA-2: The characteristic of the radiolabelled test compounds used in the experiment (structural formulas copied from the study report).

Test compound			Properties of the compound			
Name	Empirical formula	Structural formula (radiolabelling position marked with asterisk – *)	Purity [%]	Specific activity		Solvent
				expressed in [mCi/mmol]	expressed in [μCi/mg]	
FOE Methylsulfoxide	C ₁₂ H ₁₆ O ₂ SNF		98.8	21.0	81.7	CH ₃ CH ₂ OH
FOE Sulfonic acid	C ₁₁ H ₁₄ O ₄ SNF		99.3	21.0	76.4	CH ₃ CN/H ₂ O
FOE Oxalate	C ₁₁ H ₁₂ O ₃ NF		98.0	50.2	222.9	CH ₃ CN
FOE Alcohol	C ₁₁ H ₁₄ O ₂ NF		97.0	115.8	549	CH ₃ CN
FOE Thiadone	C ₃ HOSN ₂ F ₃		99.7	57	335	(CH ₃) ₂ O

The non-radiolabelled, technical grade FOE Methylsulfoxide was delivered as a liquid sample, having a purity of 93.1%. The technical grade (non-radiolabelled) FOE Sulfonic acid was delivered as a solid sample having a purity of 98.5%. The technical grade (non-radiolabelled) FOE Oxalate was delivered in form of a solid sample having a purity of 98.8%. The technical (non-radiolabelled) FOE Alcohol was delivered as solid sample having a purity of 99.4%. The technical (non-radiolabelled) FOE Thiadonewas delivered in form of a solid sample having a purity of 97.5%.

The radiolabelled test items and their non-radiolabelled counterparts were used to prepare stock solutions, separate for each test compound, subsequently used to prepare treatment solutions used at each step of the experiment.

The stock solutions were prepared by dissolving the appropriate amounts of the given technical-grade and radiolabelled test item in 5 mL of solvent. In case of FOE Sulfonic acid the solvent was CH₃CN/H₂O. The stock solutions of the remaining four test compounds were prepared in CH₃CN.

The processes of adsorption of the test compounds onto soil and their desorption were examined using the 0.01N CaCl₂ aq as the liquid phase. The blank 0.01N CaCl₂ aq was sterilised prior to use by filter-sterilisation (by passing through 0.2-μm filter).

The whole experiment consisted of the following stages:

- **First preliminary study** in which the most appropriate soil:solution ratio was determined and the possible adsorption of the test item to the test vessels was monitored;
- **Second preliminary study** aimed on the determination of the time required for adsorption equilibrium to be achieved;
- **The definitive test** in which Freundlich adsorption and Freundlich desorption isotherms were determined and their parameters derived.

All experiments were performed in glass centrifuge tubes sealed with Teflon-lined caps.

The **First preliminary study** was carried out using a treatment solutions prepared from a stock solutions by dissolving them in appropriate amount of blank sterilised 0.01N CaCl₂ aq to obtain 1000 mL of solutions having a concentration of 5 μg test item/mL. For each test compound an individual treatment solution was prepared.

For each test compound the appropriate amounts of each test soils were weighed into the test tubes and then 25 mL of treatment solution were added to obtain the following soil:solution ratios (determined on the basis of soil dry weight and assumed solution density 1 g/cm³):

- for FOE Methylsulfoxide and FOE Sulfonic acid the tested soil:solution ratios were: 1:5, 1:10, 1:20 and 1:50;
- for FOE Oxalate, FOE Alcohol and FOE Thiadone the tested soil:solution ratios were: 1:3, 1:5, 1:10 and 1:20.

In case of the three later compounds initially it was planned to test the same ratios as for FOE Methylsulfoxide and FOE Sulfonic acid, but because in the experiments with those two compounds the determined level of adsorption was relatively low, it was decided to change the examined ratios.

For each test compound and tested soil:solution ratio the samples were prepared in duplicate. Additionally for each test compound a control sample (in replicate) was prepared. The control sample contained only treatment solution of the given test compound (soilless samples).

After introduction of the treatment solution into the test vessels the test vessels were sealed with Teflon caps and shaken for 24 hours in the dark at constant temperature $T = 23.5 \pm 1.5^{\circ}\text{C}$. After that period the samples were centrifuged and from each three 1-mL aliquots of supernatant analysed by LSC.

Next test – the **Second preliminary study**, carried out to determine the optimal equilibration time, was performed using the treatment solution prepared in the same way as described above for the **First preliminary test**. The target concentration of that solution was also 5 μg test item/mL. The soil:solution ratio used in this experiment (approximate) was 1:3. To obtain it to the test vessels 6-g portions of the given test soil were weighed and 20 mL of the treatment solution containing the given test compound added (n.b. RMS on the basis of this description stated that the exact soil:solution ratio was not 1:3 but 1:3.3333). After introduction of the treatment solutions the test vessels were sealed with Teflon –lined caps and placed on the shaker to be equilibrated for up to 72 hours in the darkness and at constant temperature $T = 23.5 \pm 1.5^{\circ}\text{C}$. At pre-defined time points – 2, 8, 24, 48 and 72 hours after initiation of the experiment, duplicate samples were taken for analysis – the vessels were centrifuged and three 1-mL aliquots of the supernatant analysed by LSC for the content of the test item. Additionally the samples collected after 72 hours of equilibration were analysed by radio-HPLC to determine the stability of the test item.

For each test compound were set two control, soilless, samples, equilibrated for 72 hours and analysed after that time.

The definitive study, aimed on the determination of Freundlich adsorption and desorption isotherms and their parameters, was carried out for each test compounds using four initial concentrations: 0.04 mg/L, 0.2 mg/L, 1.0 mg/L and 5.0 mg/L.

The treatment solutions used in the experiment were prepared in the following way: firstly the stock solution of the technical grade substance was prepared in 5.0 mL of CH_3CN or $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ solution. From it on the day of initiation of the experiment the treatment solution, having a concentration approx. 5 μg test compound/mL, was prepared. This was done by transferring 0.5 mL of the characterised above stock solution and the appropriate amount of radiolabelled test substance (in less than 0.5 mL solvent) to 100-mL volumetric flask. The solution was brought to the volume with 0.01N CaCl_2 aq to obtain a treatment solution having the highest concentration – 5.0 mg/L. Next treatment solutions, having lower concentrations, were prepared by diluting that treatment solution with appropriate amount of 0.01N CaCl_2 aq in a serial-dilution procedure. The concentration of each treatment solution was verified by LSC.

Next, to examine the adsorption at equilibrium, to each pre-weighed test vessel 6-g portion of the appropriate test soil was weighed and 20 mL of appropriate treatment solution added. pH of each so prepared sample was determined, the test vessels sealed with Teflon-lined caps and placed on a shaker to be equilibrated for 24 hours in the dark at constant temperature $T = 23.5 \pm 1.5^{\circ}\text{C}$. After that time samples were centrifuged for 15 minutes at 2000 rpm, clarified supernatants collected, their volume measured and 5-mL aliquots analysed using LSC and radio-HPLC.

After removal of supernatant the test vessels with moist soil were weighed to determine the mass of the remaining soil. The volume of solution in the test vessels was brought to 20 mL using blank 0.01N CaCl_2 aq solution and so prepared samples were equilibrated for 24 hours in the same conditions as for examining the adsorption phase. After 24-hours equilibration samples were processed in the same manner as described above for the examination of the adsorption. The whole procedure was repeated three times to obtain three-step desorption.

After the last step of desorption the test vessels with remaining soil were weighed to determine the amount of the moist soil. Next the amount of the radioactivity retained by each test soil after desorption was determined. For that purpose four subsamples of each soil sample were oxidised using Harvey Model OX-550 oxidizer and generated $^{14}\text{CO}_2$ quantified by LSC. That value was subsequently used, together with the values determined in solution during the examination of adsorption and desorption, to calculate the mass balance.

All samples were quantitatively analysed by LSC. The method was not characterised, only the LOD values were reported. That parameter was determined in background checks and was defined to be $3 \times \text{SD}$ (SD = Standard Deviation). It was in range 3.2 – 9.1 dpm.

The supernatants obtained in samples equilibrated for 72 hours in the **Second preliminary study** and all supernatants obtained in **The definitive study** were examined by radio-HPLC.

The chromatographic analysis was performed in a gradient mode using Spherisorb ODS-2 chromatographic column (250 * 4.6 mm; 5 μm) maintained in a constant temperature $T = 40^\circ\text{C}$. The elution lasted for 50 minutes, of which 30 minutes was gradient elution and the remaining 20 elution in isocratic mode. The solvent system consisted of:

- **Solvent A:** 1% CH_3COOH in CH_3CN ;
- **Solvent B:** 1% CH_3COOH in H_2O

The elution programme, in relation to **Solvent A**, was following: at $t = 0.1 \text{ min}$ (beginning of chromatographic analysis) 0% **Solvent A**, linear gradient until $t = 30 \text{ min}$, at $t = 30 \text{ min}$ 100% **Solvent A**, then isocratic elution for next 20 minutes with 100% **Solvent A** until $t = 50 \text{ min}$, at $t = 50 \text{ min}$ end of chromatographic analysis. The flow rate of the solvent system was set to 1 mL/min.

The detection was performed by means of UV detection using UV detector with wavelength set to $\lambda = 230 \text{ nm}$ and LSC detector set in line after UV detector.

The identification of the test compounds was performed by means of the comparison of retention times R_t with those of the known standards. The approximate R_t values for each test compound were following:

- FOE Methylsulfoxide: $R_t = \sim 22 \text{ min}$;
- FOE Sulfonic acid: $R_t = \sim 15 \text{ min}$;
- FOE Oxalate: $R_t = \sim 16 \text{ min}$;
- FOE Alcohol: $R_t = \sim 24 \text{ min}$;
- FOE Thiadone: $R_t = \sim 20 \text{ min}$;

The results of the study are presented and discussed below.

Results and their discussion:

The characteristic of the test soils used in the study has been presented at the beginning of this summary in the table B.8.1.2.1.2._CA-1. On their basis it may be stated that while three test soils – Shpshe sandy loam soil, Drummer Silty clay loam soil and Oska-Martin Silty clay soil fully meet the acceptability criteria set by the OECD 106 Guideline, Winder Sand soil displays lower than recommended OC content – only 0.27% instead of at least 0.3%. At the same time it shall be indicated that that soil fully meets the acceptability criteria set by the reference Guidance document for this study available at the moment of its performance – the US EPA 163-1 Guideline. Therefore it should be also considered acceptable, as well as the results obtained for that soil, although they should be considered with care. RMS noticed that the pH range of the test soils was narrow, covering only slightly acidic and neutral soils. However, taking into account the fact that the compounds display low adsorption potential onto soil, that narrow range is not expected to have a significant impact on the conclusions drawn from the study.

The results of the determination of the soil:solution ratio – the first preliminary study, are presented below, individually for each test compound, in tables B.8.1.2.1.2._CA-3 – B.8.1.2.1.2._CA-8. In the first table – B.8.1.2.1.2._CA-3 are provided the results of the determination of the concentration of the treatment solution for each test compound. The results of the determination of the soil:solution ratio are presented in the tables B.8.1.2.1.2._CA-4 – B.8.1.2.1.2._CA-8. In case in the source tables the negative values were reported for the % adsorbed, RMS replaced them with the value 0%. Such values are indicated with an asterisk – *).

On the basis of the obtained results it was stated that none of the test compound displayed significant affinity to the test vessels. The selected appropriate soil:solution ratio was 1:3.

Table B.8.1.2.1.2._CA-3: The results of the determination of concentration of test compounds in treatment solutions.

Code of treatment solution	Test compound	Specific activity of radiolabelled compound [$\mu\text{Ci}/\text{mg}$]	Concentration of the test compound in solution [$\mu\text{g}/\text{mL}$]			Specific activity of treatment solution [$\mu\text{Ci}/\text{mg}$]
			Radiolabelled	Technical grade	Total	
<i>WG1-I</i>	<i>FOE Methylsulfoxide</i>	82	0.072	4.802	4.87	1.21
<i>WE1-I</i>	<i>FOE Sulfonic acid</i>	76	0.087	4.704	4.79	1.39
<i>WI1-I</i>	<i>FOE Oxalate</i>	223	0.025	5.000	5.03	1.11
<i>WLI-I</i>	<i>FOE Alcohol</i>	549	0.011	5.096	5.11	1.17
<i>WO1-I</i>	<i>FOE Thiadone</i>	335	0.018	4.606	4.62	1.29

Table B.8.1.2.1.2._CA-4: The results obtained in the experiment with FOE Methylsulfoxide.

Test system/test soil	Soil:solution ratio	Characteristic of the test system				Results		
		Repli- cate	Mass of test soil [g d. w.]	Volume of solution [mL]	Initial concentration of the test item [$\mu\text{g}/\text{mL}$]	Repli- cate	Concentration in solution at equilibrium [$\mu\text{g}/\text{mL}$]	% adsorbed onto soil
<i>Blank (no soil)</i>	Not applicable	1	----	25.0	4.87	1	4.71	3.4
		2	----	25.0	4.87	2	4.86	0.3
<i>Winder sand soil</i>	1:5	1	5.002	25.0	4.87	1	4.76	2.3
		2	5.006	25.0	4.87	2	4.76	2.4
	1:10	1	2.502	25.0	4.87	1	4.80	1.6
		2	2.502	25.0	4.87	2	4.76	2.4
	1:20	1	1.255	25.0	4.87	1	4.83	0.9
		2	1.259	25.0	4.87	2	4.79	1.7
	1:50	1	0.499	25.0	4.87	1	4.82	1.1
		2	0.500	25.0	4.87	2	4.80	1.4
<i>Shipshe Sandy loam soil</i>	1:5	1	5.004	25.0	4.87	1	4.52	7.3
		2	5.004	25.0	4.87	2	4.55	6.6
	1:10	1	2.501	25.0	4.87	1	4.72	3.2
		2	2.508	25.0	4.87	2	4.68	4.0
	1:20	1	1.247	25.0	4.87	1	4.74	2.7
		2	1.255	25.0	4.87	2	4.76	2.3
	1:50	1	0.500	25.0	4.87	1	4.82	1.1
		2	0.499	25.0	4.87	2	4.81	1.4
<i>Drummer Silty clay loam soil</i>	1:5	1	5.010	25.0	4.87	1	3.86	20.7
		2	5.005	25.0	4.87	2	3.80	22.0
	1:10	1	2.504	25.0	4.87	1	4.28	12.1
		2	2.498	25.0	4.87	2	4.27	12.4
	1:20	1	1.248	25.0	4.87	1	4.56	6.5
		2	1.255	25.0	4.87	2	4.54	6.8
	1:50	1	0.501	25.0	4.87	1	4.71	3.5
		2	0.502	25.0	4.87	2	4.71	3.5
<i>Oska-Martin Silty clay soil</i>	1:5	1	5.001	25.0	4.87	1	3.50	28.3
		2	5.007	25.0	4.87	2	3.47	28.9
	1:10	1	2.502	25.0	4.87	1	3.91	19.9
		2	2.496	25.0	4.87	2	3.95	19.1
	1:20	1	1.256	25.0	4.87	1	4.30	11.8
		2	1.251	25.0	4.87	2	4.22	13.4
	1:50	1	0.500	25.0	4.87	1	4.61	5.5
		2	0.500	25.0	4.87	2	4.60	5.7

Table B.8.1.2.1.2._CA-5: The results obtained in the experiment with FOE Sulfonic acid.

Test system/test soil	Soil:solution ratio	Characteristic of the test system				Results		
		Repli- cate	Mass of test soil [g d. w.]	Volume of solution [mL]	Initial concentration of the test item [µg/mL]	Repli- cate	Concentration in solution at equilibrium [µg/mL]	% adsorbed onto soil
<i>Blank (no soil)</i>	Not applicable	1	----	25.0	4.79	1	4/79	0.0
		2	----	25.0	4.79	2	4.75	0.9
<i>Winder sand soil</i>	1:5	1	5.003	25.0	4.79	1	4.53	5.5
		2	5.010	25.0	4.79	2	4.33	9.6
	1:10	1	2.507	25.0	4.79	1	4.75	0.9
		2	2.506	25.0	4.79	2	4.78	0.3
	1:20	1	1.257	25.0	4.79	1	4.76	0.7
		2	1.259	25.0	4.79	2	4.75	1.0
	1:50	1	0.500	25.0	4.79	1	4.65	2.9
		2	0.501	25.0	4.79	2	4.61	3.8
<i>Shipshe Sandy loam soil</i>	1:5	1	5.012	25.0	4.79	1	4.58	4.4
		2	5.008	25.0	4.79	2	4.59	4.2
	1:10	1	2.503	25.0	4.79	1	4.64	3.2
		2	2.510	25.0	4.79	2	4.63	3.3
	1:20	1	1.252	25.0	4.79	1	4.67	2.5
		2	1.255	25.0	4.79	2	3.27	31.7
	1:50	1	0.501	25.0	4.79	1	4.60	4.1
		2	0.500	25.0	4.79	2	4.67	2.5
<i>Drummer Silty clay loam soil</i>	1:5	1	5.004	25.0	4.79	1	4.44	7.3
		2	5.010	25.0	4.79	2	4.24	11.5
	1:10	1	2.502	25.0	4.79	1	4.59	4.2
		2	2.499	25.0	4.79	2	4.08	14.9
	1:20	1	1.252	25.0	4.79	1	4.71	1.8
		2	1.254	25.0	4.79	2	4.73	1.2
	1:50	1	0.501	25.0	4.79	1	4.62	3.6
		2	0.501	25.0	4.79	2	4.58	4.5
<i>Oska-Martin Silty clay soil</i>	1:5	1	5.001	25.0	4.79	1	4.80	0.0 ⁹⁾
		2	5.003	25.0	4.79	2	4.75	0.9
	1:10	1	2.502	25.0	4.79	1	4.82	0.0 ⁹⁾
		2	2.496	25.0	4.79	2	4.82	0.0 ⁹⁾
	1:20	1	1.255	25.0	4.79	1	4.74	1.2
		2	1.253	25.0	4.79	2	4.80	0.0 ⁹⁾
	1:50	1	0.500	25.0	4.79	1	4.85	0.0 ⁹⁾
		2	0.500	25.0	4.79	2	4.84	0.0 ⁹⁾

Table B.8.1.2.1.2._CA-6: The results obtained in the experiment with FOE Oxalate.

Test system/test soil	Soil:solution ratio	Characteristic of the test system				Results		
		Repli- cate	Mass of test soil [g d. w.]	Volume of solution [mL]	Initial concentration of the test item [µg/mL]	Repli- cate	Concentration in solution at equilibrium [µg/mL]	% adsorbed onto soil
<i>Blank (no soil)</i>	Not applicable	1	----	25.0	5.03	1	5.04	0.0 ^{*)}
		2	----	25.0	5.03	2	5.09	0.0 ^{*)}
<i>Winder sand soil</i>	1:3	1	7.509	25.0	5.03	1	5.03	0.0
		2	7.505	25.0	5.03	2	5.01	0.4
	1:5	1	5.011	25.0	5.03	1	5.01	0.3
		2	5.009	25.0	5.03	2	5.03	0.0
	1:10	1	2.500	25.0	5.03	1	5.05	0.0 ^{*)}
		2	2.503	25.0	5.03	2	5.08	0.0 ^{*)}
	1:20	1	1.255	25.0	5.03	1	5.09	0.0 ^{*)}
		2	1.251	25.0	5.03	2	5.07	0.0 ^{*)}
<i>Shipshe Sandy loam soil</i>	1:3	1	7.498	25.0	5.03	1	4.33	13.8
		2	7.502	25.0	5.03	2	4.18	16.9
	1:5	1	5.012	25.0	5.03	1	5.09	0.0 ^{*)}
		2	5.005	25.0	5.03	2	4.98	0.9
	1:10	1	2.505	25.0	5.03	1	5.02	0.1
		2	2.506	25.0	5.03	2	5.03	0.0 ^{*)}
	1:20	1	1.255	25.0	5.03	1	5.06	0.0 ^{*)}
		2	1.251	25.0	5.03	2	5.04	0.0 ^{*)}
<i>Drummer Silty clay loam soil</i>	1:3	1	7.503	25.0	5.03	1	4.92	2.0
		2	7.506	25.0	5.03	2	4.92	2.2
	1:5	1	5.010	25.0	5.03	1	4.97	1.1
		2	5.010	25.0	5.03	2	4.95	1.5
	1:10	1	2.499	25.0	5.03	1	5.03	0.0 ^{*)}
		2	2.500	25.0	5.03	2	4.98	0.9
	1:20	1	1.255	25.0	5.03	1	5.02	0.1
		2	1.253	25.0	5.03	2	4.99	0.6
<i>Oska-Martin Silty clay soil</i>	1:3	1	7.340	25.0	5.03	1	4.95	1.4
		2	7.343	25.0	5.03	2	4.95	1.4
	1:5	1	5.004	25.0	5.03	1	4.98	1.0
		2	5.006	25.0	5.03	2	5.02	0.2
	1:10	1	2.501	25.0	5.03	1	4.98	0.9
		2	2.500	25.0	5.03	2	4.99	0.7
	1:20	1	1.252	25.0	5.03	1	4.88	2.8
		2	1.256	25.0	5.03	2	4.84	3.7

Table B.8.1.2.1.2._CA-7: The results obtained in the experiment with FOE Alcohol.

Test system/test soil	Soil:solution ratio	Characteristic of the test system				Results		
		Repli- cate	Mass of test soil [g d. w.]	Volume of solution [mL]	Initial concentration of the test item [µg/mL]	Repli- cate	Concentration in solution at equilibrium [µg/mL]	% adsorbed onto soil
<i>Blank (no soil)</i>	Not applicable	1	----	25.0	5.11	1	4.94	3.4
		2	----	25.0	5.11	2	5.09	0.4
<i>Winder sand soil</i>	1:3	1	7.501	25.0	5.11	1	4.81	5.8
		2	7.512	25.0	5.11	2	4.87	4.6
	1:5	1	5.002	25.0	5.11	1	4.90	4.0
		2	5.004	25.0	5.11	2	4.93	3.5
	1:10	1	2.509	25.0	5.11	1	4.98	2.6
		2	2.506	25.0	5.11	2	4.99	2.4
	1:20	1	1.253	25.0	5.11	1	5.02	1.8
		2	1.257	25.0	5.11	2	5.01	1.9
<i>Shipshe Sandy loam soil</i>	1:3	1	7.503	25.0	5.11	1	4.39	14.1
		2	7.504	25.0	5.11	2	4.38	14.2
	1:5	1	5.009	25.0	5.11	1	4.54	11.0
		2	5.012	25.0	5.11	2	4.58	10.3
	1:10	1	2.502	25.0	5.11	1	4.81	5.8
		2	2.507	25.0	5.11	2	4.83	5.4
	1:20	1	1.249	25.0	5.11	1	4.94	3.3
		2	1.249	25.0	5.11	2	4.96	2.8
<i>Drummer Silty clay loam soil</i>	1:3	1	7.506	25.0	5.11	1	3.58	29.9
		2	7.507	25.0	5.11	2	3.59	29.7
	1:5	1	5.002	25.0	5.11	1	3.91	23.5
		2	5.011	25.0	5.11	2	3.81	25.5
	1:10	1	2.502	25.0	5.11	1	4.30	15.7
		2	2.496	25.0	5.11	2	4.31	15.6
	1:20	1	1.250	25.0	5.11	1	4.63	9.3
		2	1.255	25.0	5.11	2	4.65	8.9
<i>Oska-Martin Silty clay soil</i>	1:3	1	7.498	25.0	5.11	1	2.83	44.5
		2	7.501	25.0	5.11	2	3.15	38.4
	1:5	1	5.002	25.0	5.11	1	3.14	38.5
		2	5.003	25.0	5.11	2	3.28	35.7
	1:10	1	2.501	25.0	5.11	1	3.79	25.8
		2	2.502	25.0	5.11	2	3.79	25.8
	1:20	1	1.252	25.0	5.11	1	4.31	15.6
		2	1.248	25.0	5.11	2	4.28	16.2

Table B.8.1.2.1.2._CA-8: The results obtained in the experiment with FOE Thiadone.

Test system/test soil	Soil:solution ratio	Characteristic of the test system				Results		
		Repli- cate	Mass of test soil [g d. w.]	Volume of solution [mL]	Initial concentration of the test item [µg/mL]	Repli- cate	Concentration in solution at equilibrium [µg/mL]	% adsorbed onto soil
<i>Blank (no soil)</i>	Not applicable	1	----	25.0	4.62	1	4.56	1.3
		2	----	25.0	4.62	2	4.61	0.3
<i>Winder sand soil</i>	1:3	1	7.509	25.0	4.62	1	4.49	2.9
		2	7.506	25.0	4.62	2	4.49	2.9
	1:5	1	5.013	25.0	4.62	1	4.51	2.5
		2	5.009	25.0	4.62	2	4.51	2.5
	1:10	1	2.500	25.0	4.62	1	4.54	1.8
		2	2.507	25.0	4.62	2	4.55	1.7
	1:20	1	1.255	25.0	4.62	1	4.57	1.2
		2	1.251	25.0	4.62	2	4.54	1.9
<i>Shipshe Sandy loam soil</i>	1:3	1	7.505	25.0	4.62	1	4.27	7.7
		2	7.502	25.0	4.62	2	4.27	7.6
	1:5	1	5.008	25.0	4.62	1	4.34	6.1
		2	5.005	25.0	4.62	2	4.35	6.0
	1:10	1	2.503	25.0	4.62	1	4.42	4.4
		2	2.510	25.0	4.62	2	4.34	6.1
	1:20	1	1.250	25.0	4.62	1	4.50	2.7
		2	1.255	25.0	4.62	2	4.52	2.3
<i>Drummer Silty clay loam soil</i>	1:3	1	7.503	25.0	4.62	1	4.15	10.3
		2	7.503	25.0	4.62	2	4.15	10.3
	1:5	1	5.010	25.0	4.62	1	4.27	7.7
		2	5.004	25.0	4.62	2	4.23	8.5
	1:10	1	2.503	25.0	4.62	1	4.40	4.8
		2	2.501	25.0	4.62	2	4.40	4.8
	1:20	1	1.250	25.0	4.62	1	4.48	3.1
		2	1.248	25.0	4.62	2	4.48	3.1
<i>Oska-Martin Silty clay soil</i>	1:3	1	7.502	25.0	4.62	1	4.01	13.3
		2	7.505	25.0	4.62	2	4.10	11.3
	1:5	1	5.010	25.0	4.62	1	4.12	10.9
		2	5.008	25.0	4.62	2	4.17	9.8
	1:10	1	2.499	25.0	4.62	1	4.32	6.6
		2	2.502	25.0	4.62	2	4.32	6.5
	1:20	1	1.251	25.0	4.62	1	4.46	3.6
		2	1.248	25.0	4.62	2	4.46	3.6

The results of the determination of the appropriate equilibration time – the **Second preliminary study**, are presented below, individually for each test compound, in tables B.8.1.2.1.2._CA-9 – B.8.1.2.1.2._CA-15. In the first table – B.8.1.2.1.2._CA-9 are provided the results of the determination of the concentration of the treatment solution for each test compound. The results of the determination of the appropriate equilibration time are presented in the tables B.8.1.2.1.2._CA-10 – B.8.1.2.1.2._CA-14. Finally the table B.8.1.2.1.2._CA-15 presents the results of the determination of the stability of test compounds after 72-hours lasting equilibration. In case in the source tables the negative values were reported for the % adsorbed, RMS replaced them with the value 0%. Such values are indicated with an asterisk – *).

On the basis of the obtained results it was stated that the optimum equilibration time varied between substances, but in general for all them no significant change was observed for equilibration time between 24 and 72 hours. At the same time it was stated that for FOE Sulfonic acid in Drummer Silty clay loam there was a significant degradation of the test compound. As a result, the 24-hours equilibration time was proposed to be used in the definitive study for all test compounds and all test soils.

It was also demonstrated that, as in previous experiment, none of the test compound displayed significant affinity to the test vessels.

Table B.8.1.2.1.2._CA-9: The results of the determination of concentration of test compounds in treatment solutions.

Code of treatment solution	Test compound	Specific activity of radiolabelled compound [$\mu\text{Ci}/\text{mg}$]	Concentration of the test compound in solution [$\mu\text{g}/\text{mL}$]			Specific activity of treatment solution [$\mu\text{Ci}/\text{mg}$]
			Radiolabelled	Technical grade	Total	
WG1-2	FOE Methylsulfoxide	82	0.148	5.00	5.15	2.35
WE1-2	FOE Sulfonic acid	76	0.311	4.90	5.21	4.56
WE1-3	FOE Sulfonic acid	76	0.216	4.86	5.08	3.26
WI1-2	FOE Oxalate	223	0.053	5.30	5.35	2.19
WLI-2	FOE Alcohol	549	0.023	5.10	5.12	2.48
WO1-2	FOE Thiadone	335	0.037	4.90	4.94	2.52

Table B.8.1.2.1.2._CA-10: The results obtained in the experiment with FOE Methylsulfoxide.

Test system/test soil	Equilibration time [hours]	Characteristic of the test system				Results		
		Repl-icate	Mass of test soil [g d. w.]	Volume of solution [mL]	Initial concentration of the test item [$\mu\text{g}/\text{mL}$]	Repl-icate	Concentration in solution at equilibrium [$\mu\text{g}/\text{mL}$]	% adsorbed onto soil
<i>Blank (no soil)</i>	72	1	----	20.0	5.15	1	5.07	1.5
		2	----	20.0	5.15	2	4.91	4.6
<i>Winder sand soil</i>	2	1	6.003	20.0	5.15	1	4.62	10.3
		2	5.999	20.0	5.15	2	4.39	14.7
	8	1	6.002	20.0	5.15	1	4.78	7.1
		2	6.004	20.0	5.15	2	4.84	6.0
	24	1	6.002	20.0	5.15	1	5.03	2.4
		2	5.999	20.0	5.15	2	5.05	1.9
	48	1	6.004	20.0	5.15	1	4.84	6.0
		2	5.998	20.0	5.15	2	4.79	7.0
	72	1	6.004	20.0	5.15	1	5.03	2.3
		2	6.002	20.0	5.15	2	4.99	3.1
<i>Shipshe Sandy loam soil</i>	2	1	6.002	20.0	5.15	1	4.61	10.4
		2	6.004	20.0	5.15	2	4.52	12.1
	8	1	6.007	20.0	5.15	1	4.75	7.8
		2	6.001	20.0	5.15	2	4.72	8.3
	24	1	6.006	20.0	5.15	1	4.69	8.9
		2	6.008	20.0	5.15	2	4.66	9.4
	48	1	6.006	20.0	5.15	1	4.60	10.7
		2	6.002	20.0	5.15	2	4.55	11.7
	72	1	6.001	20.0	5.15	1	4.61	10.5
		2	6.007	20.0	5.15	2	4.56	11.4
<i>Drummer Silty clay loam soil</i>	2	1	6.003	20.0	5.15	1	3.93	23.6
		2	6.001	20.0	5.15	2	3.95	23.4
	8	1	6.008	20.0	5.15	1	3.84	25.4
		2	6.006	20.0	5.15	2	3.60	30.1
	24	1	6.003	20.0	5.15	1	3.52	31.7
		2	6.001	20.0	5.15	2	3.62	29.6
	48	1	6.005	20.0	5.15	1	3.35	34.9
		2	6.001	20.0	5.15	2	3.45	32.9
	72	1	6.000	20.0	5.15	1	3.02	41.2
		2	6.001	20.0	5.15	2	2.91	43.5
<i>Oska-Martin Silty clay soil</i>	2	1	6.010	20.0	5.15	1	3.24	37.1
		2	6.007	20.0	5.15	2	3.20	37.8
	8	1	6.008	20.0	5.15	1	2.26	56.1
		2	6.003	20.0	5.15	2	2.19	57.4
	24	1	6.008	20.0	5.15	1	2.29	55.6
		2	6.009	20.0	5.15	2	2.30	55.3
	48	1	6.011	20.0	5.15	1	2.06	59.9
		2	6.006	20.0	5.15	2	2.01	60.9
	72	1	6.005	20.0	5.15	1	2.07	59.7
		2	6.004	20.0	5.15	2	2.06	59.9

Table B.8.1.2.1.2._CA-11: The results obtained in the experiment with FOE Sulfonic acid.

Test system/test soil	Equilibration time [hours]	Characteristic of the test system				Results		
		Repl- cate	Mass of test soil [g d. w.]	Volume of solution [mL]	Initial concentration of the test item [µg/mL]	Repl- cate	Concentration in solution at equilibrium [µg/mL]	% adsorbed onto soil
<i>Blank (no soil)</i>	72	1	----	20.0	5.21	1	5.19	0.3
		2	----	20.0	5.21	2	5.25	0.0 ^{*)}
<i>Winder sand soil</i>	2	1	6.003	20.0	5.21	1	4.96	4.9
		2	6.003	20.0	5.21	2	4.93	5.3
	8	1	6.001	20.0	5.21	1	4.84	7.1
		2	6.003	20.0	5.21	2	4.82	7.6
	24	1	6.003	20.0	5.21	1	5.19	0.4
		2	6.001	20.0	5.21	2	5.14	1.4
	48	1	6.002	20.0	5.21	1	5.22	0.0 ^{*)}
		2	6.001	20.0	5.21	2	4.96	4.9
	72	1	6.003	20.0	5.21	1	4.98	4.4
		2	6.001	20.0	5.21	2	4.98	4.5
<i>Shipshe Sandy loam soil</i>	2	1	6.002	20.0	5.08	1	4.88	3.9
		2	6.001	20.0	5.08	2	4.91	3.3
	8	1	6.006	20.0	5.08	1	4.89	3.7
		2	6.008	20.0	5.08	2	4.88	3.8
	24	1	5.999	20.0	5.08	1	4.91	3.2
		2	6.002	20.0	5.08	2	4.90	3.4
	48	1	6.003	20.0	5.08	1	4.76	6.2
		2	6.007	20.0	5.08	2	4.36	14.2
	72	1	6.002	20.0	5.08	1	4.62	9.0
		2	6.006	20.0	5.08	2	4.86	4.2
<i>Drummer Silty clay loam soil</i>	2	1	6.004	20.0	5.08	1	4.87	4.1
		2	6.007	20.0	5.08	2	4.86	4.3
	8	1	6.002	20.0	5.08	1	4.87	4.0
		2	6.007	20.0	5.08	2	4.84	4.7
	24	1	6.005	20.0	5.08	1	4.84	4.6
		2	6.007	20.0	5.08	2	4.85	4.5
	48	1	6.002	20.0	5.08	1	4.80	5.5
		2	6.005	20.0	5.08	2	4.42	12.8
	72	1	6.008	20.0	5.08	1	4.09	19.4
		2	6.003	20.0	5.08	2	3.52	30.6
<i>Oska-Martin Silty clay soil</i>	2	1	6.009	20.0	5.08	1	4.96	2.4
		2	6.004	20.0	5.08	2	4.95	2.6
	8	1	6.007	20.0	5.08	1	4.72	7.0
		2	6.011	20.0	5.08	2	4.93	2.8
	24	1	6.009	20.0	5.08	1	4.96	2.4
		2	6.006	20.0	5.08	2	4.96	2.3
	48	1	6.008	20.0	5.08	1	4.94	2.7
		2	6.004	20.0	5.08	2	4.88	4.0
	72	1	6.006	20.0	5.08	1	4.97	2.0
		2	6.010	20.0	5.08	2	4.88	3.9

Table B.8.1.2.1.2._CA-12: The results obtained in the experiment with FOE Oxalate.

Test system/test soil	Equilibration time [hours]	Characteristic of the test system				Results		
		Repl-icate	Mass of test soil [g d. w.]	Volume of solution [mL]	Initial concentration of the test item [µg/mL]	Repl-icate	Concentration in solution at equilibrium [µg/mL]	% adsorbed onto soil
<i>Blank (no soil)</i>	72	1	----	20.0	5.35	1	5.17	3.4
		2	----	20.0	5.35	2	5.14	3.9
<i>Winder sand soil</i>	2	1	6.001	20.0	5.35	1	5.25	2.0
		2	6.002	20.0	5.35	2	5.19	3.1
	8	1	6.004	20.0	5.35	1	5.20	2.8
		2	5.999	20.0	5.35	2	5.24	2.0
	24	1	6.003	20.0	5.35	1	5.22	2.4
		2	5.998	20.0	5.35	2	5.21	2.7
	48	1	6.004	20.0	5.35	1	5.19	3.0
		2	6.001	20.0	5.35	2	5.14	4.0
	72	1	5.999	20.0	5.35	1	5.12	4.4
		2	6.001	20.0	5.35	2	5.09	4.9
<i>Shipshe Sandy loam soil</i>	2	1	6.003	20.0	5.35	1	5.18	3.2
		2	6.003	20.0	5.35	2	5.15	3.8
	8	1	6.007	20.0	5.35	1	5.11	4.5
		2	6.006	20.0	5.35	2	5.13	4.1
	24	1	6.002	20.0	5.35	1	5.10	4.6
		2	6.000	20.0	5.35	2	5.12	4.4
	48	1	6.008	20.0	5.35	1	5.03	6.0
		2	6.004	20.0	5.35	2	5.10	4.7
	72	1	6.008	20.0	5.35	1	4.97	7.2
		2	6.000	20.0	5.35	2	4.97	7.2
<i>Drummer Silty clay loam soil</i>	2	1	6.005	20.0	5.35	1	5.10	4.8
		2	6.001	20.0	5.35	2	5.09	5.0
	8	1	5.999	20.0	5.35	1	5.10	4.7
		2	6.002	20.0	5.35	2	5.09	4.8
	24	1	6.002	20.0	5.35	1	5.09	4.9
		2	6.004	20.0	5.35	2	5.09	4.9
	48	1	5.999	20.0	5.35	1	5.01	6.4
		2	5.998	20.0	5.35	2	5.03	6.0
	72	1	6.008	20.0	5.35	1	4.66	12.9
		2	6.003	20.0	5.35	2	4.81	10.1
<i>Oska-Martin Silty clay soil</i>	2	1	6.003	20.0	5.35	1	5.08	5.2
		2	6.011	20.0	5.35	2	4.99	6.7
	8	1	6.002	20.0	5.35	1	4.79	10.5
		2	6.004	20.0	5.35	2	4.88	8.8
	24	1	6.003	20.0	5.35	1	5.15	3.9
		2	6.009	20.0	5.35	2	5.18	3.3
	48	1	6.008	20.0	5.35	1	5.13	4.1
		2	6.011	20.0	5.35	2	5.22	2.5
	72	1	6.002	20.0	5.35	1	5.17	3.4
		2	6.009	20.0	5.35	2	5.14	4.0

Table B.8.1.2.1.2._CA-13: The results obtained in the experiment with FOE Alcohol.

Test system/test soil	Equilibration time [hours]	Characteristic of the test system				Results		
		Repl- cate	Mass of test soil [g d. w.]	Volume of solution [mL]	Initial concentration of the test item [µg/mL]	Repl- cate	Concentration in solution at equilibrium [µg/mL]	% adsorbed onto soil
<i>Blank (no soil)</i>	72	1	----	20.0	5.12	1	5.09	0.7
		2	----	20.0	5.12	2	5.13	0.0 ³⁾
<i>Winder sand soil</i>	2	1	5.999	20.0	5.12	1	4.83	5.8
		2	6.005	20.0	5.12	2	4.84	5.5
	8	1	6.003	20.0	5.12	1	4.74	7.4
		2	6.001	20.0	5.12	2	4.76	7.1
	24	1	6.001	20.0	5.12	1	4.82	5.8
		2	6.005	20.0	5.12	2	4.80	6.3
	48	1	6.003	20.0	5.12	1	4.60	10.2
		2	6.002	20.0	5.12	2	4.56	10.9
	72	1	6.006	20.0	5.12	1	4.66	9.1
		2	6.003	20.0	5.12	2	4.75	7.3
<i>Shipshe Sandy loam soil</i>	2	1	5.999	20.0	5.12	1	4.47	12.7
		2	6.000	20.0	5.12	2	4.51	12.0
	8	1	6.006	20.0	5.12	1	4.36	14.9
		2	5.999	20.0	5.12	2	4.27	16.7
	24	1	5.999	20.0	5.12	1	4.44	13.4
		2	6.008	20.0	5.12	2	4.37	14.7
	48	1	6.000	20.0	5.12	1	4.15	19.1
		2	6.006	20.0	5.12	2	4.13	19.4
	72	1	6.000	20.0	5.12	1	4.26	16.9
		2	6.007	20.0	5.12	2	4.28	16.5
<i>Drummer Silty clay loam soil</i>	2	1	6.002	20.0	5.12	1	3.71	27.6
		2	6.002	20.0	5.12	2	3.70	27.8
	8	1	6.005	20.0	5.12	1	3.64	28.9
		2	6.001	20.0	5.12	2	3.52	31.3
	24	1	6.004	20.0	5.12	1	3.48	32.0
		2	6.008	20.0	5.12	2	3.46	32.5
	48	1	6.004	20.0	5.12	1	3.23	37.0
		2	6.004	20.0	5.12	2	3.22	37.1
	72	1	6.001	20.0	5.12	1	3.40	33.7
		2	6.007	20.0	5.12	2	3.43	33.1
<i>Oska-Martin Silty clay soil</i>	2	1	6.004	20.0	5.12	1	3.64	29.0
		2	6.004	20.0	5.12	2	3.29	35.9
	8	1	6.008	20.0	5.12	1	3.36	34.5
		2	6.011	20.0	5.12	2	2.94	42.7
	24	1	6.006	20.0	5.12	1	2.74	46.6
		2	6.009	20.0	5.12	2	2.79	45.5
	48	1	6.004	20.0	5.12	1	2.43	52.6
		2	6.011	20.0	5.12	2	2.46	52.0
	72	1	6.008	20.0	5.12	1	2.90	43.5
		2	6.010	20.0	5.12	2	3.22	37.1

Table B.8.1.2.1.2._CA-14: The results obtained in the experiment with FOE Thiadone.

Test system/test soil	Equilibration time [hours]	Characteristic of the test system				Results		
		Repl-icate	Mass of test soil [g d. w.]	Volume of solution [mL]	Initial concentration of the test item [µg/mL]	Repl-icate	Concentration in solution at equilibrium [µg/mL]	% adsorbed onto soil
<i>Blank (no soil)</i>	72	1	----	20.0	4.94	1	4.93	0.1
		2	----	20.0	4.94	2	4.90	0.7
<i>Winder Sand soil</i>	2	1	5.999	20.0	4.49	1	4.73	4.2
		2	6.007	20.0	4.94	2	4.66	5.6
	8	1	6.004	20.0	4.94	1	4.83	2.1
		2	6.005	20.0	4.94	2	4.76	3.7
	24	1	5.998	20.0	4.94	1	4.77	3.4
		2	6.001	20.0	4.94	2	4.74	4.1
	48	1	5.997	20.0	4.94	1	4.71	4.6
		2	5.996	20.0	4.94	2	4.66	5.7
	72	1	6.003	20.0	4.94	1	4.74	4.0
		2	6.002	20.0	4.94	2	4.67	5.4
<i>Shipshe Sandy loam soil</i>	2	1	6.008	20.0	4.49	1	4.61	6.6
		2	6.006	20.0	4.94	2	4.59	7.1
	8	1	6.002	20.0	4.94	1	4.66	5.6
		2	6.006	20.0	4.94	2	4.63	6.1
	24	1	6.007	20.0	4.94	1	4.54	8.1
		2	6.007	20.0	4.94	2	4.51	8.7
	48	1	6.006	20.0	4.94	1	4.7	9.5
		2	6.005	20.0	4.94	2	4.39	11.1
	72	1	6.001	20.0	4.94	1	4.53	8.2
		2	6.007	20.0	4.94	2	4.46	9.6
<i>Drummer Silty clay loam soil</i>	2	1	6.003	20.0	4.49	1	4.75	7.4
		2	6.008	20.0	4.94	2	4.45	9.9
	8	1	6.007	20.0	4.94	1	4.49	9.2
		2	6.008	20.0	4.94	2	4.49	9.0
	24	1	6.006	20.0	4.94	1	4.40	10.9
		2	6.000	20.0	4.94	2	4.39	11.1
	48	1	6.004	20.0	4.94	1	4.13	16.3
		2	6.002	20.0	4.94	2	4.17	15.6
	72	1	6.001	20.0	4.94	1	4.28	13.3
		2	6.003	20.0	4.94	2	4.22	14.5
<i>Oska-Martin Silty clay soil</i>	2	1	6.007	20.0	4.49	1	4.54	8.1
		2	6.009	20.0	4.94	2	4.48	9.2
	8	1	6.011	20.0	4.94	1	4.45	9.9
		2	6.011	20.0	4.94	2	4.35	11.8
	24	1	6.005	20.0	4.94	1	4.39	11.0
		2	6.008	20.0	4.94	2	4.36	11.6
	48	1	6.003	20.0	4.94	1	3.87	21.6
		2	6.009	20.0	4.94	2	3.87	21.5
	72	1	6.006	20.0	4.94	1	3.91	20.8
		2	6.012	20.0	4.94	2	3.95	20.0

Table B.8.1.2.1.2._CA-15: The results of the determination of the stability of the test compounds in the experiment after 72-hours lasting equilibration.

Test soil	Replicate	The results of HPLC analysis – concentration, as % radioactivity in analysed sample, of:				
		FOE Methylsulfoxide	FOE Sulfonic acid	FOE Oxalate	FOE Alcohol	FOE Thiadone
<i>Winder Sand soil</i>	1	100.00	95.15	100.00	100.00	100.00
	2	91.93	95.40	100.00	100.00	100.00
<i>Shipshe Sandy loam soil</i>	1	90.39	84.35	100.00	100.00	100.00
	2	91.17	100.00	100.00	100.00	100.00
<i>Drummer Silty clay loam soil</i>	1	87.70	70.41	100.00	100.00	100.00
	2	100.00	0.00	100.00	100.00	100.00
<i>Oska-Martin Silty clay soil</i>	1	100.00	100.00	100.00	100.00	100.00
	2	100.00	100.00	100.00	100.00	100.00

The results of the definitive test are presented below, individually for each test compound.

a) Results obtained for FOE Methylsulfoxide:

The results of the determination of the concentrations of the test compound in treatment solutions used in the experiment are presented below in the table B.8.1.2.1.2._CA-16.

Table B.8.1.2.1.2._CA-16: The results of the verification of the concentration of treatment solutions used in the Definitive Study for FOE Methylsulfoxide.

Test soil	Treatment solution code	Theoretical concentration of the test item [µg/mL]	Measured concentration of the test item [µg/mL]		
			Radiolabelled test item	Technical grade test item	Total concentration of the test item
<i>Winder Sand soil</i>	WG1-3	5.0	1.875	3.2	5.08
	WG2-3	1.0	0.376	0.64	1.02
	WG3-3	0.2	0.075	0.128	0.203
	WG4-3	0.04	0.015	0.0256	0.0406
<i>Shipshe Sandy loam soil</i>	WG1-4	5.0	1.841	3.2	5.04
	WG2-4	1.0	0.376	0.64	1.02
	WG3-4	0.2	0.075	0.128	0.203
	WG4-4	0.04	0.015	0.0256	0.0405
<i>Drummer Silty clay loam soil</i>	WG1-5	5.0	1.879	3.2	5.08
	WG2-5	1.0	0.377	0.64	1.02
	WG3-5	0.2	0.075	0.128	0.203
	WG4-5	0.04	0.015	0.0256	0.0407
<i>Oska-Martin Silty clay soil</i>	WG1-6	5.0	1.896	3.2	5.10
	WG2-6	1.0	0.384	0.64	1.02
	WG3-6	0.2	0.077	0.128	0.205
	WG4-6	0.04	0.015	0.0256	0.0409

The numerical results of experiment examining the adsorption of FOE Methylsulfoxide onto test soils are presented below in the table B.8.1.2.1.2._CA-17. The results of the experiment examining its desorption are presented in the table B.8.1.2.1.2._CA-18. The graphical results of the experiment – the adsorption and desorption isotherms determined for each test soil, are presented on figure B.8.1.2.1.2._CA-1. The key numerical results are provided in the table B.8.1.2.1.2._CA-19. Analysing these results RMS stated that it was not possible to interpret them appropriately as the Applicant did not distinguish the isotherms representing adsorption and desorption. For that reason it was also not possible to verify the correctness of the determined parameters of each isotherm. For that reason RMS decided to repeat the determination of the isotherms using the same data as presented in tables B.8.1.2.1.2._CA-17 and B.8.1.2.1.2._CA-18 – the log-transformed data. The adsorption and desorption isotherms were determined separately. The tool used in that exercise was CurveExpert ver 1.40. The graphical results are presented on two figures – B.8.1.2.1.2._CA-2 for adsorption and B.8.1.2.1.2._CA-3 for desorption. The corresponding numerical results are provided in the table B.8.1.2.1.2._CA-20. Performing the fitting the RMS used the data for the replicates not averaging them, as had done the Applicant.

Table B.8.1.2.1.2._CA-17: The results of the examination of the adsorption of FOE Methylsulfoxide onto test soils to determine Freundlich adsorption isotherm.

Test soil	Initial concentration of the solution [µg/mL]	Replicate	Results of the experiment:					
			Concentration at equilibrium				Amount adsorbed onto soil	
			in solution		in soil		in [µg]	in [%]
			Ce [µg/mL]	Log Ce	x/m [µg/g]	Log (x/m)		
<i>Winder Sand soil</i>	5.08	1	4.84	0.68	0.80	-0.10	4.78	4.7
		2	4.89	0.69	0.62	-0.21	3.73	3.7
		3	4.89	0.69	0.61	-0.22	3.63	3.6
	1.02	1	0.963	-0.02	0.18	-0.75	1.06	5.2
		2	0.978	-0.01	0.13	-0.90	0.76	3.7
		3	0.979	-0.01	0.12	-0.91	0.73	3.6
	0.203	1	0.196	-0.71	0.02	-1.61	0.15	3.6
		2	0.196	-0.71	0.02	-1.62	0.14	3.5
		3	0.195	-0.71	0.03	-1.59	0.15	3.8
	0.0406	1	0.0369	-1.43	0.01	-1.91	0.07	9.1
		2	0.0389	-1.41	0.01	-2.26	0.03	4.1
		3	0.0403	-1.39	0.00	-3.03	0.01	0.7
<i>Shipshe Sandy loam soil</i>	5.04	1	4.67	0.67	1.23	0.09	7.41	7.3
		2	4.67	0.67	1.22	0.09	7.33	7.3
		3	4.70	0.67	1.14	0.06	6.86	6.8
	1.02	1	0.909	-0.04	0.35	-0.45	2.12	10.5
		2	0.903	-0.04	0.38	-0.42	2.26	11.1
		3	0.905	-0.04	0.37	-0.43	2.21	10.9
	0.203	1	0.176	-0.75	0.09	-1.05	0.54	13.2
		2	0.176	-0.75	0.09	-1.04	0.54	13.3
		3	0.178	-0.75	0.08	-1.07	0.51	12.5
	0.0405	1	0.0359	-1.44	0.02	-1.82	0.09	11.3
		2	0.0355	-1.45	0.02	-1.78	0.10	12.4
		3	0.0366	-1.44	0.01	-1.89	0.08	9.6
<i>Drummer Silty clay loam soil</i>	5.08	1	3.38	0.53	5.67	0.75	34.05	33.5
		2	3.42	0.53	5.54	0.74	33.22	32.7
		3	3.39	0.53	5.63	0.75	33.82	33.3
	1.02	1	0.565	-0.25	1.51	0.18	9.04	44.5
		2	0.574	-0.24	1.47	0.17	8.85	43.5
		3	0.608	-0.22	1.36	0.13	8.18	40.2
	0.203	1	0.116	-0.94	0.29	-0.54	1.75	43.0
		2	0.116	-0.93	0.29	-0.54	1.74	42.9
		3	0.115	-0.94	0.29	-0.53	1.77	43.4
	0.0407	1	0.0215	-1.67	0.06	-1.19	0.38	47.2
		2	0.0217	-1.66	0.06	-1.20	0.38	46.8
		3	0.0214	-1.67	0.06	-1.19	0.39	47.5
<i>Oska-Martin Silty clay soil</i>	5.10	1	1.94	0.29	10.49	1.02	63.05	61.9
		2	2.03	0.31	10.20	1.01	61.25	60.1
		3	2.00	0.30	10.29	1.01	61.87	60.7
	1.02	1	0.362	-0.44	2.20	0.34	13.24	64.7
		2	0.363	-0.44	2.20	0.34	13.22	64.6
		3	0.359	-0.45	2.21	0.35	13.30	65.0
	0.205	1	0.0625	-1.20	0.48	-0.32	2.86	69.6
		2	0.0641	-1.19	0.47	-0.33	2.83	68.8
		3	0.0626	-1.20	0.48	-0.32	2.86	69.5
	0.0409	1	0.0123	-1.91	0.09	-1.02	0.57	69.8
		2	0.0122	-1.91	0.10	-1.02	0.57	70.2
		3	0.0119	-1.92	0.10	-1.02	0.58	70.9

Table B.8.1.2.1.2._CA-18: The results of the examination of the desorption of FOE Methylsulfoxide from the test soils to determine Freundlich desorption isotherm.

Test soil	Initial concentration of the solution [µg/mL]	Replicate	Results of the experiment:					
			Concentration at equilibrium				Amount desorbed from soil	
			in solution		in soil		in [µg] ¹⁾	in [%] ²⁾
			Ce [µg/mL]	Log Ce	x/m [µg/g]	Log (x/m)		
<i>Winder Sand soil</i>	5.08	1	0.618	-0.21	0.19	-0.73	3.67	76.6
		2	0.608	-0.22	0.06	-1.21	3.36	90.2
		3	0.619	-0.21	0.01	-1.93	3.56	98.1
	1.02	1	0.126	-0.90	0.04	-1.36	0.79	75.0
		2	0.117	-0.93	0.03	-1.54	0.59	77.2
		3	0.115	-0.94	0.01	-1.50	0.54	74.2
	0.203	1	0.0234	-1.63	0.01	-2.30	0.12	79.5
		2	0.0232	-1.63	0.01	-2.29	0.11	78.5
		3	0.0235	-1.63	0.01	-2.25	0.12	78.0
	0.0406	1	0.0050	-2.30	0.01	-2.17	0.03	54.4
		2	0.0046	-2.34	0.00	-2.74	0.02	67.2
		3	0.0058	----	----	----	0.04	> 100
<i>Shipshe Sandy loam soil</i>	5.04	1	0.759	-0.12	0.03	-1.54	7.23	97.7
		2	0.720	-0.14	0.15	-0.84	6.45	88.0
		3	0.669	-0.17	0.24	-0.61	5.40	78.6
	1.02	1	0.155	-0.81	0.10	-1.02	1.55	72.8
		2	0.152	-0.82	0.13	-0.90	1.50	66.5
		3	0.145	-0.84	0.14	-0.85	1.35	61.3
	0.203	1	0.0334	-1.48	0.03	-1.55	0.37	68.5
		2	0.0354	-1.45	0.02	-1.65	0.41	75.4
		3	0.0368	-1.43	0.01	-1.91	0.43	85.4
	0.0405	1	0.0075	-2.13	0.00	-3.21	0.09	96.0
		2	0.0074	-2.13	0.00	-2.69	0.09	87.8
		3	0.0076	----	----	----	0.09	> 100
<i>Drummer Silty clay loam soil</i>	5.08	1	1.26	0.10	3.10	0.49	15.45	45.4
		2	1.31	0.12	2.84	0.45	16.20	48.8
		3	1.33	0.12	2.83	0.45	16.83	49.8
	1.02	1	0.254	-0.59	0.93	-0.03	3.45	38.2
		2	0.246	-0.61	0.84	-0.03	3.26	36.8
		3	0.246	-0.61	0.18	-0.08	3.15	38.5
	0.203	1	0.0511	-1.29	0.18	-0.75	0.69	39.3
		2	0.0505	-1.30	0.18	-0.75	0.67	38.6
		3	0.0514	-1.29	0.18	-0.75	0.69	39.3
	0.0407	1	0.0102	-1.99	0.04	-1.39	0.14	37.0
		2	0.0099	-2.01	0.04	-1.39	0.13	35.3
		3	0.0101	-2.00	0.04	-1.39	0.14	36.1
<i>Oska-Martin Silty clay soil</i>	5.10	1	1.26	0.10	7.69	0.89	16.87	26.8
		2	1.27	0.10	7.42	0.87	16.67	27.2
		3	1.29	0.11	7.44	0.87	17.13	27.7
	1.02	1	0.243	-0.61	1.65	0.22	3.30	24.9
		2	0.238	-0.62	1.67	0.22	3.20	24.2
		3	0.239	-0.62	1.67	0.22	3.24	24.4
	0.205	1	0.0463	-1.33	0.37	-0.44	0.66	23.0
		2	0.0467	-1.33	0.36	-0.44	0.66	23.3
		3	0.0447	-1.35	0.37	-0.43	0.63	21.9
	0.0409	1	0.0089	-2.05	0.07	-1.13	0.13	22.0
		2	0.0086	-2.07	0.08	-1.12	0.12	20.9
		3	0.0085	-2.07	0.08	-1.11	0.12	20.4

Footnotes to the table:

- 1) all values as reported in the study report;
 2) all values as reported in the study report.

The graphical results of the experiment presented in the study report are given below on figure B.8.1.2.1.2._CA-1 and the numerical ones in the table B.8.1.2.1.2._CA-19.

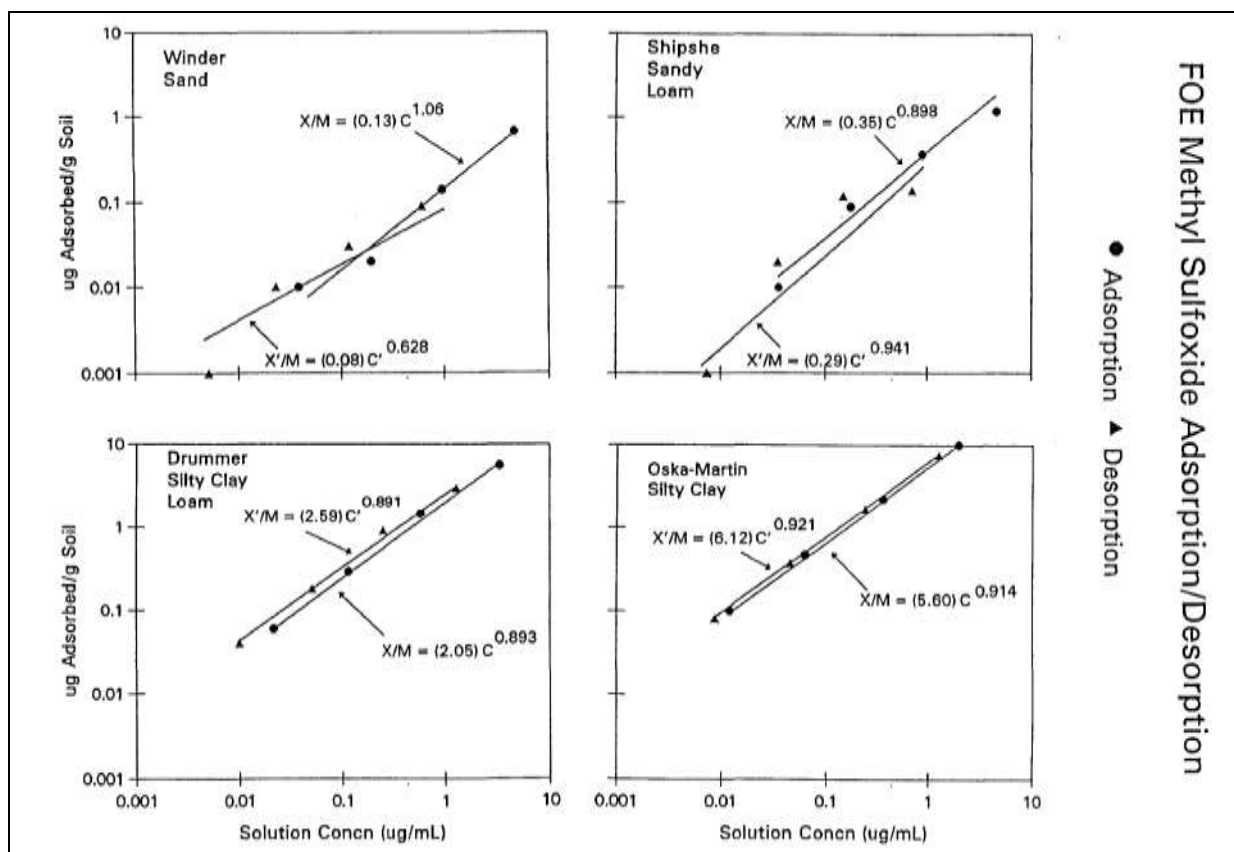


Figure B.8.1.2.1.2_CA-1: The adsorption and desorption isotherms for FOE Methylsulfoxide provided by the Applicant (copied from the study report).

Table B.8.1.2.1.2_CA-19: The key numerical results of the experiment presented in the study report – parameters of Freundlich adsorption and desorption isotherms for FOE Methylsulfoxide, including the correlation coefficient r

Test soil	Parameters of Freundlich adsorption isotherm					Parameters of Freundlich desorption isotherm				
	$\text{Log } K_{fads}$	$K_{fads} [\text{mL/g}]$	$1/n$	$K_{fOCads} [\text{mL/g}]$	r	$\text{Log } K_{fdes}$	$K_{fdes} [\text{mL/g}]$	$1/n$	$K_{fOCdes} [\text{mL/g}]$	r
Winder Sand soil	-0.877	0.13	1.06	49	0.958	-1.08	0.08	0.628	31	0.827
Shipshe Sandy loam soil	-0.458	0.35	0.898	46	0.994	-0.538	0.29	0.941	39	0.841
Drummer Silty clay loam soil	0.311	2.05	0.893	96	0.999	0.413	2.59	0.891	121	0.997
Oska-Martin Silty clay soil	0.748	5.60	0.914	463	1.000	0.787	6.12	0.921	506	1.000

The graphical and numerical results of the repeated analysis, performed by the RMS, of the data from the tables B.8.1.2.1.2_CA-17 (for adsorption) and B.8.1.2.1.2_CA-18 (for desorption) are presented below on figures B.8.1.2.1.2_CA-2 (adsorption) and B.8.1.2.1.2_CA-3 (desorption) and in the table B.8.1.2.1.2_CA-20.

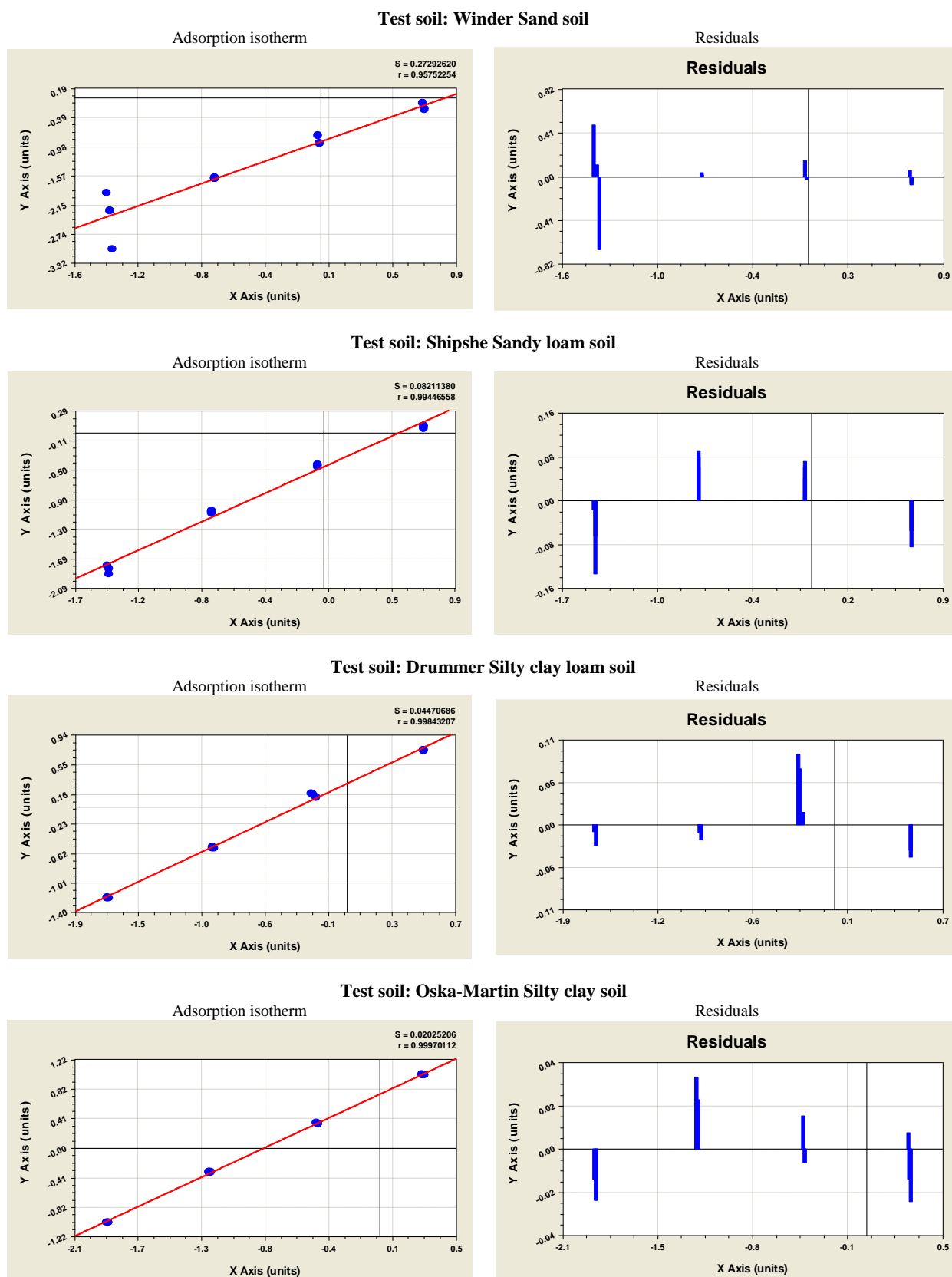


Figure B.8.1.2.1.2._CA-2: The adsorption isotherms for FOE Methylsulfoxide determined by the RMS.

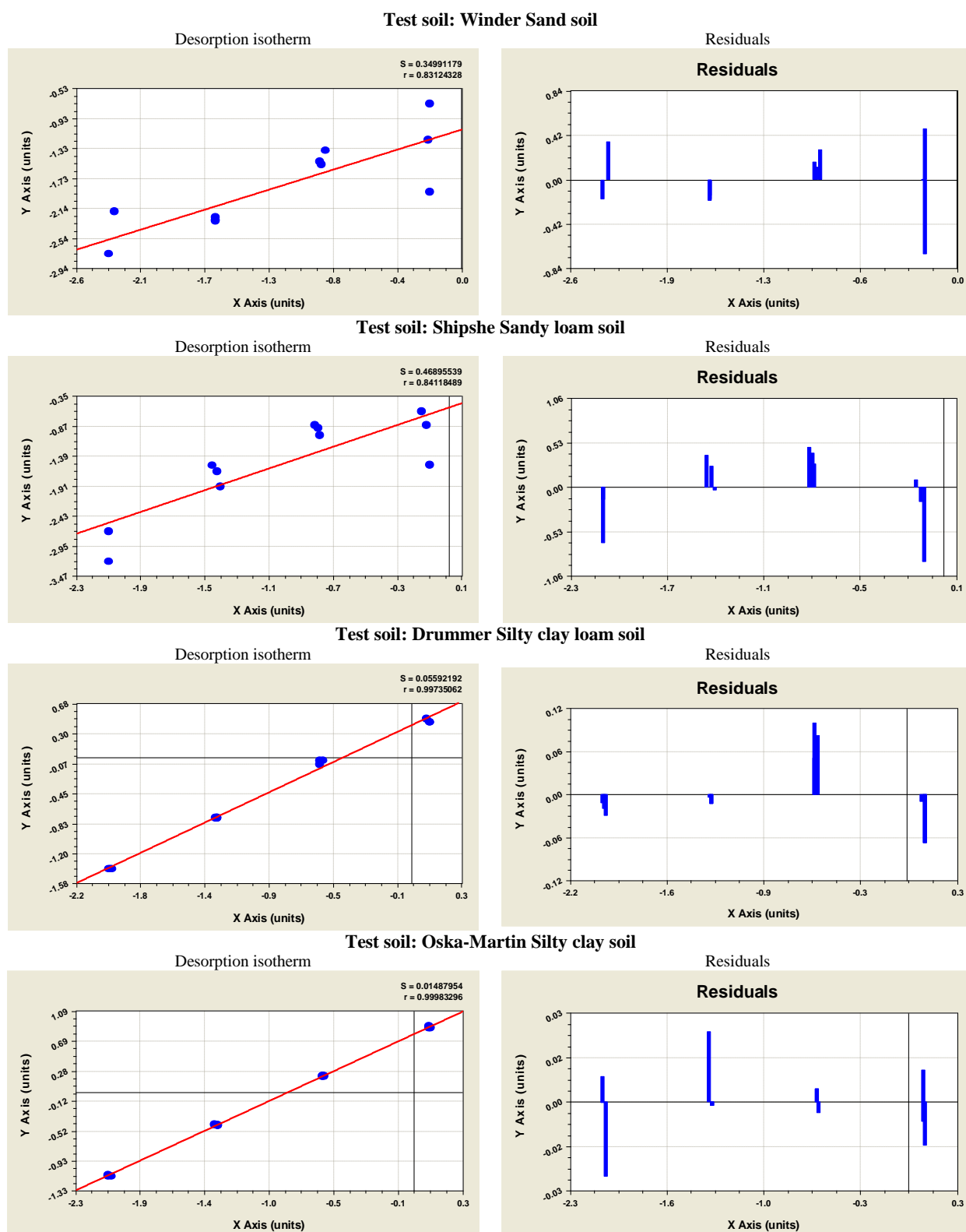


Figure B.8.1.2.1.2._CA-3: The desorption isotherms for FOE Methylsulfoxide determined by the RMS.

Table B.8.1.2.1.2._CA-20: The parameters of the Freundlich adsorption and desorption isotherms determined for FOE Methylsulfoxide by the RMS

Test soil	Process	Parameters of isotherm				Statistical evaluation	
		Log K _F	K _F [mL/g]	K _{F OC} [mL/g]	1/n	SD	Correlation coefficient <i>r</i>
<i>Winder, Sand soil</i>	Adsorption	-0.876	0.133	49.26	1.059	0.2729	0.9575
	Desorption	-1.077	0.084	31.11	0.630	0.3499	0.8312
<i>Shipshe, Sandy loam soil</i>	Adsorption	-0.457	0.349	46.53	0.900	0.0821	0.9945
	Desorption	-0.542	0.287	38.27	0.938	0.4689	0.8412
<i>Drummer, Silty clay loam soil</i>	Adsorption	0.310	2.042	95.87	0.893	0.0447	0.9984
	Desorption	0.411	2.576	120.94	0.890	0.0559	0.9973
<i>Oska-Martin, Silty clay soil</i>	Adsorption	0.748	5.598	462.64	0.914	0.0202	0.9997
	Desorption	0.786	6.109	504.88	0.921	0.0149	0.9998

Conclusions of the experiment:

The comparison of the results presented in the study report and those obtained by the RMS showed that the parameters of the adsorption and desorption isotherms obtained by the Applicant and RMS were almost identical. At the same time RMS stated that the determined adsorption isotherms displayed, except that determined for Winder Sand soil, good conformity with the experimental results. That conformity was not so good in case of the desorption isotherms, especially in case of Winder Sand soil and Shipshe Sandy loam soil, but that in turn may be partly attributed to low level of adsorption recorded in these two soils. The 1/n values for the adsorption isotherms were in range 0.893 – 1.059, indicating that the isotherms well complied with the assumed model. In case of the results obtained in Winder Sand soil it was stated that the adsorption isotherm was robust and well complied with the model – Freundlich sorption isotherm. For that reason RMS decided to include the results into the data set, even though the OC content was lower than the recommended minimum – 0.3%.

The definitive set of the results from this experiment is presented below in the table B.8.1.2.1.2._CA-21. RMS decided to present the values determined as a result of the repeated analysis of the data set.

Table B.8.1.2.1.2._CA-21: The definitive set of Freundlich adsorption and desorption parameters determined for FOE Methylsulfoxide.

Test soil – USDA type (name)	Key soil properties		Freundlich adsorption isotherm parameters			Freundlich desorption isotherm parameters		
	pH ¹⁾	OC [%]	K _F [mL/g]	K _{F OC} [mL/g]	1/n	K _F [mL/g]	K _{F OC} [mL/g]	1/n
<i>Sand (Winder)</i>	5.8	0.27	0.133	49.26	1.059	0.084	31.11	0.630
<i>Sandy loam (Shipshe)</i>	6.3	0.75	0.349	46.53	0.900	0.287	38.27	0.938
<i>Silty clay loam (Drummer)</i>	6.6	2.13	2.042	95.87	0.893	2.576	120.94	0.890
<i>Silty clay (Oska-Martin)</i>	6.0	1.21	5.598	462.64	0.914	6.109	504.88	0.921

Footnotes to the table:

1) Measured in water;

b) Results obtained for FOE Sulfonic acid:

The results of the determination of the concentrations of the test compound in treatment solutions used in the experiment are presented below in the table B.8.1.2.1.2._CA-22.

Table B.8.1.2.1.2._CA-22: The results of the verification of the concentration of treatment solutions used in the Definitive Study for FOE Sulfonic acid.

Test soil	Treatment solution code	Theoretical concentration of the test item [µg/mL]	Measured concentration of the test item [µg/mL]		
			Radiolabelled test item	Technical grade test item	Total concentration of the test item
<i>Winder Sand soil</i>	WE1-4	5.0	2.364	3.0	5.36
	WE2-4	1.0	0.475	0.60	1.07
	WE3-4	0.2	0.095	0.12	0.215
	WE4-4	0.04	0.019	0.024	0.0431
<i>Shipshe Sandy loam soil</i>	WE1-5	5.0	1.875	3.0	4.88
	WE2-5	1.0	0.375	0.60	0.975
	WE3-5	0.2	0.074	0.12	0.194
	WE4-5	0.04	0.015	0.024	0.0389
<i>Drummer Silty clay loam soil</i>	WE1-6	5.0	1.928	3.0	4.93
	WE2-6	1.0	0.392	0.60	0.992
	WE3-6	0.2	0.077	0.12	0.197
	WE4-6	0.04	0.016	0.024	0.0396
<i>Oska-Martin Silty clay soil</i>	WE1-7	5.0	2.033	3.0	5.03
	WE2-7	1.0	0.405	0.60	1.01
	WE3-7	0.2	0.080	0.12	0.200
	WE4-7	0.04	0.016	0.024	0.0410

The numerical results of experiment examining the adsorption of FOE Sulfonic acid onto test soils are presented below in the table B.8.1.2.1.2._CA-23. The results of the experiment examining its desorption are presented in the table B.8.1.2.1.2._CA-24. The results obtained during examination of the adsorption showed that the adsorption of the test compound onto soil was very low, generally below 10%. For that reason the results of the desorption bear a significant level of uncertainty as the initial concentrations of the test compound retained by soil were very low. RMS decided to report the results presented by the Applicant noticing at the same time that they should be considered with extreme care, as in many instances the reported level of desorption is either above 100%, or a negative value, what is due to the fact that the concentrations were determined at levels close to LOQ.

For that reason the Applicant decided not to determine the desorption isotherms (the available data base did not enable doing that). The graphical results of the experiment – the adsorption isotherms reported in the study report, are given on figure B.8.1.2.1.2._CA-4 and in numerical form in the table B.8.1.2.1.2._CA-25. RMS decided to verify them using the values presented in the table B.8.1.2.1.2._CA-21 – the log-transformed concentrations in soil and solution at equilibrium. The results are provided on figure B.8.1.2.1.2._CA-5 and in numerical form in the table B.8.1.2.1.2._CA-26. The tool used in that exercise was CurveExpert ver. 1.4. Performing the fitting the RMS used the data for the replicates not averaging them, as had done the Applicant.

Table B.8.1.2.1.2._CA-23: The results of the examination of the adsorption of FOE Sulfonic acid onto test soils to determine Freundlich adsorption isotherm.

Test soil	Initial concentration of the solution [µg/mL]	Replicate	Results of the experiment:					
			Concentration at equilibrium				Amount adsorbed onto soil	
			in solution		in soil		in [µg]	in [%]
			Ce [µg/mL]	Log Ce	x/m [µg/g]	Log (x/m)		
<i>Winder Sand soil</i>	5.36	1	5.28	0.72	0.30	-0.53	1.78	1.7
		2	5.30	0.72	0.20	-0.70	1.91	1.1
		3	5.29	0.72	0.24	-0.63	1.42	1.3
	1.07	1	1.07	0.03	0.02	-1.71	0.12	0.5
		2	1.06	0.03	0.05	-1.33	0.28	1.3
		3	1.06	0.02	0.06	-1.22	0.36	1.7
	0.215	1	0.210	-0.68	0.02	-1.73	0.11	2.6
		2	0.209	-0.68	0.02	-1.67	0.13	3.0
		3	0.211	-0.68	0.02	-1.80	0.09	2.2
	0.0431	1	0.0424	-1.37	0.00	-2.60	0.02	1.8
		2	0.0423	-1.37	0.00	-2.54	0.02	2.0
		3	0.0421	-1.38	0.00	-2.46	0.02	2.4
<i>Shipshe Sandy loam soil</i>	4.88	1	4.69	0.67	0.62	-0.20	3.75	3.8
		2	4.72	0.67	0.53	-0.27	3.21	3.3
		3	4.73	0.67	0.48	-0.32	2.90	3.0
	0.975	1	0.937	-0.03	0.13	-0.90	0.75	3.9
		2	0.941	-0.03	0.11	-0.96	0.66	3.4
		3	0.938	-0.03	0.12	-0.92	0.73	3.7
	0.194	1	0.188	-0.73	0.02	-1.69	0.12	3.1
		2	0.190	-0.72	0.01	-1.86	0.08	2.1
		3	0.190	-0.72	0.01	-1.88	0.08	2.0
	0.0389	1	0.0376	-1.43	0.00	-2.34	0.03	3.5
		2	0.0375	-1.43	0.00	-2.33	0.03	3.6
		3	0.0373	-1.43	0.001	-2.25	0.03	4.3
<i>Drummer Silty clay loam soil</i>	4.93	1	4.69	0.67	0.80	-0.10	4.82	4.9
		2	4.65	0.67	0.93	-0.03	5.60	5.7
		3	4.66	0.67	0.89	-0.05	5.36	5.4
	0.992	1	0.921	-0.04	0.24	-0.63	1.42	7.2
		2	0.922	-0.04	0.23	-0.63	1.40	7.0
		3	0.920	-0.04	0.24	-0.62	1.44	7.3
	0.197	1	0.193	-0.71	0.01	-1.90	0.08	1.9
		2	0.185	-0.73	0.04	-1.41	0.23	5.9
		3	0.185	-0.73	0.04	-1.41	0.23	6.0
	0.0396	1	0.0367	-1.44	0.01	-2.02	0.06	7.3
		2	0.0346	-1.46	0.02	-1.78	0.10	12.6
		3	0.0365	-1.44	0.01	-2.00	0.06	7.7
<i>Oska-Martin Silty clay soil</i>	5.03	1	4.93	0.69	0.36	-0.45	2.14	2.1
		2	4.91	0.69	0.41	-0.39	2.44	2.4
		3	4.92	0.69	0.38	-0.42	2.30	2.3
	1.01	1	0.977	-0.01	0.09	-1.03	0.56	2.8
		2	0.976	-0.01	0.10	-1.02	0.58	2.9
		3	0.971	-0.01	0.11	-0.95	0.68	3.4
	0.200	1	0.199	-0.70	0.01	-2.29	0.03	0.8
		2	0.196	-0.71	0.01	-1.85	0.08	2.1
		3	0.196	-0.71	0.01	-1.91	0.07	1.8
	0.0401	1	0.0396	-1.40	0.00	-2.86	0.01	1.0
		2	0.0395	-1.40	0.00	-2.72	0.01	1.4
		3	0.0397	-1.40	0.00	-2.91	0.01	0.9

Table B.8.1.2.1.2._CA-24: The results of the examination of the desorption of FOE Sulfonic acid from the test soils to determine Freundlich desorption isotherm.

Test soil	Initial concentration of the solution [µg/mL]	Replicate	Results of the experiment:					
			Concentration at equilibrium				Amount desorbed from soil	
			in solution		in soil		in [µg] ³⁾	in [%] ⁴⁾
			Ce [µg/mL]	Log Ce	x/m [µg/g]	Log (x/m)		
<i>Winder Sand soil</i>	5.36	1	0.539	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	2.33	131.3
		2	0.526	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	2.03	171.2
		3	0.523	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	1.99	140.5
	1.07	1	0.1007	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	0.30	263.2
		2	0.0997	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	0.30	105.1
		3	0.0961	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	0.23	64.3
	0.215	1	0.0185	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	0.04	31.8
		2	0.0181	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	0.03	22.5
		3	0.0194	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	0.05	54.2
	0.0431	1	0.0039	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	0.01	69.2
		2	0.0036	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	0.00	22.4
		3	0.0041	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	0.01	69.7
<i>Shipshe Sandy loam soil</i>	4.88	1	0.373	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	-0.04	-1.2
		2	0.397	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	0.39	12.1
		3	0.368	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	-0.21	-7.3
	0.975	1	0.0791	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	0.08	10.9
		2	0.0796	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	0.09	12.9
		3	0.0777	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	0.05	7.2
	0.194	1	0.0283	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	0.26	218.6
		2	0.0194	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	0.08	101.1
		3	0.0199	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	0.09	119.5
	0.0389	1	0.0049	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	0.04	140.5
		2	0.0041	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	0.02	79.6
		3	0.0042	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	0.03	75.2
<i>Drummer Silty clay loam soil</i>	4.93	1	0.530	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	-3.47	-72.0
		2	0.489	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	-41.6	-74.2
		3	0.529	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	-3.41	-63.5
	0.992	1	0.154	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	0.32	22.8
		2	0.153	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	0.29	20.5
		3	0.152	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	0.28	19.1
	0.197	1	0.0349	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	0.12	156.3
		2	0.0344	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	0.13	56.7
		3	0.0339	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	0.12	52.1
	0.0396	1	0.0067	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	0.02	42.3
		2	0.0067	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	0.03	30.7
		3	0.0067	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	0.03	41.4
<i>Oska-Martin Silty clay soil</i>	5.03	1	1.06	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	-1.88	-87.6
		2	1.09	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	-1.31	-53.7
		3	1.15	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	-0.06	-2.8
	1.01	1	0.221	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	-0.18	-32.4
		2	0.219	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	-0.20	-34.6
		3	0.234	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	0.12	18.1
	0.200	1	0.0476	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	0.02	58.3
		2	0.0474	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	0.03	31.5
		3	0.0476	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	0.03	37.9
	0.0401	1	0.0094	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	0.00	29.1
		2	0.0092	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	0.00	-5.1
		3	0.0093	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	0.00	-6.9

Footnotes to the table:

- 1) n. c. = not calculated;
- 2) n. r. = not reported, probably not determined;
- 3) all values as reported in the study report;
- 4) all values as reported in the study report.

The graphical results of the experiment presented in the study report are given below on figure B.8.1.2.1.2._CA-4 and in numerical form in the table B.8.1.2.1.2._CA-25.

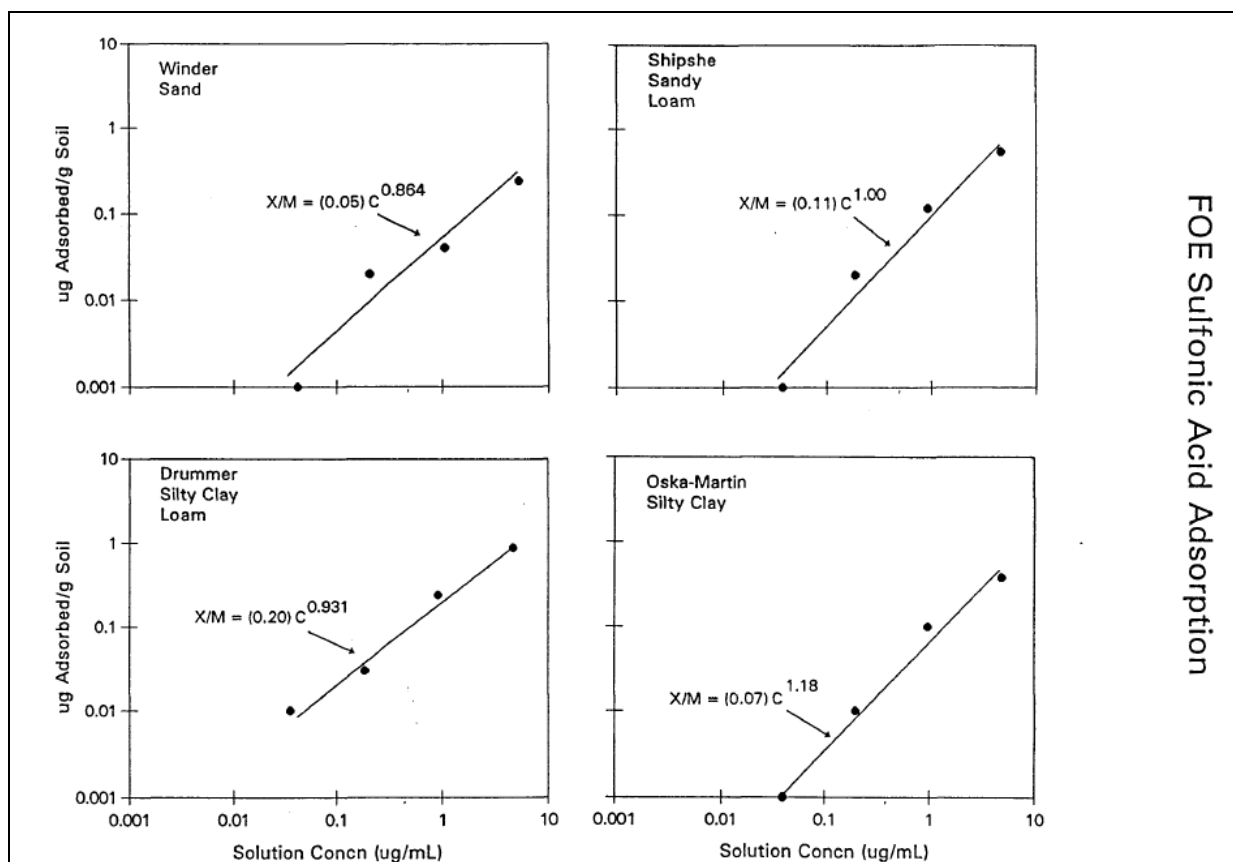


Figure B.8.1.2.1.2._CA-4: The adsorption isotherms for FOE Sulfonic acid provided by the Applicant (copied from the study report).

Table B.8.1.2.1.2._CA-25: The key numerical results of the experiment presented in the study report – parameters of Freundlich adsorption isotherm for FOE Sulfonic acid, including the correlation coefficient r

Test soil	Parameters of Freundlich adsorption isotherm					Parameters of Freundlich desorption isotherm				
	$\text{Log } K_{f \text{ ads}}$	$K_{f \text{ ads}} [\text{mL/g}]$	$1/n$	$K_{fOC \text{ ads}} [\text{mL/g}]$	r	$\text{Log } K_{f \text{ des}}$	$K_{f \text{ des}} [\text{mL/g}]$	$1/n$	$K_{fOC \text{ des}} [\text{mL/g}]$	r
Winder Sand soil	-1.30	0.05	0.864	19	0.973	Not determined				
Shipshe Sandy loam soil	-0.950	0.11	1.000	15	0.992	Not determined				
Drummer Silty clay loam soil	-0.689	0.20	0.931	10	0.970	Not determined				
Oska-Martin Silty clay soil	-1.14	0.07	1.180	6	0.988	Not determined				

The graphical and numerical results of the repeated analysis, performed by the RMS, of the data from the table B.8.1.2.1.2._CA-23 (for adsorption) are presented below on figure B.8.1.2.1.2._CA-5 and in the table B.8.1.2.1.2._CA-26.

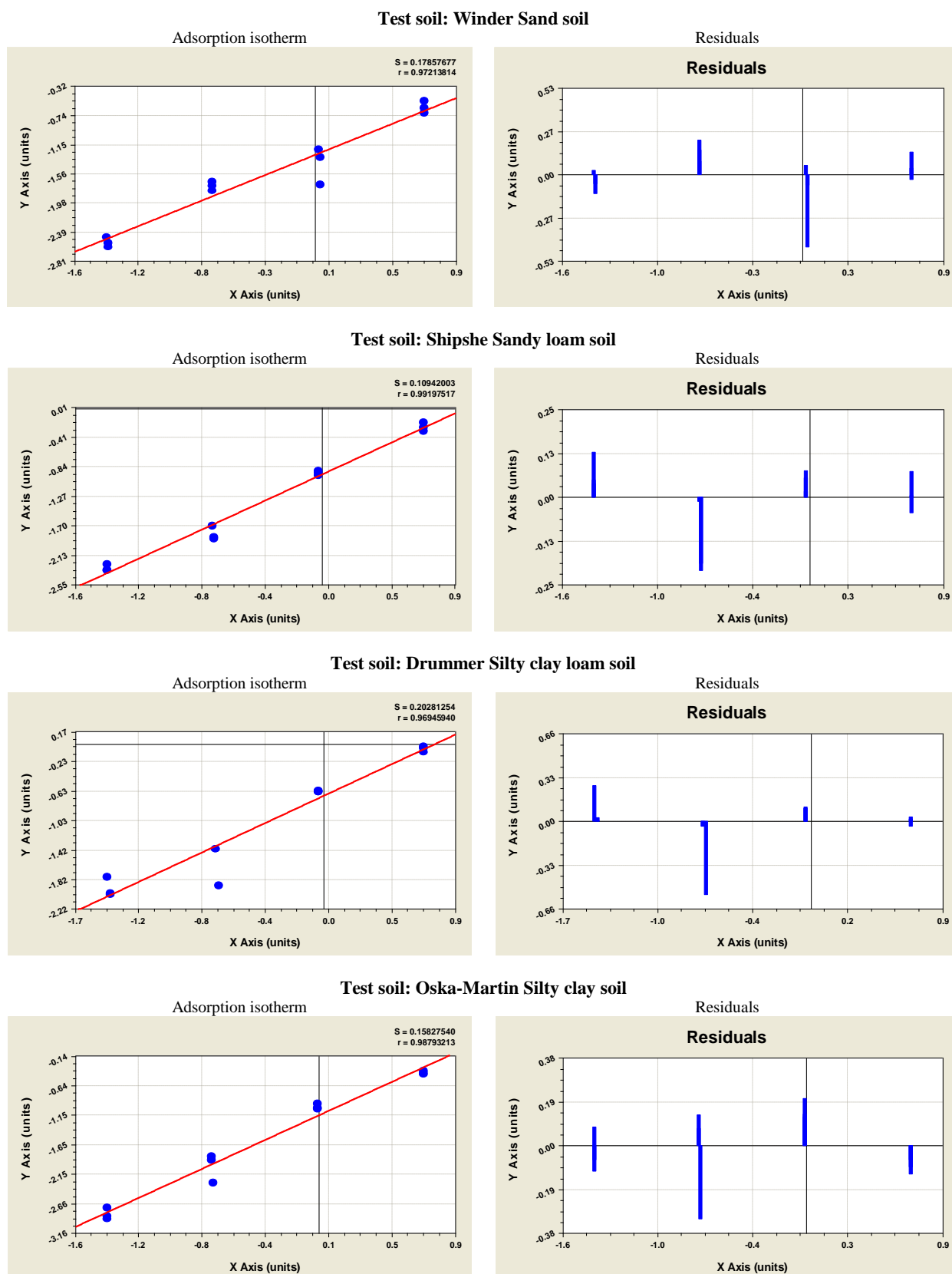


Figure B.8.1.2.1.2._CA-5: The adsorption isotherms for FOE Sulfonic acid determined by the RMS.

Table B.8.1.2.1.2._CA-26: The parameters of the Freundlich adsorption isotherm determined for FOE Sulfonic acid by the RMS

Test soil	Process	Parameters of isotherm				Statistical evaluation	
		Log K _F	K _F [mL/g]	K _{F OC} [mL/g]	1/n	SD	Correlation coefficient <i>r</i>
<i>Winder, Sand soil</i>	Adsorption	-1.294	0.051	18.88	0.865	0.1786	0.9721
<i>Shipshe, Sandy loam soil</i>	Adsorption	-0.974	0.106	14.13	1.002	0.1094	0.9920
<i>Drummer, Silty clay loam soil</i>	Adsorption	-0.690	0.204	9.58	0.931	0.2028	0.9695
<i>Oska-Martin, Silty clay soil</i>	Adsorption	-1.145	0.072	5.95	1.183	0.1583	0.9879

Conclusions of the experiment:

The comparison of the results presented in the study report and those obtained by the RMS showed that the parameters of the adsorption isotherms obtained by the Applicant and RMS were very similar. At the same time RMS stated that the determined adsorption isotherms displayed good conformity with the experimental results. It was not possible to determine the desorption isotherms. That was due to the fact that because of low level adsorption of FOE Sulfonic acid onto every test soil used in the experiment, the results obtained for the desorption bore very high level of uncertainty. The 1/n values for the adsorption isotherms were in range 0.865 – 1.183, indicating that the isotherms generally well complied with the assumed model. However, in case of the isotherm determined for Oska-Martin Silty clay soil the that value was close to 1.2, indicating that the mechanism other than that described by Freundlich equation may also be involved. This is not a definitive conclusion, because the high 1/n value may also be due to generally low level of adsorption and resulting preferential occupation of the sorption sites.

In case of the results obtained in Winder Sand soil it was stated that the adsorption isotherm was robust and well complied with the model – Freundlich sorption isotherm. For that reason RMS decided to include the results into the data set even though the OC content was lower than the recommended minimum – 0.3%.

The definitive set of the results from this experiment is presented below in the table B.8.1.2.1.2._CA-27. RMS decided to present the values determined as a result of the repeated analysis of the data set.

Table B.8.1.2.1.2._CA-27: The definitive set of Freundlich adsorption parameters determined for FOE Sulfonic acid.

Test soil – USDA type (name)	Key soil properties		Freundlich adsorption isotherm parameters			Freundlich desorption isotherm parameters		
	pH ¹⁾	OC [%]	K _F [mL/g]	K _{F OC} [mL/g]	1/n	K _F [mL/g]	K _{F OC} [mL/g]	1/n
<i>Sand (Winder)</i>	5.8	0.27	0.051	18.88	0.865	Not determined		
<i>Sandy loam (Shipshe)</i>	6.3	0.75	0.106	14.13	1.002	Not determined		
<i>Silty clay loam (Drummer)</i>	6.6	2.13	0.204	9.58	0.931	Not determined		
<i>Silty clay (Oska-Martin)</i>	6.0	1.21	0.072	5.95	1.183	Not determined		

Footnotes to the table:

1) Measured in water;

c) Results obtained for FOE Oxalate:

The results of the determination of the concentrations of the test compound in treatment solutions used in the experiment are presented below in the table B.8.1.2.1.2._CA-28.

Table B.8.1.2.1.2._CA-28: The results of the verification of the concentration of treatment solutions used in the Definitive Study for FOE Oxalate.

Test soil	Treatment solution code	Theoretical concentration of the test item [µg/mL]	Measured concentration of the test item [µg/mL]		
			Radiolabelled test item	Technical grade test item	Total concentration of the test item
<i>Winder Sand soil</i>	WI1-3	5.0	0.718	4.4	5.12
	WI2-3	1.0	0.143	0.88	1.02
	WI3-3	0.2	0.029	0.176	0.205
	WI4-3	0.04	0.006	0.0352	0.0408
<i>Shipshe Sandy loam soil</i>	WI1-4	5.0	0.738	4.4	5.14
	WI2-4	1.0	0.146	0.88	1.03
	WI3-4	0.2	0.030	0.176	0.206
	WI4-4	0.04	0.006	0.0352	0.0411
<i>Drummer Silty clay loam soil</i>	WI1-5	5.0	0.716	4.4	5.12
	WI2-5	1.0	0.142	0.88	1.02
	WI3-5	0.2	0.029	0.176	0.205
	WI4-5	0.04	0.006	0.0352	0.0410
<i>Oska-Martin Silty clay soil</i>	WI1-6	5.0	0.735	4.4	5.14
	WI2-6	1.0	0.147	0.88	1.03
	WI3-6	0.2	0.029	0.176	0.205
	WI4-6	0.04	0.006	0.0352	0.0412

The numerical results of experiment examining the adsorption of FOE Oxalate onto test soils are presented below in the table B.8.1.2.1.2._CA-29. The results of the experiment examining its desorption are presented in the table B.8.1.2.1.2._CA-30. The results obtained during examination of the adsorption showed that the adsorption of the test compound onto soil was very low, generally below 10%. For that reason the results of the desorption bear a significant level of uncertainty as the initial concentrations of the test compound retained by soil were very low. RMS decided to report the results presented by the Applicant noticing at the same time that they should be considered with extreme care, as in many instances the reported level of desorption is either above 100%, or a negative value, what is due to the fact that the concentrations were determined at levels close to LOQ.

For that reason the Applicant decided not to determine the desorption isotherms (the available data base did not enable doing that). The graphical results of the experiment – the adsorption isotherms reported in the study report, are given on figure B.8.1.2.1.2._CA-6 and in numerical form in the table B.8.1.2.1.2._CA-31. RMS decided to verify them using the values presented in the table B.8.1.2.1.2._CA-29 – the log-transformed concentrations in soil and solution at equilibrium. The results are provided on figure B.8.1.2.1.2._CA-7 and in numerical form in the table B.8.1.2.1.2._CA-32. The tool used in that exercise was CurveExpert ver. 1.4. Performing the fitting the RMS used the data for the replicates not averaging them, as had done the Applicant.

Table B.8.1.2.1.2._CA-29: The results of the examination of the adsorption of FOE Oxalate onto test soils to determine Freundlich adsorption isotherm.

Test soil	Initial concentration of the solution [µg/mL]	Replicate	Results of the experiment:					
			Concentration at equilibrium				Amount adsorbed onto soil	
			in solution		in soil		in [µg]	in [%]
			Ce [µg/mL]	Log Ce	x/m [µg/g]	Log (x/m)		
<i>Winder Sand soil</i>	5.12	1	4.97	0.70	0.51	-0.29	3.05	3.0
		2	5.04	0.70	0.25	-0.60	1.52	1.5
		3	4.93	0.69	0.63	-0.20	3.77	3.7
	1.02	1	1.01	0.00	0.05	-1.27	0.32	1.6
		2	1.00	0.00	0.07	-1.18	0.39	1.9
		3	1.01	0.00	0.05	-1.27	0.32	1.6
	0.205	1	0.199	-0.70	0.02	-1.71	0.12	2.8
		2	0.200	-0.70	0.02	-1.77	0.10	2.5
		3	0.199	-0.70	0.02	-1.72	0.11	2.8
	0.0408	1	0.0405	-1.39	0.00	-3.01	0.01	0.7
		2	0.0408	-1.39	0.00	-4.31	0.00	0.0
		3	0.0410	----	0.00	----	0.00	-0.4
<i>Shipshe Sandy loam soil</i>	5.14	1	4.99	0.70	0.51	-0.30	3.04	3.0
		2	4.94	0.69	0.66	-0.18	3.98	3.9
		3	4.97	0.70	0.55	-0.26	3.30	3.2
	1.03	1	1.00	0.00	0.08	-1.11	0.46	2.3
		2	1.01	0.00	0.06	-1.21	0.37	1.8
		3	1.01	0.01	0.04	-1.35	0.27	1.3
	0.206	1	0.199	-0.70	0.02	-1.67	0.13	3.1
		2	0.198	-0.70	0.03	-1.59	0.15	3.7
		3	0.198	-0.70	0.02	-1.61	0.15	3.6
	0.0411	1	0.0394	-1.40	0.01	-2.24	0.03	4.2
		2	0.0395	-1.40	0.01	-2.25	0.03	4.1
		3	0.0299	-1.40	0.00	-2.37	0.03	3.1
<i>Drummer Silty clay loam soil</i>	5.12	1	4.91	0.69	0.69	-0.16	4.17	4.1
		2	4.94	0.69	0.60	-0.22	3.60	3.5
		3	4.91	0.69	0.69	-0.16	4.17	4.1
	1.02	1	0.982	-0.01	0.13	-0.87	0.80	3.9
		2	0.984	-0.01	0.13	-0.89	0.77	3.7
		3	0.984	-0.01	0.13	-0.89	0.77	3.8
	0.205	1	0.194	-0.71	0.03	-1.47	0.20	4.9
		2	0.194	-0.71	0.03	-1.47	0.20	5.0
		3	0.194	-0.71	0.03	-1.46	0.21	5.0
	0.0410	1	0.0377	-1.42	0.01	-1.97	0.06	7.9
		2	0.0358	-1.45	0.02	-1.76	0.10	12.7
		3	0.0383	-1.42	0.01	-2.05	0.05	6.6
<i>Oska-Martin Silty clay soil</i>	5.14	1	4.91	0.69	0.75	-0.13	4.49	4.4
		2	4.92	0.69	0.73	-0.14	4.39	4.3
		3	4.93	0.69	0.68	-0.17	4.07	4.0
	1.03	1	0.978	-0.01	0.16	-0.79	0.98	4.8
		2	0.980	-0.01	0.16	-0.80	0.94	4.6
		3	0.981	-0.01	0.15	-0.81	0.93	4.5
	0.205	1	0.195	-0.71	0.04	-1.44	0.22	5.3
		2	0.196	-0.71	0.03	-1.50	0.19	4.6
		3	0.196	-0.71	0.03	-1.49	0.19	4.7
	0.0412	1	0.0397	-1.40	0.00	-2.30	0.03	3.6
		2	0.0390	-1.41	0.01	-2.14	0.04	5.3
		3	0.0391	-1.41	0.01	-2.16	0.04	5.0

Table B.8.1.2.1.2._CA-30: The results of the examination of the desorption of FOE Oxalate from the test soils to determine Freundlich desorption isotherm.

Test soil	Initial concentration of the solution [µg/mL]	Replicate	Results of the experiment:					
			Concentration at equilibrium				Amount desorbed from soil	
			in solution		in soil		in [µg] ³⁾	in [%] ⁴⁾
			Ce [µg/mL]	Log Ce	x/m [µg/g]	Log (x/m)		
<i>Winder Sand soil</i>	5.12	1	0.445	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	0.46	15.2
		2	0.456	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	0.54	35.4
		3	0.519	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	2.00	52.9
	1.02	1	0.0924	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	0.14	42.2
		2	0.0974	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	0.23	61.5
		3	0.0921	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	0.13	40.2
	0.205	1	0.0197	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	0.06	48.1
		2	0.0201	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	0.06	60.7
		3	0.0210	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	0.08	70.8
	0.0408	1	0.0030	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	-0.01	-164.0
		2	0.0039	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	0.01	3170.6
		3	0.0030	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	0.02	-636.8
<i>Shipshe Sandy loam soil</i>	5.14	1	0.391	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	-1.15	-37.8
		2	0.369	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	-1.52	-38.1
		3	0.362	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	-1.71	-51.9
	1.03	1	0.0862	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	-0.08	-17.8
		2	0.0844	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	-0.13	-34.4
		3	0.0879	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	-0.07	-24.5
	0.206	1	0.0188	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	0.02	14.1
		2	0.0216	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	0.08	48.8
		3	0.0206	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	0.06	37.8
	0.0411	1	0.0042	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	0.01	35.7
		2	0.0039	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	0.01	21.4
		3	0.0043	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	0.01	53.4
<i>Drummer Silty clay loam soil</i>	5.12	1	0.598	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	-0.97	-23.3
		2	0.584	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	-1.15	-31.9
		3	0.631	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	-0.14	-3.3
	1.02	1	0.125	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	-0.06	-7.4
		2	0.133	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	0.10	12.5
		3	0.134	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	0.12	16.2
	0.205	1	0.0287	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	0.07	34.3
		2	0.0279	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	0.05	16.0
		3	0.0284	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	0.06	30.1
	0.0410	1	0.0058	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	0.02	29.0
		2	0.0053	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	0.01	12.5
		3	0.0056	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	0.01	24.8
<i>Oska-Martin Silty clay soil</i>	5.14	1	1.08	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	1.43	31.8
		2	1.09	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	1.64	37.5
		3	0.84	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	-3.39	-83.3
	1.03	1	0.212	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	0.22	23.0
		2	0.215	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	0.28	26.9
		3	0.221	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	0.39	41.9
	0.205	1	0.0411	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	0.02	11.3
		2	0.0395	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	-0.01	-7.9
		3	0.0450	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	0.10	50.1
	0.0412	1	0.0078	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	-0.01	-23.5
		2	0.0074	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	-0.01	-25.7
		3	0.0082	n. c. ¹⁾	n. r. ²⁾	n. c. ¹⁾	0.01	10.8

Footnotes to the table:

- 1) n. c. = not calculated;
- 2) n. r. = not reported, probably not determined;
- 3) all values as reported in the study report;
- 4) all values as reported in the study report.

The graphical results of the experiment presented in the study report are given below on figure B.8.1.2.1.2._CA-6 and in numerical form in the table B.8.1.2.1.2._CA-31.

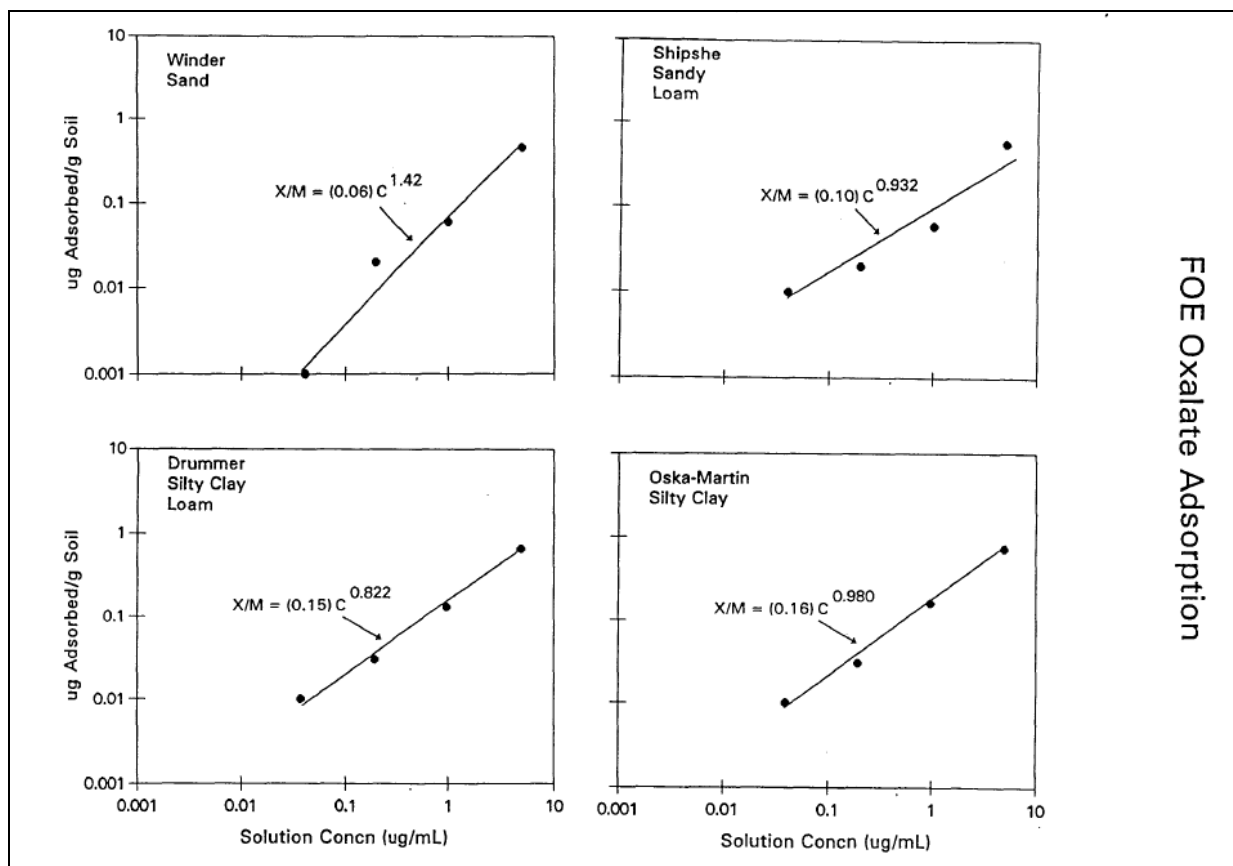


Figure B.8.1.2.1.2_CA-6: The adsorption isotherm for FOE Oxalate provided by the Applicant (copied from the study report).

Table B.8.1.2.1.2_CA-31: The key numerical results of the experiment presented in the study report – parameters of Freundlich adsorption isotherm for FOE Oxalate, including the correlation coefficient r

Test soil	Parameters of Freundlich adsorption isotherm					Parameters of Freundlich desorption isotherm				
	$\text{Log } K_{f \text{ ads}}$	$K_{f \text{ ads}} [\text{mL/g}]$	$1/n$	$K_{f \text{ OC ads}} [\text{mL/g}]$	r	$\text{Log } K_{f \text{ des}}$	$K_{f \text{ des}} [\text{mL/g}]$	$1/n$	$K_{f \text{ OC des}} [\text{mL/g}]$	r
Winder Sand soil	-1.22	0.06	1.42	23	0.923	Not determined				
Shipshe Sandy loam soil	-1.02	0.10	0.932	13	0.981	Not determined				
Drummer Silty clay loam soil	-0.816	0.15	0.822	7	0.989	Not determined				
Oska-Martin Silty clay soil	-0.806	0.16	0.980	13	1.00	Not determined				

The graphical and numerical results of the repeated analysis, performed by the RMS, of the data from the table B.8.1.2.1.2_CA-29 (for adsorption) are presented below on figure B.8.1.2.1.2_CA-7 and in the table B.8.1.2.1.2_CA-32.

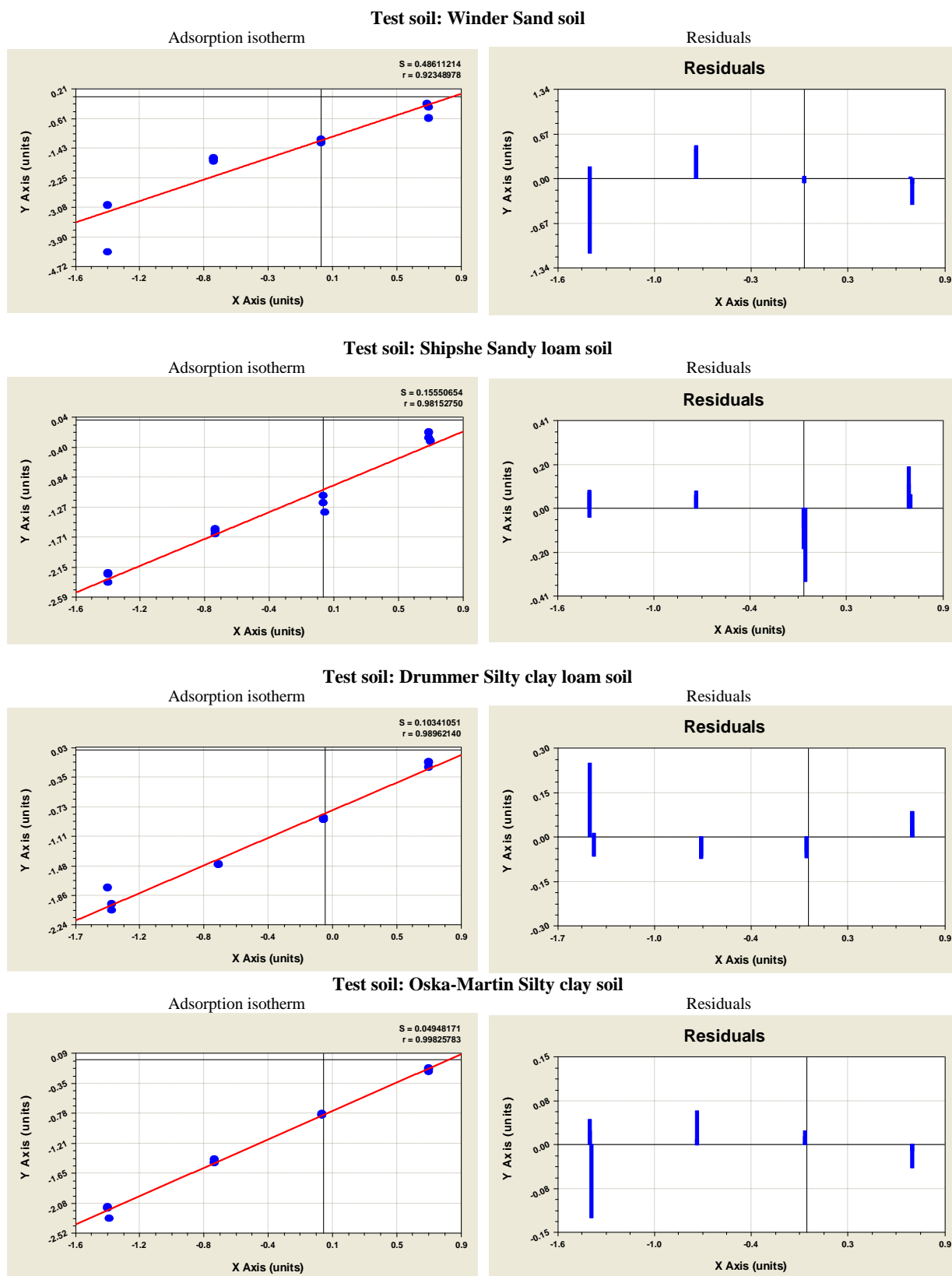


Figure B.8.1.2.1.2._CA-7: The adsorption isotherms for FOE Oxalate determined by the RMS.

Table B.8.1.2.1.2._CA-32: The parameters of the Freundlich adsorption isotherm determined for FOE Oxalate by the RMS

Test soil	Process	Parameters of isotherm				Statistical evaluation	
		Log K _F	K _F [mL/g]	K _{F OC} [mL/g]	1/n	SD	Correlation coefficient <i>r</i>
<i>Winder, Sand soil</i>	Adsorption	-1.214	0.061	22.59	1.423	0.4861	0.9230
<i>Shipshe, Sandy loam soil</i>	Adsorption	-1.018	0.096	12.80	0.933	0.1555	0.9815
<i>Drummer, Silty clay loam soil</i>	Adsorption	-0.814	0.153	7.18	0.824	0.1034	0.9896
<i>Oska-Martin, Silty clay soil</i>	Adsorption	-0.805	0.157	12.97	0.978	0.0495	0.9983

Conclusions of the experiment:

The comparison of the results presented in the study report and those obtained by the RMS showed that the parameters of the adsorption isotherms obtained by the Applicant and RMS were very similar. At the same time RMS stated that the determined adsorption isotherms displayed good conformity with the experimental results. It was not possible to determine the desorption isotherms. That was due to the fact that because of low level adsorption of FOE Oxalate onto every test soil used in the experiment, the results obtained for the desorption bore very high level of uncertainty. The 1/n values for the adsorption isotherms were in range 0.824 – 1.423, with the highest value obtained for Winder Sand soil. In case of three remaining soil the 1/n were in range 0.824 – 0.978, indicating that for these three soils the isotherms well complied with the assumed model. In case of the isotherm determined for Winder Sand soil the high 1/n value of 1.423 may indicate that the mechanism other than that described by Freundlich equation could also be involved. This however is not a definitive conclusion, because the high 1/n value may also be due to generally low level of adsorption and resulting preferential occupation of the sorption sites.

However, because of high 1/n value, indicating the adsorption mechanism other than that described by Freundlich isotherm, and also due to the fact that the OC = 0.27% was below the recommended lowest level of 0.3%, the parameters of Freundlich adsorption isotherm obtained in Winder Sand soil cannot be considered reliable. For that reason RMS decided not to include these results into the final data set.

The definitive set of the results from this experiment is presented below in the table B.8.1.2.1.2._CA-33. RMS decided to present the values determined as a result of the repeated analysis of the data set.

Table B.8.1.2.1.2._CA-33: The definitive set of Freundlich adsorption and desorption parameters determined for FOE Oxalate.

Test soil – USDA type (name)	Key soil properties		Freundlich adsorption isotherm parameters			Freundlich desorption isotherm parameters		
	pH ¹⁾	OC [%]	K _F [mL/g]	K _{F OC} [mL/g]	1/n	K _F [mL/g]	K _{F OC} [mL/g]	1/n
<i>Sandy loam (Shipshe)</i>	6.3	0.75	09.096	12.80	0.933	Not determined		
<i>Silty clay loam (Drummer)</i>	6.6	2.13	0.153	7.18	0.824	Not determined		
<i>Silty clay (Oska-Martin)</i>	6.0	1.21	0.157	12.97	0.978	Not determined		

Footnotes to the table:

1) Measured in water;

d) Results obtained for FOE Alcohol:

The results of the determination of the concentrations of the test compound in treatment solutions used in the experiment are presented below in the table B.8.1.2.1.2._CA-34.

Table B.8.1.2.1.2._CA-34: The results of the verification of the concentration of treatment solutions used in the Definitive Study for FOE Alcohol.

Test soil	Treatment solution code	Theoretical concentration of the test item [µg/mL]	Measured concentration of the test item [µg/mL]		
			Radiolabelled test item	Technical grade test item	Total concentration of the test item
<i>Winder Sand soil</i>	WL1-3	5.0	0.279	4.80	5.08
	WL2-3	1.0	0.056	0.96	1.02
	WL3-3	0.2	0.011	0.192	0.203
	WL4-3	0.04	0.002	0.0384	0.0406
<i>Shipshe Sandy loam soil</i>	WL1-4	5.0	0.289	4.80	5.09
	WL2-4	1.0	0.058	0.96	1.02
	WL3-4	0.2	0.012	0.192	0.204
	WL4-4	0.04	0.002	0.0384	0.0407
<i>Drummer Silty clay loam soil</i>	WL1-5	5.0	0.281	4.80	5.08
	WL2-5	1.0	0.057	0.96	1.02
	WL3-5	0.2	0.011	0.192	0.203
	WL4-5	0.04	0.002	0.0384	0.0407
<i>Oska-Martin Silty clay soil</i>	WL1-6	5.0	0.289	4.80	5.09
	WL2-6	1.0	0.058	0.96	1.02
	WL3-6	0.2	0.012	0.192	0.204
	WL4-6	0.04	0.002	0.0384	0.0407

The numerical results of experiment examining the adsorption of FOE Alcohol onto test soils are presented below in the table B.8.1.2.1.2._CA-35. The results of the experiment examining its desorption are presented in the table B.8.1.2.1.2._CA-36. The graphical results of the experiment – the adsorption and desorption isotherms determined for each test soil, are presented on figure B.8.1.2.1.2._CA-8. The key numerical results are provided in the table B.8.1.2.1.2._CA-37. Analysing these results RMS stated that it was not possible to interpret them appropriately as the Applicant did not distinguish the isotherms representing adsorption and desorption. For that reason it was also not possible to verify the correctness of the determined parameters of each isotherm. For that reason RMS decided to repeat the determination of the isotherms using the same data as presented in tables B.8.1.2.1.2._CA-35 and B.8.1.2.1.2._CA-36 – the log-transformed data. The adsorption and desorption isotherms were determined separately. The tool used in that exercise was CurveExpert ver 1.40. The graphical results are presented on two figures – B.8.1.2.1.2._CA-9 for adsorption and B.8.1.2.1.2._CA-10 for desorption. The corresponding numerical results are provided in the table B.8.1.2.1.2._CA-38. Performing the fitting the RMS used the data for the replicates not averaging them, as had done the Applicant.

Table B.8.1.2.1.2._CA-35: The results of the examination of the adsorption of FOE Alcohol onto test soils to determine Freundlich adsorption isotherm.

Test soil	Initial concentration of the solution [µg/mL]	Replicate	Results of the experiment:					
			Concentration at equilibrium				Amount adsorbed onto soil	
			in solution		in soil		in [µg]	in [%]
			Ce [µg/mL]	Log Ce	x/m [µg/g]	Log (x/m)		
<i>Winder Sand soil</i>	5.08	1	4.78	0.68	1.00	0.00	5.97	5.9
		2	4.81	0.68	0.91	-0.04	5.46	5.4
		3	4.78	0.68	0.98	-0.01	5.88	5.8
	1.02	1	0.947	-0.02	0.23	-0.64	1.38	6.8
		2	0.952	-0.02	0.21	-0.67	1.28	6.3
		3	0.951	-0.02	0.22	-0.66	1.30	6.4
	0.203	1	0.186	-0.73	0.06	-1.23	0.35	8.6
		2	0.189	-0.72	0.05	-1.33	0.28	6.9
		3	0.189	-0.72	0.05	-1.33	0.28	6.8
	0.0406	1	0.0373	-1.43	0.01	-1.96	0.07	8.2
		2	0.0376	-1.42	0.01	-1.99	0.06	7.5
		3	0.0383	-1.42	0.01	-2.10	0.05	5.8
<i>Shipshe Sandy loam soil</i>	5.09	1	4.29	0.63	2.68	0.43	16.08	15.8
		2	4.32	0.64	2.55	0.41	15.30	15.0
		3	4.28	0.63	2.68	0.43	16.13	15.8
	1.02	1	0.803	-0.10	0.72	-0.15	4.30	21.1
		2	0.807	-0.09	0.70	-0.15	4.20	20.7
		3	0.811	-0.09	0.69	-0.16	4.13	20.3
	0.204	1	0.156	-0.81	0.16	-0.80	0.96	23.5
		2	0.158	-0.80	0.15	-0.82	0.92	22.6
		3	0.155	-0.81	0.16	-0.79	0.97	23.8
	0.0407	1	0.0306	-1.51	0.03	-1.48	0.20	24.7
		2	0.0306	-1.51	0.03	-1.47	0.20	24.8
		3	0.0306	-1.51	0.03	-1.47	0.20	24.7
<i>Drummer Silty clay loam soil</i>	5.08	1	3.34	0.52	5.81	0.76	34.88	34.3
		2	3.39	0.53	5.63	0.75	33.80	33.3
		3	3.37	0.53	5.70	0.76	34.20	33.7
	1.02	1	0.610	-0.21	1.35	0.13	8.13	40.0
		2	0.588	-0.23	1.43	0.16	8.58	42.2
		3	0.600	-0.22	1.39	0.14	8.33	41.0
	0.203	1	0.115	-0.94	0.29	-0.53	1.77	43.4
		2	0.117	-0.93	0.29	-0.54	1.73	42.7
		3	0.115	-0.94	0.29	-0.53	1.76	43.3
	0.0407	1	0.0293	-1.62	0.06	-1.25	0.34	41.2
		2	0.0237	-1.63	0.06	-1.25	0.34	41.8
		3	0.0250	-1.60	0.05	-1.28	0.31	38.6
<i>Oska-Martin Silty clay soil</i>	5.09	1	2.41	0.38	8.92	0.95	53.62	52.7
		2	2.47	0.39	8.73	0.94	52.46	51.5
		3	2.45	0.39	8.77	0.94	52.69	51.8
	1.02	1	0.467	-0.33	1.84	0.26	11.02	54.1
		2	0.461	-0.34	1.85	0.27	11.14	54.7
		3	0.465	-0.33	1.84	0.27	11.07	54.3
	0.204	1	0.0873	-1.06	0.39	-0.41	2.33	57.1
		2	0.0884	-1.05	0.38	-0.42	2.30	56.6
		3	0.0892	-1.05	0.38	-0.42	2.29	56.2
	0.0407	1	0.0168	-1.78	0.08	-1.10	0.48	58.8
		2	0.0163	-1.79	0.08	-1.09	0.49	59.9
		3	0.0182	-1.74	0.07	-1.13	0.45	55.2

Table B.8.1.2.1.2._CA-36: The results of the examination of the desorption of FOE Alcohol from the test soils to determine Freundlich desorption isotherm.

Test soil	Initial concentration of the solution [µg/mL]	Replicate	Results of the experiment:					
			Concentration at equilibrium				Amount desorbed from soil	
			in solution		in soil		in [µg] ¹⁾	in [%] ²⁾
			Ce [µg/mL]	Log Ce	x/m [µg/g]	Log (x/m)		
<i>Winder Sand soil</i>	5.08	1	0.632	-0.20	0.40	-0.39	3.55	59.5
		2	0.678	-0.17	0.17	-0.76	4.42	81.0
		3	0.676	-0.17	0.24	-0.62	4.43	75.3
	1.02	1	0.140	-0.85	0.06	-1.20	1.00	72.5
		2	0.140	-0.85	0.05	-1.33	0.99	77.8
		3	0.131	-0.88	0.08	-1.09	0.81	62.4
	0.203	1	0.0269	-1.57	0.03	-1.56	0.19	51.9
		2	0.0294	-1.53	0.01	-2.07	0.23	81.8
		3	0.0275	-1.56	0.01	-1.84	0.19	68.7
	0.0406	1	0.0055	-2.26	0.00	-2.34	0.04	58.6
		2	0.0054	-2.27	0.00	-2.39	0.04	59.7
		3	0.0057	-2.24	0.00	-3.00	0.04	87.4
<i>Shipshe Sandy loam soil</i>	5.09	1	0.876	-0.06	1.33	0.12	8.09	50.3
		2	0.929	-0.03	1.04	0.02	9.06	59.3
		3	0.936	-0.03	1.14	0.06	9.30	57.7
	1.02	1	0.202	-0.70	0.34	-0.47	2.26	52.7
		2	0.206	-0.69	0.31	-0.51	2.35	55.6
		3	0.200	-0.70	0.32	-0.50	2.21	53.7
	0.204	1	0.0412	-1.38	0.08	-1.10	0.48	50.4
		2	0.0436	-1.36	0.07	-1.18	0.53	57.2
		3	0.0452	-1.35	0.07	-1.17	0.56	58.1
	0.0407	1	0.0091	-2.04	0.01	-1.84	0.11	56.6
		2	0.0094	-2.03	0.01	-1.87	0.12	60.3
		3	0.0094	-2.03	0.01	-1.87	0.12	59.8
<i>Drummer Silty clay loam soil</i>	5.08	1	1.15	0.06	3.33	0.52	14.90	42.7
		2	1.14	0.06	3.18	0.50	14.73	43.6
		3	1.04	0.02	3.57	0.55	12.76	37.3
	1.02	1	0.270	-0.57	0.70	-0.16	3.94	48.5
		2	0.257	-0.59	0.81	-0.09	3.73	43.5
		3	0.266	-0.58	0.74	-0.13	3.88	46.6
	0.203	1	0.0572	-1.24	0.15	-0.83	0.87	49.2
		2	0.0614	-1.21	0.13	-0.88	0.95	54.7
		3	0.0608	-1.22	0.14	-0.86	0.94	53.3
	0.0407	1	0.0131	-1.88	0.02	-1.66	0.21	61.1
		2	0.0130	-1.89	0.02	-1.64	0.20	59.6
		3	0.0133	-1.88	0.02	-1.75	0.21	65.8
<i>Oska-Martin Silty clay soil</i>	5.09	1	1.46	0.16	5.95	0.77	17.84	33.3
		2	1.48	0.17	5.74	0.76	17.98	34.3
		3	1.50	0.18	5.69	0.75	18.53	35.2
	1.02	1	0.306	-0.51	1.18	0.07	3.92	35.6
		2	0.293	-0.53	1.24	0.09	3.69	33.1
		3	0.296	-0.53	1.22	0.09	3.73	33.7
	0.204	1	0.0613	-1.21	0.25	-0.60	0.82	35.1
		2	0.0636	-1.20	0.24	-0.62	0.86	37.2
		3	0.0604	-1.22	0.25	-0.60	0.79	34.5
	0.0407	1	0.0118	-1.93	0.05	-1.27	0.16	32.7
		2	0.0111	-1.95	0.06	-1.24	0.15	29.9
		3	0.0139	-1.86	0.04	-1.37	0.19	42.7

Footnotes to the table:

- 1) all values as reported in the study report;
 2) all values as reported in the study report.

The graphical results of the experiment presented in the study report are given below on figure B.8.1.2.1.2._CA-8 and in numerical form in the table B.8.1.2.1.2._CA-37.

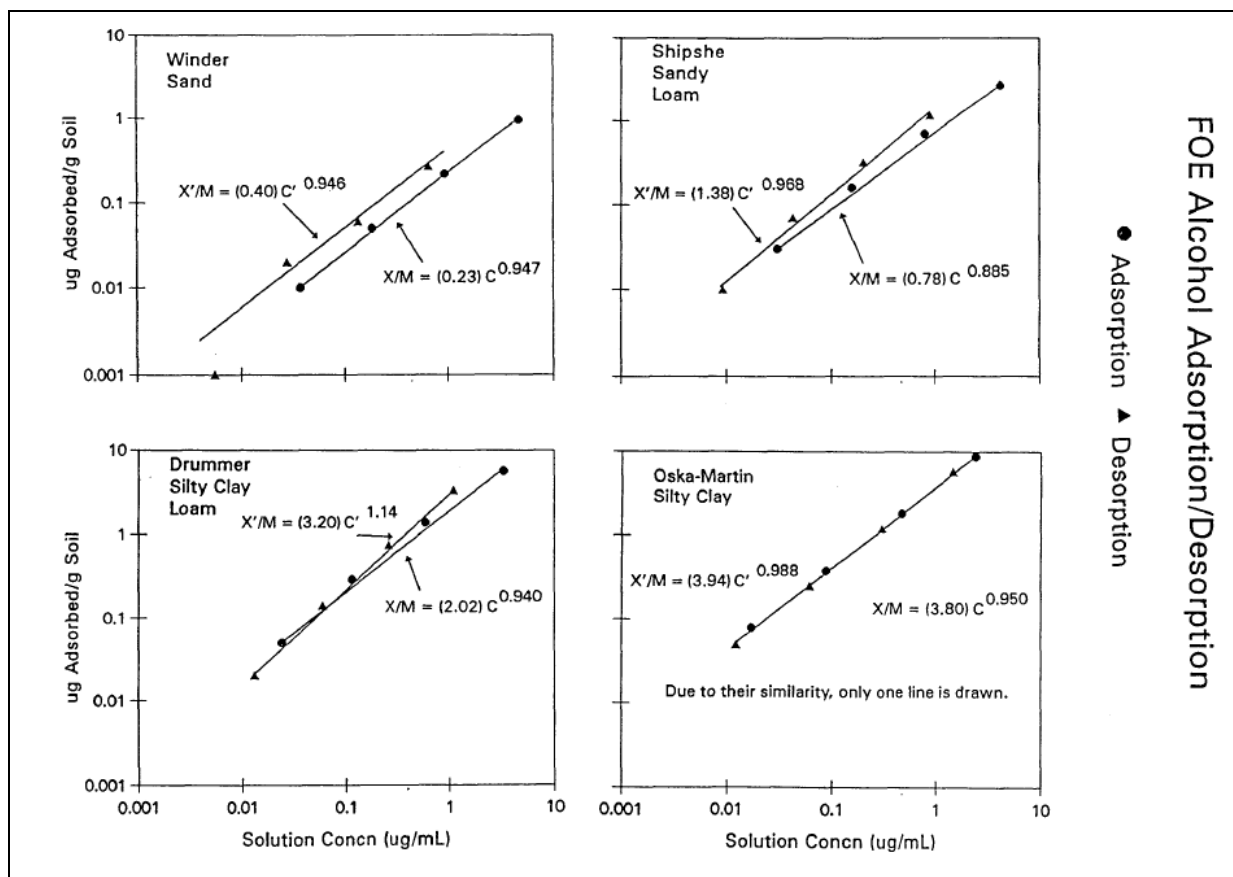


Figure B.8.1.2.1.2_CA-8: The adsorption and desorption isotherms for FOE Alcohol provided by the Applicant (copied from the study report).

Table B.8.1.2.1.2_CA-37: The key numerical results of the experiment presented in the study report – parameters of Freundlich adsorption and desorption isotherms for FOE Alcohol, including the correlation coefficient r

Test soil	Parameters of Freundlich adsorption isotherm					Parameters of Freundlich desorption isotherm				
	$\text{Log } K_{fads}$	K_{fads} [mL/g]	$1/n$	K_{fOCads} [mL/g]	r	$\text{Log } K_{fdes}$	K_{fdes} [mL/g]	$1/n$	K_{fOCdes} [mL/g]	r
Winder Sand soil	-0.645	0.23	0.947	84	0.998	-0.40	0.40	0.946	147	0.959
Shipshe Sandy loam soil	-0.108	0.78	0.885	104	0.999	0.140	1.38	0.968	184	0.997
Drummer Silty clay loam soil	0.305	2.02	0.940	95	0.998	0.506	3.20	1.14	150	0.998
Oska-Martin Silty clay soil	0.580	3.80	0.950	314	1.000	0.596	3.94	0.988	326	1.000

The graphical and numerical results of the repeated analysis, performed by the RMS, of the data from the tables B.8.1.2.1.2_CA-35 (for adsorption) and B.8.1.2.1.2_CA-36 (for desorption) are presented below on figures B.8.1.2.1.2_CA-9 (adsorption) and B.8.1.2.1.2_CA-10 (desorption) and in the table B.8.1.2.1.2_CA-38.

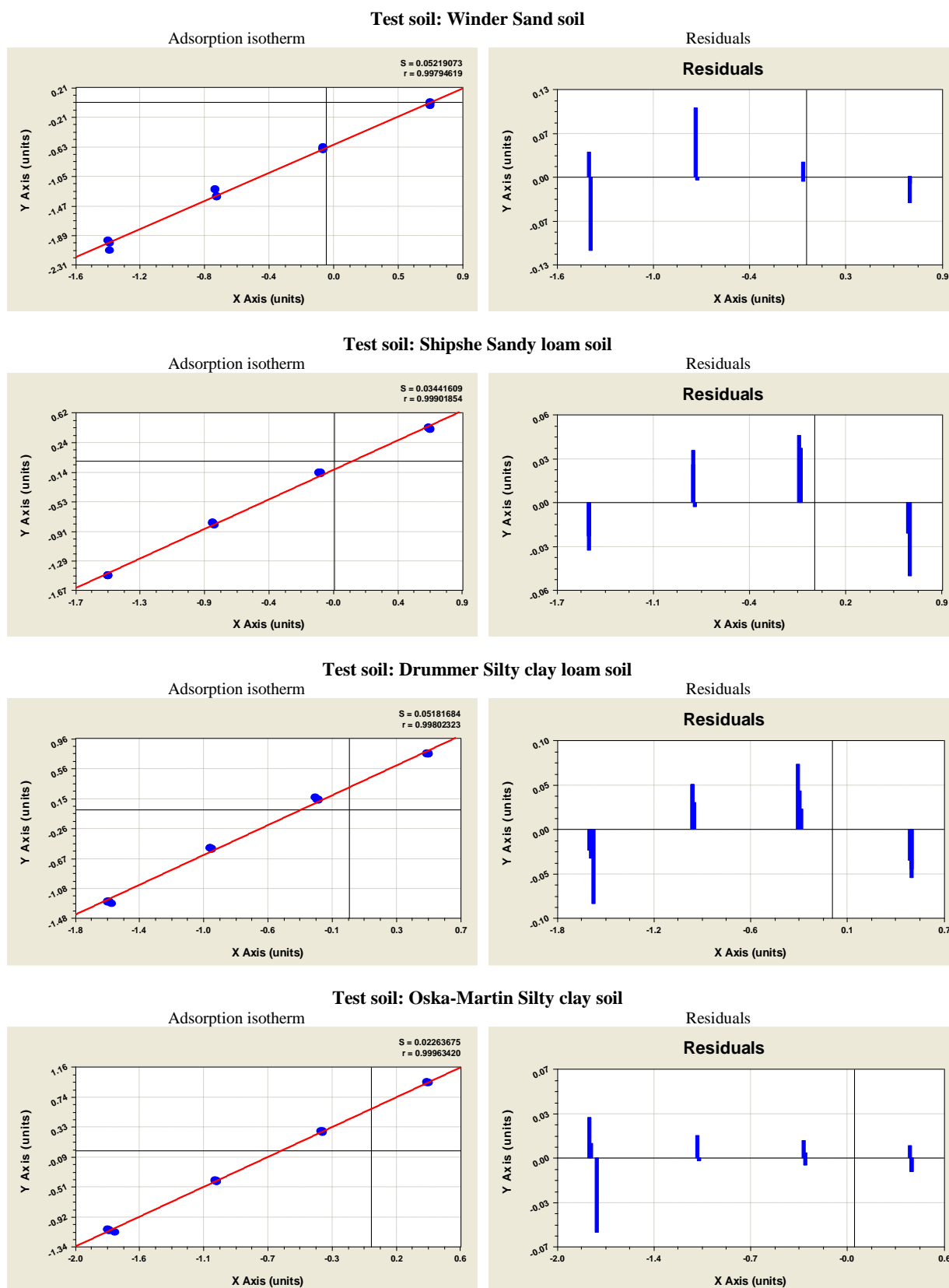


Figure B.8.1.2.1.2._CA-32: The adsorption isotherms for FOE Alcohol determined by the RMS.

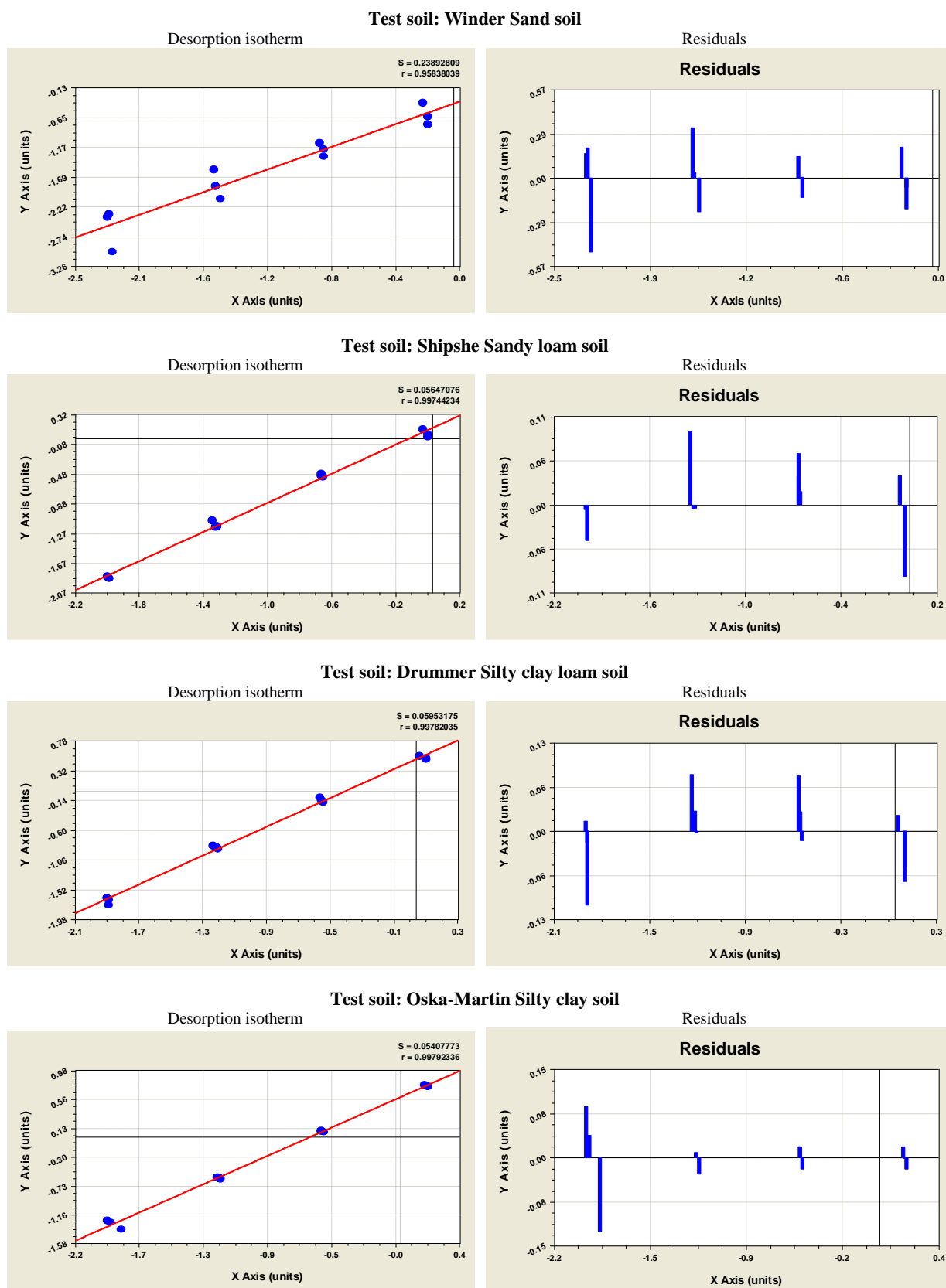


Figure B.8.1.2.1.2_CA-33: The desorption isotherms for FOE Alcohol determined by the RMS.

Table B.8.1.2.1.2._CA-38: The parameters of the Freundlich adsorption and desorption isotherms determined for FOE Alcohol by the RMS

Test soil	Process	Parameters of isotherm				Statistical evaluation	
		Log K _F	K _F [mL/g]	K _{F OC} [mL/g]	1/n	SD	Correlation coefficient <i>r</i>
<i>Winder, Sand soil</i>	Adsorption	-0.645	0.226	83.70	0.947	0.0522	0.9979
	Desorption	-0.403	0.395	52.67	0.946	0.2389	0.9584
<i>Shipshe, Sandy loam soil</i>	Adsorption	-0.108	0.780	104.00	0.887	0.0344	0.9990
	Desorption	0.141	1.384	184.53	0.970	0.0565	0.9974
<i>Drummer, Silty clay loam soil</i>	Adsorption	0.305	2.018	94.74	0.940	0.0518	0.9980
	Desorption	0.504	3.191	149.81	1.142	0.0595	0.9978
<i>Oska-Martin, Silty clay soil</i>	Adsorption	0.580	3.802	314.21	0.950	0.0226	0.9996
	Desorption	0.593	3.917	323.72	0.986	0.0541	0.9979

Conclusions of the experiment:

The comparison of the results presented in the study report and those obtained by the RMS showed that the parameters of the adsorption and desorption isotherms obtained by the Applicant and RMS were almost identical. At the same time RMS stated that the determined adsorption isotherms displayed very good conformity with the experimental results. That conformity was also good in case of the desorption isotherms.

The 1/n values for the adsorption isotherms were in range 0.887 – 0.950, indicating that the isotherms well complied with the assumed model. In case of the results obtained in Winder Sand soil it was stated that the adsorption isotherm was robust and well complied with the model – Freundlich sorption isotherm. For that reason RMS decided to include the results into the data set even though the OC content was lower than the recommended minimum – 0.3%.

The definitive set of the results from this experiment is presented below in the table B.8.1.2.1.2._CA-39. RMS decided to present the values determined as a result of the repeated analysis of the data set.

Table B.8.1.2.1.2._CA-39: The definitive set of Freundlich adsorption and desorption parameters determined for FOE Alcohol.

Test soil – USDA type (name)	Key soil properties		Freundlich adsorption isotherm parameters			Freundlich desorption isotherm parameters		
	pH ¹⁾	OC [%]	K _F [mL/g]	K _{F OC} [mL/g]	1/n	K _F [mL/g]	K _{F OC} [mL/g]	1/n
<i>Sand (Winder)</i>	5.8	0.27	0.226	83.70	0.947	0.395	52.67	0.946
<i>Sandy loam (Shipshe)</i>	6.3	0.75	0.780	104.00	0.887	1.384	184.53	0.970
<i>Silty clay loam (Drummer)</i>	6.6	2.13	2.018	94.74	0.940	3.191	149.81	1.142
<i>Silty clay (Oska-Martin)</i>	6.0	1.21	3.802	314.21	0.950	3.917	323.72	0.986

Footnotes to the table:

1) Measured in water;

e) Results obtained for FOE Thiadone:

The results of the determination of the concentrations of the test compound in treatment solutions used in the experiment are presented below in the table B.8.1.2.1.2._CA-40.

Table B.8.1.2.1.2._CA-40: The results of the verification of the concentration of treatment solutions used in the Definitive Study for FOE Thiadone.

Test soil	Treatment solution code	Theoretical concentration of the test item [µg/mL]	Measured concentration of the test item [µg/mL]		
			Radiolabelled test item	Technical grade test item	Total concentration of the test item
<i>Winder Sand soil</i>	WO1-3	5.0	0.525	4.90	5.43
	WO2-3	1.0	0.105	0.98	1.09
	WO3-3	0.2	0.021	0.196	0.217
	WO4-3	0.04	0.004	0.0392	0.0435
<i>Shipshe Sandy loam soil</i>	WO1-4	5.0	0.544	4.90	5.44
	WO2-4	1.0	0.109	0.98	1.09
	WO3-4	0.2	0.022	0.196	0.218
	WO4-4	0.04	0.004	0.0392	0.0435
<i>Drummer Silty clay loam soil</i>	WO1-7	5.0	0.568	4.90	5.47
	WO2-7	1.0	0.114	0.98	1.09
	WO3-7	0.2	0.023	0.196	0.219
	WO4-7	0.04	0.005	0.0392	0.0438
<i>Oska-Martin Silty clay soil</i>	WO1-8	5.0	0.586	4.90	5.49
	WO2-8	1.0	0.118	0.98	1.10
	WO3-8	0.2	0.024	0.196	0.220
	WO4-8	0.04	0.005	0.0392	0.0440

The numerical results of experiment examining the adsorption of FOE Thiadone onto test soils are presented below in the table B.8.1.2.1.2._CA-41. The results of the experiment examining its desorption are presented in the table B.8.1.2.1.2._CA-42. The graphical results of the experiment – the adsorption and desorption isotherms determined for each test soil, are presented on figure B.8.1.2.1.2._CA-11. The key numerical results are provided in the table B.8.1.2.1.2._CA-43. Analysing these results RMS stated that it was not possible to interpret them appropriately as the Applicant did not distinguish the isotherms representing adsorption and desorption. For that reason it was also not possible to verify the correctness of the determined parameters of each isotherm. For that reason RMS decided to repeat the determination of the isotherms using the same data as presented in tables B.8.1.2.1.2._CA-41 and B.8.1.2.1.2._CA-42 – the log-transformed data. The adsorption and desorption isotherms were determined separately. The tool used in that exercise was CurveExpert ver 1.40. The graphical results are presented on two figures – B.8.1.2.1.2._CA-12 for adsorption and B.8.1.2.1.2._CA-13 for desorption. The corresponding numerical results are provided in the table B.8.1.2.1.2._CA-44. Performing the fitting the RMS used the data for the replicates not averaging them, as had done the Applicant.

Table B.8.1.2.1.2._CA-41: The results of the examination of the adsorption of FOE Thiadone onto test soils to determine Freundlich adsorption isotherm.

Test soil	Initial concentration of the solution [µg/mL]	Replicate	Results of the experiment:					
			Concentration at equilibrium				Amount adsorbed onto soil	
			in solution		in soil		in [µg]	in [%]
			Ce [µg/mL]	Log Ce	x/m [µg/g]	Log (x/m)		
<i>Winder Sand soil</i>	5.43	1	5.31	0.72	0.40	-0.40	2.40	2.2
		2	5.23	0.72	0.67	-0.18	4.00	3.7
		3	5.31	0.73	0.38	-0.42	2.27	2.1
	1.09	1	1.07	0.03	0.06	-1.24	0.35	1.6
		2	1.04	0.02	0.16	-0.79	0.97	4.4
		3	1.04	0.02	0.14	-0.85	0.85	3.9
	0.217	1	0.211	-0.68	0.02	-1.69	0.12	2.8
		2	0.206	-0.69	0.04	-1.42	0.23	5.3
		3	0.206	-0.69	0.04	-1.45	0.21	4.9
	0.0435	1	0.0403	-1.39	0.01	-1.97	0.06	7.3
		2	0.0401	-1.40	0.01	-1.95	0.07	7.8
		3	0.0408	-1.39	0.01	-2.04	0.05	6.2
<i>Shipshe Sandy loam soil</i>	5.44	1	5.08	0.71	1.21	0.08	7.27	6.7
		2	5.07	0.70	1.26	0.10	7.56	6.9
		3	5.07	0.71	1.24	0.09	7.43	6.8
	1.09	1	0.996	0.00	0.31	-0.51	1.84	8.5
		2	0.990	0.00	0.33	-0.48	1.98	9.1
		3	0.980	-0.01	0.36	-0.44	2.18	10.0
	0.218	1	0.194	-0.71	0.08	-1.10	0.48	11.0
		2	0.191	-0.72	0.09	-1.05	0.54	12.3
		3	0.190	-0.72	0.09	-1.04	0.55	12.7
	0.0435	1	0.0363	-1.44	0.02	-1.62	0.14	16.6
		2	0.0364	-1.44	0.02	-1.62	0.14	16.4
		3	0.0369	-1.43	0.02	-1.66	0.13	15.2
<i>Drummer Silty clay loam soil</i>	5.47	1	4.92	0.69	1.81	0.26	10.88	9.9
		2	4.90	0.69	1.88	0.27	11.28	10.3
		3	5.00	0.70	1.56	0.19	9.38	8.6
	1.09	1	0.920	-0.04	0.58	-0.24	3.47	15.9
		2	0.918	-0.04	0.59	-0.23	3.53	16.1
		3	0.917	-0.04	0.59	-0.23	3.54	1.62
	0.219	1	0.162	-0.79	0.19	-0.72	1.14	26.1
		2	0.163	-0.79	0.19	-0.73	1.11	25.5
		3	0.161	-0.79	0.19	-0.72	1.15	26.2
	0.0438	1	0.0277	-1.56	0.05	-1.27	0.32	36.6
		2	0.0277	-1.56	0.05	-1.27	0.32	36.7
		3	0.0282	-1.55	0.05	-1.29	0.31	35.5
<i>Oska-Martin Silty clay soil</i>	5.49	1	4.76	0.68	2.42	0.38	14.55	13.3
		2	4.81	0.68	2.25	0.35	13.53	12.3
		3	4.87	0.69	2.06	0.31	12.40	11.3
	1.10	1	0.885	-0.05	0.71	-0.15	4.27	19.4
		2	0.879	-0.06	0.73	-0.14	4.39	20.0
		3	0.885	-0.05	0.71	-0.15	4.27	19.4
	0.220	1	0.165	-0.78	0.18	-0.74	1.09	24.7
		2	0.164	-0.79	0.19	-0.73	1.12	25.5
		3	0.166	-0.78	0.18	-0.75	1.07	24.2
	0.0440	1	0.0316	-1.50	0.04	-1.38	0.25	28.3
		2	0.0314	-1.50	0.04	-1.38	0.25	28.6
		3	0.0320	-1.49	0.04	-1.40	0.25	27.2

Table B.8.1.2.1.2._CA-42: The results of the examination of the desorption of FOE Thiadone from the test soils to determine Freundlich desorption isotherm.

Test soil	Initial concentration of the solution [µg/mL]	Replicate	Results of the experiment:					
			Concentration at equilibrium				Amount desorbed from soil	
			in solution		in soil		in [µg] ¹⁾	in [%] ²⁾
			Ce [µg/mL]	Log Ce	x/m [µg/g]	Log (x/m)		
<i>Winder Sand soil</i>	5.43	1	0.545	-0.26	0.17	-0.76	1.35	56.3
		2	0.565	-0.25	0.35	-0.46	1.90	47.6
		3	0.549	-0.26	0.14	-0.85	1.41	62.2
	1.09	1	0.116	----	----	----	0.40	116.4
		2	0.107	-0.97	0.11	-0.94	0.28	28.7
		3	0.104	-0.98	0.11	-0.96	0.20	23.0
	0.217	1	0.0221	-1.66	0.01	-1.99	0.06	50.4
		2	0.0238	-1.62	0.02	-1.69	0.11	46.4
		3	0.0212	-1.67	0.03	-1.57	0.05	24.5
	0.0435	1	0.0045	-2.34	0.01	-2.12	0.02	28.8
		2	0.0041	-2.39	0.01	-2.01	0.01	13.4
		3	0.0043	-2.37	0.01	-2.15	0.01	21.7
<i>Shipshe Sandy loam soil</i>	5.44	1	0.631	-0.20	0.89	-0.05	1.95	26.8
		2	0.591	-0.23	1.06	0.03	1.17	15.5
		3	0.628	-0.20	0.92	-0.04	1.90	25.6
	1.09	1	0.132	-0.88	0.22	-0.67	0.55	30.0
		2	0.129	-0.89	0.25	-0.61	0.50	25.3
		3	0.133	-0.89	0.26	-0.58	0.60	27.7
	0.218	1	0.0287	-1.54	0.05	-1.29	0.17	35.0
		2	0.0274	-1.56	0.06	-1.19	0.15	27.5
		3	0.0299	-1.52	0.06	-1.23	0.20	36.0
	0.0435	1	0.0059	-2.23	0.02	-1.77	0.04	29.4
		2	0.0058	-2.24	0.02	-1.76	0.04	27.8
		3	0.0058	-2.23	0.02	-1.81	0.04	29.5
<i>Drummer Silty clay loam soil</i>	5.47	1	0.946	-0.02	1.37	0.14	2.67	24.5
		2	0.926	-0.03	1.49	0.17	2.34	20.8
		3	0.874	-0.06	1.40	0.15	0.97	10.4
	1.09	1	0.181	-0.74	0.48	-0.32	0.58	16.6
		2	0.176	-0.76	0.51	-0.30	0.49	13.8
		3	0.182	-0.74	0.49	-0.31	0.61	17.1
	0.219	1	0.0289	-1.54	0.18	-0.74	0.05	4.0
		2	0.0284	-1.55	0.18	-0.74	0.03	2.8
		3	0.0275	-1.56	0.19	-0.73	0.02	1.5
	0.0438	1	0.0055	-2.26	0.05	-1.30	0.02	6.0
		2	0.0062	-2.21	0.05	-1.32	0.03	10.1
		3	0.0062	-2.21	0.05	-1.33	0.03	9.7
<i>Oska-Martin Silty clay soil</i>	5.49	1	1.08	0.03	2.63	0.42	-1.27	-8.7
		2	1.11	0.05	2.39	0.38	-0.85	-6.3
		3	1.13	0.05	2.18	0.34	-0.69	-5.6
	1.10	1	0.260	-0.58	0.55	-0.26	0.96	22.4
		2	0.245	-0.61	0.62	-0.21	0.69	15.6
		3	0.258	-0.56	0.56	-0.25	0.91	21.4
	0.220	1	0.0493	-1.31	0.15	-0.83	0.19	17.6
		2	0.0479	-1.32	0.16	-0.80	0.17	15.4
		3	0.0492	-1.31	0.15	-0.83	0.19	17.4
	0.0440	1	0.0099	-2.00	0.03	-1.47	0.05	19.0
		2	0.0094	-2.03	0.04	-1.45	0.04	14.9
		3	0.0098	-2.01	0.03	-1.48	0.04	17.5

Footnotes to the table:

- 1) all values as reported in the study report;
 2) all values as reported in the study report.

The graphical results of the experiment presented in the study report are given below on figure B.8.1.2.1.2._CA-11 and in numerical form in the table B.8.1.2.1.2._CA-43.

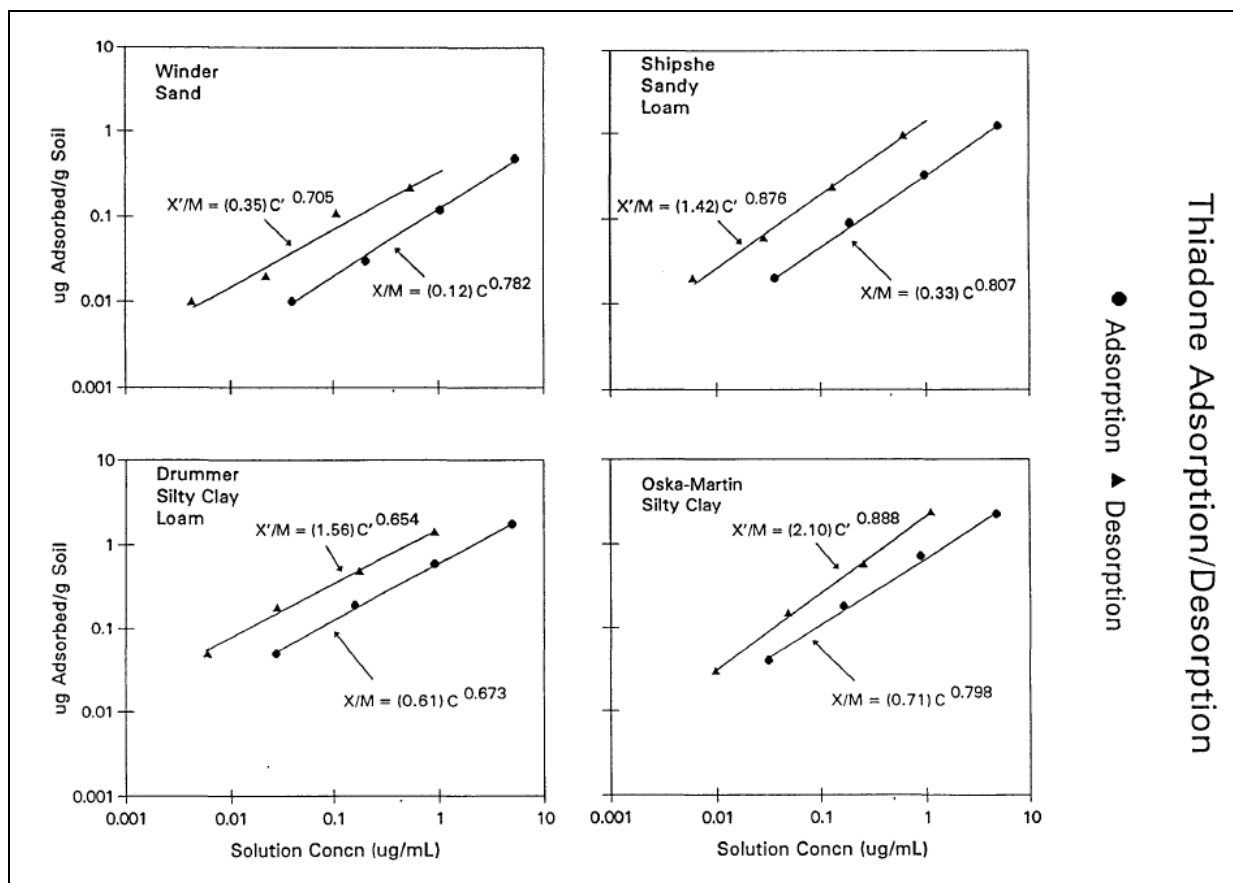


Figure B.8.1.2.1.2_CA-11: The adsorption and desorption isotherms for FOE Thiadone provided by the Applicant (copied from the study report).

Table B.8.1.2.1.2_CA-43: The key numerical results of the experiment presented in the study report – parameters of Freundlich adsorption and desorption isotherms for FOE Thiadone, including the correlation coefficient r

Test soil	Parameters of Freundlich adsorption isotherm					Parameters of Freundlich desorption isotherm				
	$\text{Log } K_{f \text{ ads}}$	$K_{f \text{ ads}} [\text{mL/g}]$	$1/n$	$K_{f \text{ OC ads}} [\text{mL/g}]$	r	$\text{Log } K_{f \text{ des}}$	$K_{f \text{ des}} [\text{mL/g}]$	$1/n$	$K_{f \text{ OC des}} [\text{mL/g}]$	r
Winder Sand soil	-0.939	0.12	0.782	43	0.975	-0.462	0.35	0.705	128	0.958
Shipshe Sandy loam soil	-0.477	0.33	0.807	44	0.999	0.152	1.42	0.876	189	0.998
Drummer Silty clay loam soil	-0.214	0.61	0.673	29	0.999	0.193	1.56	0.654	73	0.995
Oska-Martin Silty clay soil	-0.151	0.71	0.798	58	0.998	0.322	2.10	0.888	174	0.998

The graphical and numerical results of the repeated analysis, performed by the RMS, of the data from the tables B.8.1.2.1.2_CA-41 (for adsorption) and B.8.1.2.1.2_CA-42 (for desorption) are presented below on figures B.8.1.2.1.2_CA-12 (adsorption) and B.8.1.2.1.2_CA-13 (desorption) and in the table B.8.1.2.1.2_CA-44.

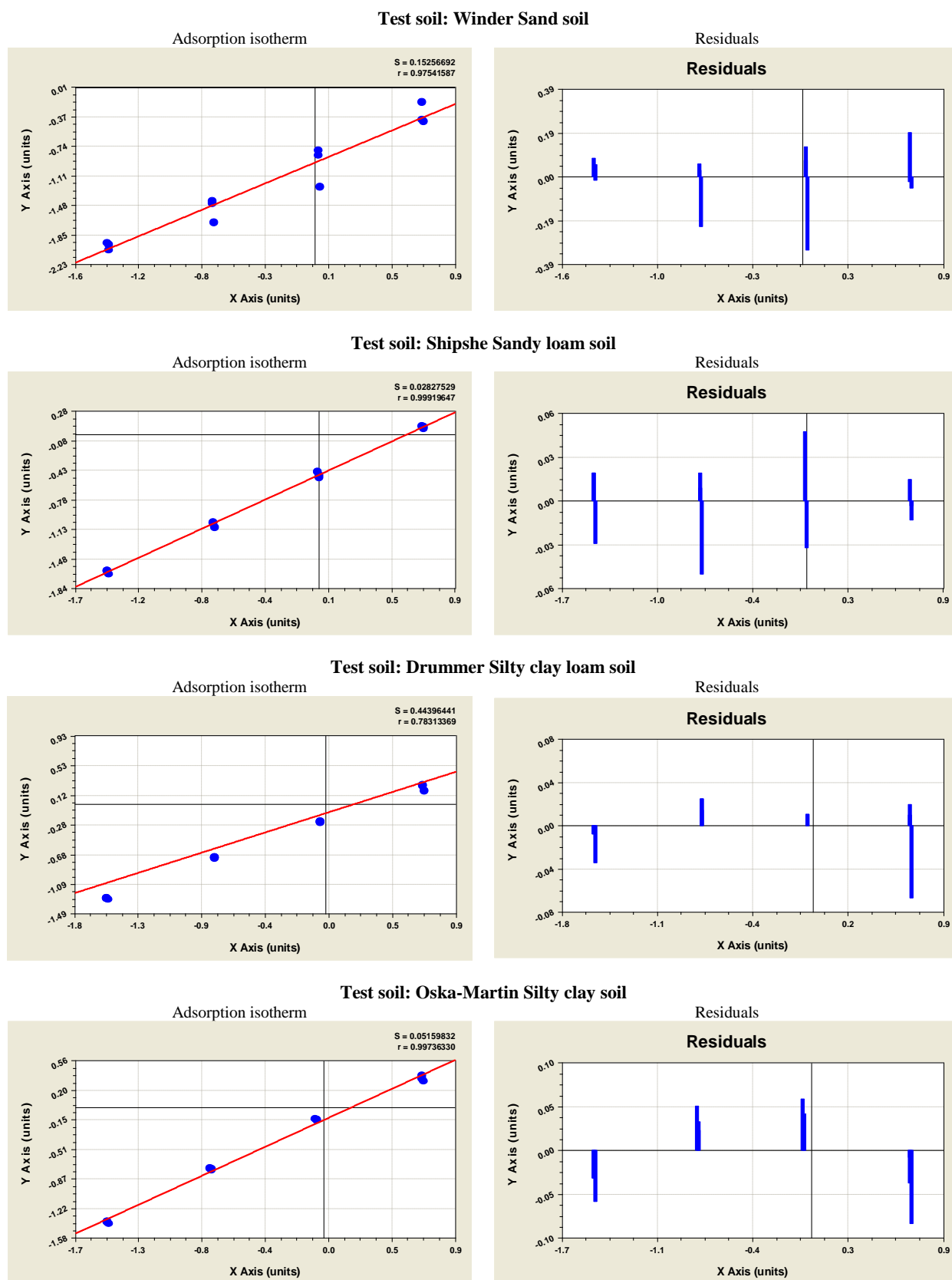


Figure B.8.1.2.1.2._CA-12: The adsorption isotherms for FOE Thiadone determined by the RMS.

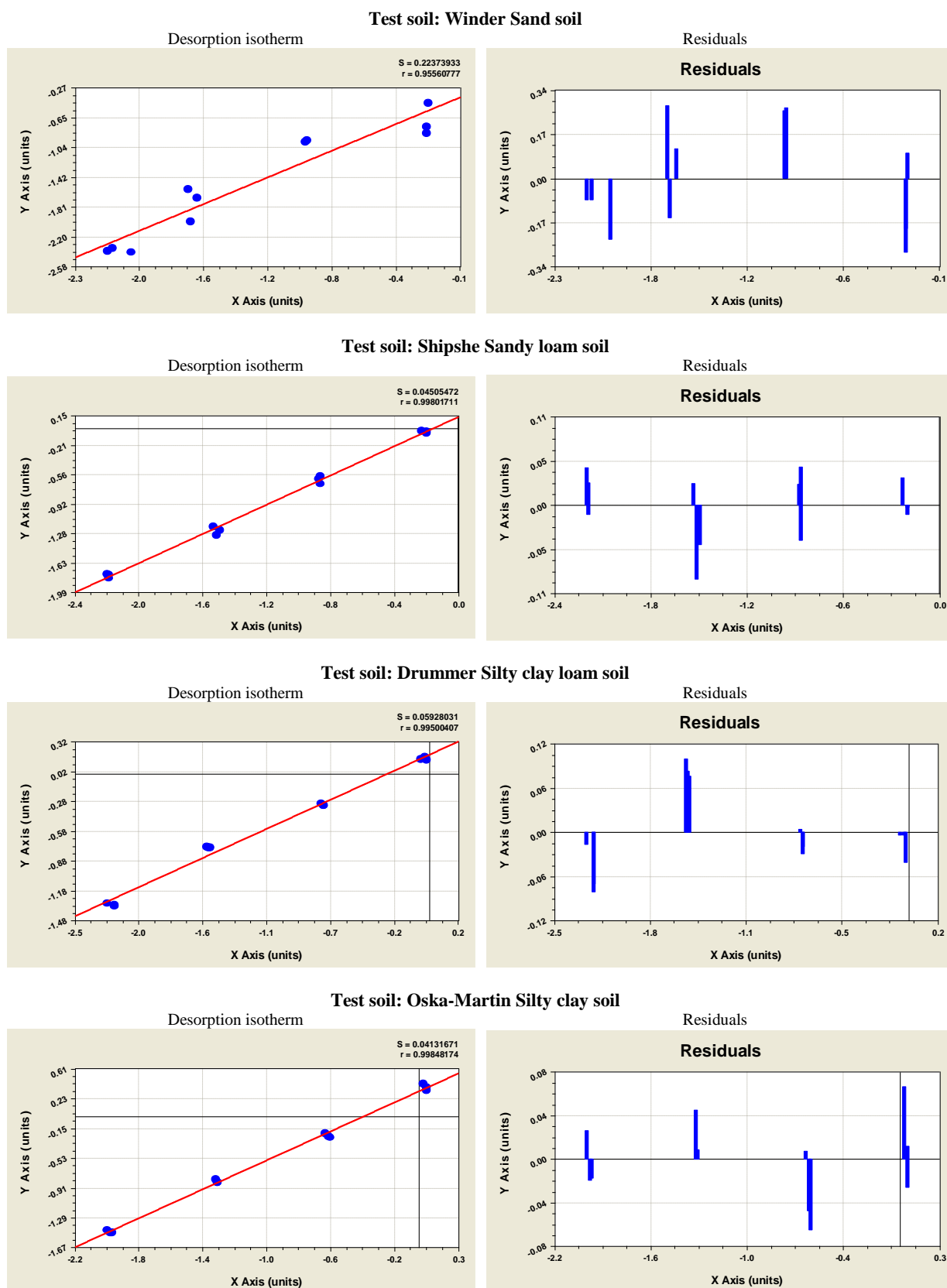


Figure B.8.1.2.1.2._CA-13: The desorption isotherms for FOE Thiadone determined by the RMS.

Table B.8.1.2.1.2._CA-44: The parameters of the Freundlich adsorption and desorption isotherms determined for FOE Thiadone by the RMS

Test soil	Process	Parameters of isotherm				Statistical evaluation	
		Log K _F	K _F [mL/g]	K _{F OC} [mL/g]	1/n	SD	Correlation coefficient <i>r</i>
<i>Winder, Sand soil</i>	Adsorption	-0.940	0.115	42.59	0.781	0.1526	0.9754
	Desorption	-0.331	0.467	172.96	0.909	0.2237	0.9556
<i>Shipshe, Sandy loam soil</i>	Adsorption	-0.479	0.332	44.27	0.806	0.0283	0.9991
	Desorption	0.136	1.368	182.40	0.867	0.0450	0.9980
<i>Drummer, Silty clay loam soil</i>	Adsorption	-0.214	0.611	28.68	0.672	0.0281	0.9990
	Desorption	0.193	1.559	73.19	0.654	0.0592	0.9950
<i>Oska-Martin, Silty clay soil</i>	Adsorption	-0.153	0.703	58.10	0.796	0.0516	0.9974
	Desorption	0.323	2.104	173.88	0.887	0.0413	0.9985

Conclusions of the experiment:

The comparison of the results presented in the study report and those obtained by the RMS showed that the parameters of the adsorption isotherms obtained by the Applicant and RMS were very similar. In case however of the desorption isotherms the obtained results displayed some differences. That was stated in particular for Winder Sand soil and Shipshe Sandy loam soil.

RMS also stated that the determined adsorption isotherms displayed good conformity with the experimental results. Similar statement can be made in case of the desorption isotherms.

The 1/n values for the adsorption isotherms were in range 0.672 – 0.806, indicating that the isotherms complied to the acceptable degree with the assumed model. In case of the results obtained in Winder Sand soil it was stated that the adsorption isotherm was robust and well complied with the model – Freundlich sorption isotherm. For that reason RMS decided to include the results into the data set even though the OC content was lower than the recommended minimum – 0.3%.

The definitive set of the results from this experiment is presented below in the table B.8.1.2.1.2._CA-45. RMS decided to present the values determined as a result of the repeated analysis of the data set.

Table B.8.1.2.1.2._CA-45: The definitive set of Freundlich adsorption and desorption parameters determined for FOE Thiadone.

Test soil – USDA type (name)	Key soil properties		Freundlich adsorption isotherm parameters			Freundlich desorption isotherm parameters		
	pH ¹⁾	OC [%]	K _F [mL/g]	K _{F OC} [mL/g]	1/n	K _F [mL/g]	K _{F OC} [mL/g]	1/n
<i>Sand (Winder)</i>	5.8	0.27	0.115	42.59	0.781	0.467	172.96	0.909
<i>Sandy loam (Shipshe)</i>	6.3	0.75	0.332	44.27	0.806	1.368	182.40	0.867
<i>Silty clay loam (Drummer)</i>	6.6	2.13	0.611	28.68	0.672	1.559	73.91	0.654
<i>Silty clay (Oska-Martin)</i>	6.0	1.21	0.703	58.10	0.796	2.104	173.88	0.887

Footnotes to the table:

1) Measured in water;

Final conclusions of the study:

The examination of the soil sorption of five degradation products of Flufenacet – FOE Methylsulfoxide, FOE Sulfonic acid, FOE Oxalate, FOE Alcohol and FOE Thiadone was carried out using four different agricultural US soils. The test soils had representative range of OC content, but relatively narrow range of pH – one of them was acidic, the remaining three neutral. That relatively narrow range of soil pH does not enable to make a definitive conclusion concerning the would-be pH-dependence of the adsorption, but generally low level of adsorption indicates that that phenomenon, if occurs, may not have a significant influence on the sorption properties of the test compounds.

It was stated that the test compounds were weakly to moderately sorbed onto soil, what was correlated with their properties, such as acidity (e.g. FOE Sulfonic acid and FOE Oxalate are relatively strong organic acid, in soil expected to be present in dissociated state) or water solubility.

In general FOE Sulfonic acid and FOE Oxalate were weakly sorbed onto soil and the process was fully reversible. FOE Methylsulfoxide, FOE Alcohol and FOE Thiadone were sorbed onto soil more strongly, although they should be classified in general as weakly to moderately sorbed onto soil, and the adsorption was to the significant degree reversible.

In case of four test compounds – FOE Methylsulfoxide, FOE Sulfonic acid, FOE Alcohol and FOE Thiadone, it was possible to determine reliable Freundlich isotherm adsorption parameters in all four test soils. In case of FOE Oxalate reliable Freundlich isotherm adsorption parameters were determined for three test soils, all having pH in neutral range (between 6.0 and 6.6), what limits the possibility of the examination of the pH-dependence of the soil sorption for that compound. On the other hand, the analysis of the physicochemical properties of that compound, and in particular its acidity, may indicate that that phenomenon may play only minor role in its sorptive behaviour in soil.

The definitive results of the study – the Freundlich adsorption parameters for each test compound, are presented below in reporting format recommended for EU-agreed List of End Points.

Soil adsorption transformation products (Regulation (EU) N° 283/2013, Annex Part A, point 7.1.3.1.2 and Regulation (EU) N° 284/2013, Annex Part A, point 9.1.2.1)

FOE Methylsulfoxide							
Soil Type (USDA)	OC %	Soil pH ^{a)}	K _d (mL/g)	K _d _{oc} (mL/g)	K _F (mL/g)	K _F _{oc} (mL/g)	1/n
Sand	0.27	5.8	----	----	0.133	49.26	1.059
Sandy loam	0.75	6.3	----	----	0.349	46.53	0.900
Silty clay loam	2.13	6.6	----	----	2.042	95.87	0.893
Silty clay	1.21	6.0	----	----	5.598	462.64	0.914
Geometric mean (if not pH dependent)					0.853	100.41	----
Arithmetic mean (if not pH dependent)					----	----	0.942
pH dependence, <i>Yes or No</i>			No				
^{a)} All values measured in water;							

FOE Sulfonic acid							
Soil Type	OC %	Soil pH ^{a)}	K _d (mL/g)	K _d _{oc} (mL/g)	K _F (mL/g)	K _F _{oc} (mL/g)	1/n
Sand	0.27	5.8	----	----	0.051	18.88	0.865
Sandy loam	0.75	6.3	----	----	0.106	14.13	1.002
Silty clay loam	2.13	6.6	----	----	0.204	9.58	0.931
Silty clay	1.21	6.0	----	----	0.072	5.95	1.183
Geometric mean (if not pH dependent)*					0.094	11.10	----
Arithmetic mean (if not pH dependent)					----	----	0.995
pH dependence, <i>Yes or No</i>			No				
^{a)} All values measured in water;							

FOE Oxalate

Soil Type	OC %	Soil pH ^{a)}	K _d (mL/g)	K _{doc} (mL/g)	K _F (mL/g)	K _{Foc} (mL/g)	1/n
Sandy loam	0.75	6.3	----	----	0.096	12.80	0.933
Silty clay loam	2.13	6.6	----	----	0.153	7.18	0.824
Silty clay	1.21	6.0	----	----	0.157	12.97	0.978
Geometric mean (if not pH dependent)*					0.132	10.60	----
Arithmetic mean (if not pH dependent)					----	----	0.912
pH dependence, <i>Yes or No</i>			No				

^{a)} All values measured in water;**FOE Alcohol**

Soil Type	OC %	Soil pH ^{a)}	K _d (mL/g)	K _{doc} (mL/g)	K _F (mL/g)	K _{Foc} (mL/g)	1/n
Sand	0.27	5.8	----	----	0.226	83.70	0.947
Sandy loam	0.75	6.3	----	----	0.780	104.00	0.887
Silty clay loam	2.13	6.6	----	----	2.018	94.74	0.940
Silty clay	1.21	6.0	----	----	3.802	314.21	0.950
Geometric mean (if not pH dependent)*					1.078	126.88	----
Arithmetic mean (if not pH dependent)					----	----	0.931
pH dependence, <i>Yes or No</i>			No				

^{a)} All values measured in water;**FOE Thiadone**

Soil Type	OC %	Soil pH ^{a)}	K _d (mL/g)	K _{doc} (mL/g)	K _F (mL/g)	K _{Foc} (mL/g)	1/n
Sand	0.27	5.8	----	----	0.115	42.59	0.781
Sandy loam	0.75	6.3	----	----	0.332	44.27	0.806
Silty clay loam	2.13	6.6	----	----	0.611	28.68	0.672
Silty clay	1.21	6.0	----	----	0.703	58.10	0.796
Geometric mean (if not pH dependent)*					0.358	42.10	----
Arithmetic mean (if not pH dependent)					----	----	0.764
pH dependence, <i>Yes or No</i>			No				

^{a)} All values measured in water;

Study 2:

Report: Hein W., (2011): “[Phenyl-UL-¹⁴C] BCS-CO62475: Adsorption/Desorption in Five Different Soils.”; RLP AgroScience GmbH, Breitenweg 71, 67435 Neustadt a. d. Weinstrasse, Germany (performing laboratory) for Bayer CropScience Aktiengesellschaft, Development, Environmental Safety Metabolism/ADME and Environmental Fate, Alfred Nobel Str. 50, D-40789 Monheim, Germany; Study number (RLP AgroSciences GmbH) AS158; Bayer Report No. M-411141-01-1; 30 June 2011; study reference number: M-411141-01-1.

Guidelines: The study was performed to comply with the following Guidelines:

- OECD Guideline for Testing of Chemicals No 106 “Adsorption/Desorption”, Jan. 21, 2000;
- US. EPA Fate, Transport and Transformation Test Guidelines OPPTS 835. 1220 Sediment and Soil Adsorption/Desorption Isotherm;
- Canada Pest Management Regulatory Agency (PMRA), Environmental Chemistry and Fate, Guidelines for Registration of Pesticides in Canada, 1987.

GLP: Yes;

RMS comments: This is a newly submitted study, aimed on the examination of the soil sorption of FOE Methylsulfone – one of the major soil degradation products of Flufenacet. For the purpose of the current assessment it was evaluated for compliance with the following Guidelines:

- OECD Guideline for Testing of Chemicals No 106, Adsorption – Desorption Using a Batch Equilibrium Method, adopted 21st January 2000;
- US. EPA Fate, Transport and Transformation Test Guidelines OPPTS 835.1220, Sediment and Soil Adsorption/Desorption Isotherm, January 1998;
- US. EPA Fate, Transport and Transformation Test Guidelines OPPTS 835.1230, Adsorption/Desorption (Batch Equilibrium), October 2000;

It was stated that the study complied with the provisions of the evoked Guidelines. However, the RMS examining the study report stated that the Freundlich adsorption and desorption isotherms were determined using the averaged equilibrium data for each initial concentration of the test compound, although the values for each replicate were reported. Additionally the linearised Freundlich adsorption and desorption isotherms for the given test soil were presented on the same graph and they were not clearly distinguished, what caused problems with the interpretation of the results. For that reason RMS decided to repeat the fitting of the data using the replicates as individual input data and separating adsorption and desorption isotherms. The study is summarised below.

Summary:

The aim of the study was to examine the adsorption and desorption of FOE Methylsulfone (for the purpose of this study bearing a codename BCS-CO62475) – a major soil degradation product of Flufenacet, onto soil. The examination was performed using five test soils, three EU and two US soils. Their characteristic is provided below in the table B.8.1.2.1.2._CA-46.

The test soils were sampled from the agriculturally used areas. In case of the EU soils, they were sampled from fields on which no pesticides were used for at least 5 years prior to the sampling. They were collected from the 0-20 cm layer using the shovel. The soil samples were air-dried and sieved through 2-mm sieve before being delivered to the test facility. There they were stored first in ambient conditions and then at T = 0-10°C until being used.

One of the US soils was sampled from the field on which different pesticides used on cabbage, broccoli and lettuce were applied until December 2007. After that, until sampling in March 2009 (for approx. 15 consecutive months), no use of any plant protection products was recorded. The second US soil was sampled from the field on which no pesticides were used for at least three consecutive years before sampling. Soil samples were collected by shovel from the top 6- to 8-inch layer (corresponding to the soil depth of 0-15 cm or 0-20 cm). The soil samples were air-dried and sieved through 2-mm sieve before being delivered to the test facility. There they were stored first in ambient conditions and then at T = 0-10°C until being used.

The storage period was following:

- for the EU soils: 740 days after delivery to the test facility;
- for the US soils: 718 days after delivery to the test facility.

Table B.8.1.2.1.2._CA-46: The characteristic of soils used in the study.

Parameter	Soil				
	<i>Wurmwiese</i>	<i>Höfchen am Hohenseh 4a</i>	<i>Dollendorf II</i>	<i>Guadalupe CA</i>	<i>Springfield NE</i>
Soil origin	Monheim am Rhein, Northrhine-Westfalia, Germany	Burscheid, Northrhine-Westfalia, Germany	Blankenheim, Northrhine-Westfalia, Germany	Guadalupe, CA, USA	Springfield, NE, USA
Soil type (USDA)	Loam	Silt loam	Clay loam	Sandy loam	Silt loam
Particle size distribution	Sand [%]	51	27	31	56.0
	Silt [%]	28	54	38	32.6
	Clay [%]	21	19	31	11.4
Soil pH	in CaCl ₂	5.3	6.6	7.3	6.7
	in water	5.5	6.8	7.4	6.8
Organic matter content (OM) [%]	3.10	4.14	7.93	1.1	2.9
Organic carbon content (OC) [%]	1.8	2.4	4.6	0.7	1.7
CEC [meq/100 g]	10.8	13.9	21.9	16.1	16.1

The test compound used in the experiment was the ¹⁴C-FOE Methylsulfone uniformly radiolabelled in phenyl ring, as shown below on figure B.8.1.2.1.2._CA-14.

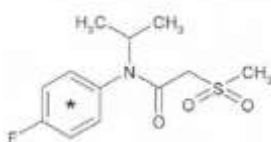


Figure B.8.1.2.1.2._CA-14: The structural formula of the radiolabelled FOE Methylsulfone (BCS-CO62475) used in the experiment; the asterisk (*) indicates radiolabelling position (copied from the study report).

The test compound had specific activity of 3.26 MBq/mg (88 µCi/mg), radiochemical purity (determined by HPLC) of > 98% and chemical purity (also determined by HPLC) of > 98%. It was delivered to the test facility as a transparent, vacuum-dried solid. It was stored in the test facility at $T \leq -18^{\circ}\text{C}$ until being used.

The whole delivered sample was used to prepare the **Standard Stock Solution I**, bearing the code-name **SSL I**. That was done by transferring the whole amount of the radiolabelled test compound into a 10-mL volumetric flask and dissolving it in CH₃CN added up to calibration mark. The so prepared stock solution was analysed for its concentration of the test item by LSC. That was done using two 0.1-mL aliquots of the stock solution diluted 50 times before being analysed.

The so determined concentration of the test item in the standard solution was 0.537 mg/mL. Additionally the radiopurity of the solution was determined using radio-HPLC. It was > 98.5%.

Additionally, as a reference compound for chromatography, the non-radiolabelled FOE Methylsulfone was used in the experiment. It was delivered to the test facility as a white solid, having a chemical purity of 97.2%. It was used to prepare the **Standard Stock Solution II** by weighing 3.6 mg of it and dissolving it in 3.6 mL CH₃CN.

The whole experiment was carried out using 0.01M CaCl₂ aq solution, prepared by dissolving 2.94 g CaCl₂ x 2 H₂O in 2 litres of distilled water. The so prepared solutions were used throughout the whole study. Their pH was in range 6.57 – 6.77. They were generally labelled **Stock Solution I_{Bio}** (**SL I_{Bio}**) and as such used to prepare the treatment solutions used in the experiment.

The whole study consisted of three steps, further called experiments:

- the **Preliminary Test I**, aimed on the determination of the appropriate soil:solution ratio for each test soil, stability of the test item in 0.01M CaCl₂ aq solution and its potential adsorption to the test vessels; the experiment was performed using a single initial concentration of the test item – 1.00 mg/L (highest concentration of FOE Methylsulfone used in the study);

- the **Preliminary Test II**, in which was determined the appropriate equilibration time and parental mass balance in order to demonstrate the stability of the test compound during incubation for determining sorption isotherms; the experiment was performed using a single initial concentration of the test item – 1.00 mg/L (highest concentration of FOE Methylsulfone used in the study);
- the **Definitive Test**, aimed on the determination of the Freundlich adsorption and desorption isotherm and calculation of their parameters - K_F and $1/n$ values; at this stage five different nominal initial concentrations of the test compound – FOE Methylsulfone, were used: 0.01 mg/L, 0.03 mg/L, 0.10 mg/L, 0.30 mg/L and 1.00 mg/L.

The test compound was administered in form of the application solutions prepared from the **Standard Stock Solution I (SSL I)** as aqueous solutions in 0.01M $\text{CaCl}_{2\text{aq}}$.

In case of the **Preliminary Test I** the application solution was prepared by transferring 0.745 mL of the solution **SSL I** into the appropriate flask. The organic solvent was evaporated under the gentle stream of N_2 and residue redissolved in 40 mL of **SL I_{Bio}** solution. The so prepared solution was then analysed by LSC for concentration of the test item and by radio-HPLC for its radiopurity.

In case of the **Preliminary Test II** the application solution was prepared by transferring 2.7 mL of the solution **SSL I** into the appropriate flask. The organic solvent was evaporated under the gentle stream of N_2 and residue redissolved in 145 mL of **SL I_{Bio}** solution. The so prepared solution was then analysed by LSC for concentration of the test item and by radio-HPLC for its radiopurity.

The application solutions for the **Definitive Test** were prepared by a serial dilution of the solution **SSL I**. As a first step the **Solution A**, having a nominal concentration 10 mg/L, was prepared from a solution **SSL I**. That was done by transferring 0.838 mL of the solution **SSL I** into the appropriate flask. The organic solvent was evaporated under the gentle stream of N_2 and the residue redissolved in 45 mL of **SL I_{Bio}** solution. The so prepared solution was then analysed by LSC for concentration of the test item and by radio-HPLC for its radiopurity. Next, the four remaining application solutions, marked **B**, **C**, **D** and **E** were prepared by diluting the **Solution A** with the **SL I_{Bio}** solution. The procedure looked as follows:

- the **Solution B**, having a nominal concentration of 3.0 mg/L, was prepared by transferring 7.50 mL of the **Solution A** into 25-mL volumetric flask and filling it to the volume with **SL I_{Bio}** solution;
- the **Solution C**, having a nominal concentration of 1.0 mg/L, was prepared by transferring 2.50 mL of the **Solution A** into 25-mL volumetric flask and filling it to the volume with **SL I_{Bio}** solution;
- the **Solution D**, having a nominal concentration of 0.30 mg/L, was prepared by transferring 0.75 mL of the **Solution A** into 25-mL volumetric flask and filling it to the volume with **SL I_{Bio}** solution;
- the **Solution E**, having a nominal concentration of 0.10 mg/L, was prepared by transferring 0.25 mL of the **Solution A** into 25-mL volumetric flask and filling it to the volume with **SL I_{Bio}** solution.

The so prepared solutions were then analysed by LSC for concentration of the test item and by radio-HPLC for their radiopurity.

The measured concentrations of the so prepared application solutions were following:

- **Solution A** (nominal concentration 10.0 mg/L): 9.90 mg/L;
- **Solution B** (nominal concentration 3.00 mg/L): 2.95 mg/L;
- **Solution C** (nominal concentration 1.00 mg/L): 0.98 mg/L;
- **Solution D** (nominal concentration 0.30 mg/L): 0.29 mg/L;
- **Solution E** (nominal concentration 0.10 mg/L): 0.10 mg/L;

Their radiopurity was > 98%.

The study was performed using the following general conditions:

- all experiments were performed in the darkness and at constant temperature $T = 20 \pm 2^\circ\text{C}$;
- test vessels were borosilicate glass centrifuge tubes with Teflon lined screw caps;
- the **Preliminary Test I** and the **Definitive Test** were carried out in 42-mL test vessels using the total volume of solution (not corrected for the soil residual moisture content) of 20 mL;
- the **Preliminary Test II** was performed in 83-mL test vessels using the total volume of solution (not corrected for the soil residual moisture content) of 50 mL;
- equilibration was performed by shaking the test vessels for the pre-defined amount of time on the horizontal overhead shaker at ~20 rpm;
- at the end of equilibration samples containing soil were centrifuged for about 10 minutes at ~5000 rpm (~4200 g) to separate liquid and solid phases;

- in all experiments with the test soils the samples were pre-equilibrated for at least 16 hours before introduction of the test compound; the pre-equilibration procedure is characterised in details for each experiment, as they differed due to the different amounts of solution used.

The **Preliminary Test I** was aimed on the determination of the appropriate soil:solution ratio for each test soil and the stability of the test compound in 0.01M CaCl₂ _{aq} solution.

The examination of the stability of FOE Methylsulfone in 0.01M CaCl₂ _{aq} solution was carried out in soilless systems. First two 42-mL test vessels were filled each with 18 mL of **SL I_{Bio}** solution. Next, to each of them 2 mL of the **Solution A** were added to obtain the final volume of 20 mL and the concentration of the test item (nominal) 1.0 mg/L. So prepared test vessels were capped and equilibrated for up to 96 hours. At pre-defined time points – 24 hours, 48 hours, 72 hours and 96 hours of shaking, aliquots of each test solution were analysed by LSC and HPLC.

The experiment aimed on the determination of the appropriate soil:solution ratio began by weighing 2-g, 10-g and 20-g portions of each test soil into 42-mL test vessels. All samples were prepared in duplicate. Next, to each test vessel 18 mL of **SL I_{Bio}** solution were added, test vessels capped and so prepared samples pre-equilibrated overnight (for ≥16 hours). After pre-equilibration samples were centrifuged for 5 minutes at 1000 rpm and 2 mL of the **Solution A** were added to obtain the final volume of 20 mL and the concentration of the test item (nominal) 1.0 mg/L. So prepared samples were then equilibrated, by shaking on horizontal shaker, for 24 hours. After that period samples were centrifuged and radioactivity content in supernatants determined by LSC. Additionally, for each test soil and each tested soil:solution ratio, pH of the supernatants was determined using one of the replicates.

The appropriate soil:solution ratio was determined on the basis of the results of LSC analysis of supernatants after equilibration and in comparison to the initial measured concentration of the test item in solution, which was 1.018 mg/L.

The **Preliminary Test II** was aimed on the determination of the appropriate equilibration time and the stability of the test compound in the test system.

The experiment was performed using 83-mL test vessels and the total volume of the solution (not corrected for residual soil moisture content) of 50 mL. It was carried out using the soil:solution ratio determined individually for each test soil at preceeding step.

The experiment was initiated by weighing the appropriate amount of the test soil into the test vessels. For each test soil five replicates were prepared. Next, to each test vessel 45 mL of **SL I_{Bio}** solution were added, test vessels capped and so prepared samples pre-equilibrated overnight (for ≥16 hours). After pre-equilibration 5 mL of the **Solution A** were added to obtain the final volume of 50 mL and the concentration of the test item (nominal) 1.0 mg/L. So prepared samples were then equilibrated, by shaking on horizontal shaker, for up to 120 hours. At pre-defined time points – after 2 hours, 4 hours, 6 hours 24 hours, 30 hours, 48 hours, 72 hours 96 hours and 120 hours of shaking, samples were taken for analysis. The sampling procedure, as characterised in the study report, is presented below on figure B.8.1.2.1.2._CA-15.

Sampling Procedure for the Determination of Adsorption Equilibrium Times and Matrix Stability Analysis per Soil:

Time	2 h	4 h	6 h	24 h	30 h	48 h	72 h	96 h	120 h
Rep 1		X		○					
Rep 2			X	X		○			
Rep 3	X		X			X	○		
Rep 4	X				X		X	○	
Rep 5		X			X			X	○

X =

- 1) Removed from shaker
- 2) Centrifuged, 10 min, 5000 rpm = 4200^g, 20°C
- 3) An aliquot of the supernatant was taken and afterwards analysed by LSC
- 4) Return to shaker

○ =

- 1) Centrifuged (Conditions see above)
- 2) Complete removal of supernatant
- 3) LSC and HPLC supernatant
- 4) Extracted soil and analyzed by HPLC
- 5) Combustion of soil residue and LSC-measurement

At each sampling interval the mentioned test vessels were centrifuged and aliquots of 100 µL were taken from the supernatants for LSC.

Figure B.8.1.2.1.2._CA-15: The sampling procedure used in the **Preliminary Test II** (copied from the study report).

The soil extraction was a 4-step cold-extraction process. At each step soil was extracted for 30 minutes with 40 mL of CH₃CN/H₂O 1:1 (v:v) solution. The extracts were combined and analysed by LSC for radioactivity content and by radio-HPLC to determine the nature of the extracted radioactivity.

The **Definitive Test** was carried out using the the procedure presented below on figure B.8.1.2.1.2._CA-16. The experiment was performed in 42-mL test vessels and using 20 mL of the test solution. The nominal initial concentrations of the test item – FOE Methylsulfone, used in the experiment were following: 1.00 mg/L, 0.30 mg/L, 0.10 mg/L, 0.03 mg/L and 0.01 mg/L. The measured initial concentrations of the test item in solution were calculated using the actual volume of the solution, corrected by addition of the residual soil moisture content. The resulting total volume of the solution in the test system were:

- **20.13 mL** for Wurmwiese Loam soil (the determined residual soil moisture content was 0.13 mL);
- **20.18 mL** for Höfchen am Hohenseh Silt loam soil (the determined residual soil moisture content was 0.18 mL);
- **20.27 mL** for Dollendorf II Clay loam soil (the determined residual soil moisture content was 0.27 mL);
- **20.24 mL** for Guadalupe Sandy loam soil (the determined residual soil moisture content was 0.24 mL);
- **20.07 mL** for Springfield Silt loam soil (the determined residual soil moisture content was 0.07 mL).

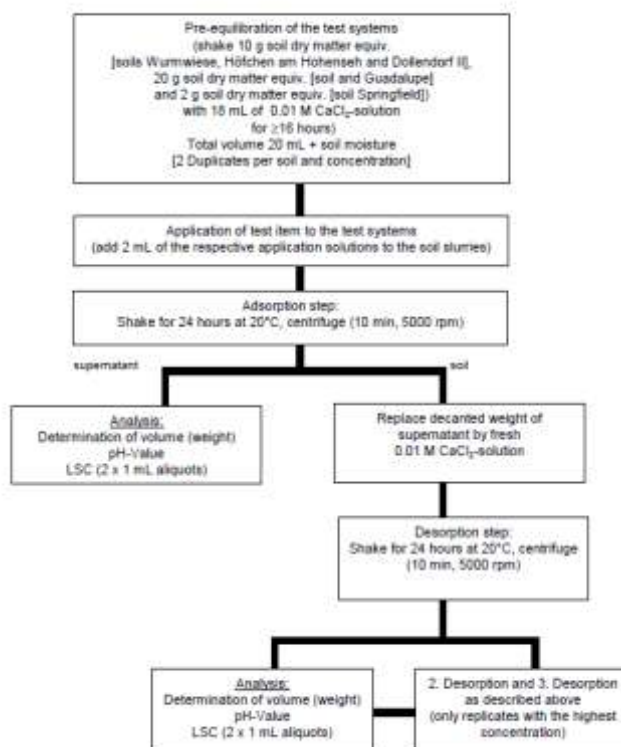


Figure B.8.1.2.1.2._CA-16: The conceptual scheme of the experimental procedure used in the **Definitive Test** (copied from the study report).

The examination of the 1st step of desorption was carried out for all five nominal concentrations of the test item, in order to determine the Freundlich desorption isotherms. The next steps – 2nd and 3rd, were examined using the samples with the highest initial (nominal) concentration of the test item – 1.00 mg/L.

In all samples left after the examination of the desorption the mass balance was established. That was done by mixing the remaining soil sample with cellulose added in amount 0.4 g/g soil. So prepared samples were air-dried, homogenised and analysed after combustion by LSC. In case of Wurmwiese, Höfchen am Hohenseh, Dollendorf II and Guadalupe test soils the aliquots of the soil samples were taken for analysis, while the samples of the Springfield test soil were analysed entirely.

All liquid samples were analysed for their radioactivity content using LSC method. The analysis was carried out using TRI-CARB 2800 TR or TRI-CARB 2300 TR liquid scintillation counters. Samples were analysed in Ultima Gold LS cocktail. The counting time was usually 10 minutes. The background was determined using

blank samples and automatically subtracted from the analysed samples during the LSC analysis. Also automatically, by the instrument, was performed quench and counting efficiency correction for transformation of gross count (cpm) into dmp.

The solid samples used to determine the mass balance were oxidised using Sample Oxidiser OX 500. Generated $^{14}\text{CO}_2$ was absorbed in Oxisolve C-400 or CarboSorb-E/Permafluor E+ LS cocktail and analysed using TRI-CARB 2800 TR or TRI-CARB 2300 TR liquid scintillation counters.

The chromatographic analysis was performed in a gradient mode using Jasco HPLC system equipped with radio-HPLC detector and UV detector set at $\lambda = 210$ nm. The chromatographic separation was carried out on Nucleodur C18 Gravity (125 x 4 mm; 5 μm) chromatographic column, preceded by LiChroCart 4-4 LiChrospher 100-RP-18 (5 μm) per-column. The chromatographic column was kept in HPLC oven set at a constant temperature $T = 20^\circ\text{C}$. The elution was performed in one of the two gradient modes (**Gradient 1** and **Gradient 2**), characterised below in the table B.8.1.2.1.2._CA-47. The solvent system used in elution consisted of:

- **Solvent A:** bidistilled water + 0.2% H_3PO_4 (85%),
- **Solvent B:** CH_3CN .

The flow rate was set to 1.5 mL/min. The retention time of the test item – [^{14}C] FOE Methylsulfone was $R_t = \text{approx } 18$ min.

Table B.8.1.2.1.2._CA-47: The gradient modes used in the HPLC analysis of samples collected during the study.

Gradient 1			Gradient 2		
Time [minutes]	Solvent system		Time [minutes]	Solvent system	
	% Solvent A	% Solvent B		% Solvent A	% Solvent B
0	100	0	0	100	0
5	100	0	5	100	0
35	0	100	18	57	43
40	0	100	20	0	100
42	100	0	23	0	100
45	100	0	25	100	0
			28	100	0

The calculations of the Freundlich sorption parameters were performed using the equations presented below on figure B.8.1.2.1.2._CA-17.

Freundlich isotherm	Log-transformed Freundlich isotherm	Equation used in calculation of $K_{F,OC}$
$x/m = K_F \cdot c_e^{1/n}$ <p> K_F = Freundlich coefficient x/m = Equilibrium concentration of adsorbed test item in $\mu\text{g/g}$ dry weight soil c_e = Equilibrium concentration of test item in solution $\mu\text{g/mL}$ $1/n$ = Constant </p>	$\log\left(\frac{x}{m}\right) = \frac{1}{n} \cdot \log c_e + \log K_F$	$K_{F,OC} = \frac{K_F \cdot 100}{\% \text{ org. C}}$ <p> $K_{F,OC}$ = Adsorption coefficient related to organic carbon $\% \text{ org. C}$ = portion of organic carbon in soil expressed as % of weight </p>

Figure B.8.1.2.1.2._CA-17: The equations used in the calculations of the Freundlich sorption parameters (copied from the study report).

The results of the study are presented and discussed below.

Results and their discussion:

The characteristic of the test soils used in the study has been presented at the beginning of this summary in table B.8.1.2.1.2._CA-46. On their basis it may be stated that all test soils fully meet the acceptability criteria set by the OECD 106 Guideline.

The results of the monitoring of the temperature during the definitive test are presented below on figure B.8.1.2.1.2._CA-18. On their basis it was stated that the mean $T = 19.9^{\circ}\text{C}$ and its range $19.1 - 20.6^{\circ}\text{C}$. It was therefore within the pre-defined limits of $T = 20 \pm 2^{\circ}\text{C}$.



Figure B.8.1.2.1.2._CA-18: The graphical results of the monitoring of the temperature during the study (copied from the study report).

The numerical results of the examination of stability of the test item – FOE Methylsulfone in 0.01M CaCl_2 aq solution are presented below in the table B.8.1.2.1.2._CA-48. On their basis it was stated that the compound was stable.

Table B.8.1.2.1.2._CA-48: The results of the examination of the stability of the test item in the test solution.

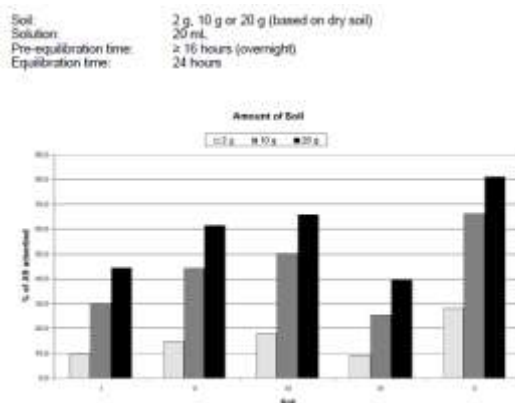
I) Experimental conditions				
Amount of soil:		Test system without soil		
Amount of test solution in test vessel:		20 mL		
Concentration of the test item:		1.001 mg/L (measured highest concentration used in experiment)		
Equilibration time:		0 – 96 h		
II) Results				
Equilibraion time [Hours]	Replicate	Obtained results		
		Total radioactivity in the test vessel in [Bq/20 mL]	Total radioactivity in the test vessel [%AR]	Amount of the test item [%]
0		65257.5	100%	99.5
24	1	64413.3	98.7	98.7
	2	63602.7	97.5	96.7
48	1	62019.6	95.0	94.6
	2	63347.5	97.1	96.3
72	1	64886.6	99.4	98.9
	2	64309.1	98.5	98.1
96	1	63903.0	97.9	97.3
	2	63778.4	97.7	97.7

The results of the determination of the appropriate soil:solution ratio are presented below, in numerical form in the table B.8.1.2.1.2._CA-49 and in graphical form on figure B.8.1.2.1.2._CA-197. The symbols used on that graph to denominate test soils were following:

- I for Wurmwiess test soil;
- II for Höfchen am Hohenseh test soil;
- III for Dollendorf II test soil;
- IV for Guadalupe test soil;
- V for Springfield test soil.

Table B.8.1.2.1.2._CA-49: The numerical results of the determination of the appropriate soil:solution ratio.

Test soil	Soil solution ratio		Amount of FOE Methylsulfone remaining in solution [% AR]	Amount of FOE Methylsulfone sorbed onto soil [% AR]
	in g soil/mL solution	as ratio		
<i>Wurmwiese</i> <i>Loam soil</i>	2/20	1:10	90.4	9.6
	10/20	1:2	69.9	30.1
	20/20	1:1	55.7	44.3
<i>Höfchen am Hohenseh</i> <i>Silt loam soil</i>	2/20	1:10	85.4	14.6
	10/20	1:2	55.9	44.1
	20/20	1:1	38.6	61.4
<i>Dollendorf II</i> <i>Clay loam soil</i>	2/20	1:10	82.2	17.8
	10/20	1:2	49.9	50.1
	20/20	1:1	34.2	65.8
<i>Guadalupe</i> <i>Sandy loam soil</i>	2/20	1:10	91.0	9.0
	10/20	1:2	74.6	25.4
	20/20	1:1	60.4	39.6
<i>Springfield</i> <i>Silt loam soil</i>	2/20	1:10	72.0	28.0
	10/20	1:2	33.7	66.3
	20/20	1:1	18.9	81.1

**Figure B.8.1.2.1.2._CA-19:** The graphical results of the determination of the appropriate soil:solution ratio – amount of FOE Methylsulfone adsorbed onto soil (copied from the study report).

On the basis of the obtained results, presented above, the following soil:solution ratios were selected to be used in further tests:

- for Wurmwiese Loam soil: 1:2;
- for Höfchen am Hohenseh Silt loam soil: 1:2;
- for Dollendorf II Clay loam soil: 1:2;
- for Guadalupe Sandy loam soil: 1:1;
- for Springfield Silt loam soil: 1:10.

The results obtained during the **Preliminary Test II** are presented below in numerical and graphical form. In the table B.8.1.2.1.2._CA-50 are provided the numerical results of the determination of the appropriate equilibration time. These results are also given in graphical form on figure B.8.1.2.1.2._CA-20. Below them, in the table B.8.1.2.1.2._CA-51 are presented the results of the determination of the mass balance aimed on the determination of the stability of the test item – FOE Methylsulfone in the test system containing soil during the equilibration period. On the basis of these results the selected appropriate equilibration time was 24 hours. It was also stated that the recovery of radioactivity and the test item was > 90% during the whole incubation period indicating that FOE Methylsulfone was stable in the test system for up to 120 hours.

Table B.8.1.2.1.1._CA-26: The numerical results of the determination of the appropriate equilibration time.

Equilibration time [hours]	Results									
	Concentration of applied radioactivity in the test system with soil Wurmwiese, expressed as:		Concentration of applied radioactivity in the test system with soil Höfchen am Hohenseh, expressed as:		Concentration of applied radioactivity in the test system with soil Dollendorf II, expressed as:		Concentration of applied radioactivity in the test system with soil Guadalupe, expressed as:		Concentration of applied radioactivity in the test system with soil Springfield, expressed as:	
	Test item equivalents [mg/L]	Test item [mg/L]	Test item equivalents [mg/L]	Test item [mg/L]	Test item equivalents [mg/L]	Test item [mg/L]	Test item equivalents [mg/L]	Test item [mg/L]	Test item equivalents [mg/L]	Test item [mg/L]
2	0.77	----	0.67	----	0.61	----	0.68	----	0.80	----
4	0.75	----	0.66	----	0.59	----	0.65	----	0.79	----
6	0.75	----	0.65	----	0.58	----	0.65	----	0.73	----
24	0.72	0.71	0.59	0.59	0.54	0.53	0.62	0.62	0.75	0.75
30	0.71	----	0.57	----	0.52	----	0.61	----	0.73	----
48	0.71	0.70	0.56	0.55	0.51	0.51	0.60	0.60	0.73	0.72
72	0.70	0.70	0.55	0.55	0.50	0.50	0.60	0.59	0.72	0.71
96	0.69	0.68	0.54	0.54	0.50	0.49	0.59	0.59	0.72	0.71
120	0.68	0.68	0.52	0.52	0.50	0.50	0.59	0.59	0.72	0.71

Soil: 25 g soil for the soils Wurmwiese, Höfchen am Hohenseh and Dollendorf II
50 g soil for the soil Guadalupe
5 g soil for the soil Springfield

Solution: 50 mL

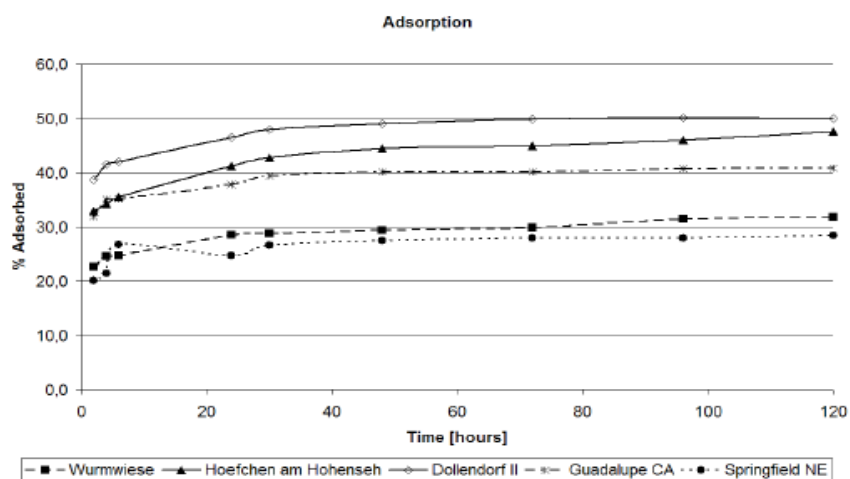
**Figure B.8.1.2.1.2._CA-20:** The graphical results of the determination of the appropriate equilibration time (copied from the study report).

Table B.8.1.2.1.2._CA-51: The results of the determination of the mass balance carried out in **Preliminary Test II.**

Test soil	Rep.	Equili- bration time [hours]	Radioactivity – [% AR] recovered in:					Test item – FOE Methylsulfone, in [%], recovered in:		
			Supernatant	Soil extract	Soil residue	ADS activity	Total	Supernatant	Soil extract	Total
Wurmweise Loam soil	1	24	54.12	40.99	1.27	0.30	96.68	54.02	40.74	94.76
	2	48	53.12	42.51	1.49	0.59	97.71	53.20	42.49	95.70
	3	72	51.90	42.62	1.91	0.89	97.33	51.92	42.83	94.75
	4	96	50.88	42.64	2.56	0.87	96.95	50.86	42.85	93.70
	5	120	50.13	41.66	3.47	0.86	96.13	50.16	41.48	91.64
Höfchen am Hohenseh Silt loam soil	1	24	43.21	51.67	1.49	0.26	96.63	43.27	51.92	95.19
	2	48	39.71	54.11	1.89	0.49	96.20	39.63	54.08	93.71
	3	72	39.79	54.04	2.09	0.75	96.67	39.62	54.14	93.76
	4	96	38.97	54.74	2.20	0.71	96.61	38.83	55.01	93.84
	5	120	37.47	54.69	2.77	0.71	95.65	37.45	54.96	92.41
Dollendorf II Clay loam soil	1	24	38.77	55.36	2.46	0.22	96.82	38.77	55.33	94.10
	2	48	34.99	57.32	3.24	0.44	95.99	34.93	57.60	92.53
	3	72	34.73	57.08	4.12	0.68	96.62	34.90	56.99	91.90
	4	96	33.31	57.16	5.11	0.65	96.23	33.08	57.44	90.52
	5	120	33.70	57.42	4.39	0.66	96.16	33.60	57.49	91.08
Guadalupe Sandy loam soil	1	24	42.80	51.35	2.55	0.26	96.97	42.66	51.40	94.06
	2	48	38.31	54.84	3.04	0.51	96.70	38.24	55.11	93.36
	3	72	37.17	55.34	3.23	0.77	96.51	36.98	55.61	92.59
	4	96	35.99	56.60	3.25	0.76	96.60	35.73	56.88	92.62
	5	120	35.69	56.52	3.72	0.74	96.66	35.53	56.53	92.06
Springfield Silt loam soil	1	24	69.84	27.02	0.30	0.31	97.47	69.97	27.15	97.12
	2	48	67.13	28.07	0.55	0.61	96.36	67.11	28.20	95.31
	3	72	66.12	28.29	0.45	0.89	95.75	65.89	28.43	94.32
	4	96	66.46	28.71	0.70	0.90	96.77	65.98	28.85	94.84
	5	120	65.59	29.14	0.87	0.90	96.49	65.22	29.28	94.50

The results of the **Definitive Test** are presented below. The verification of the application rate of FOE Methylsulfone in the **Definitive Test** gave the following results:

- for the solution having a nominal concentration **1.0 mg FOE Methylsulfone/L** the measured concentration was **0.99 mg FOE Methylsulfone/L**;
- for the solution having a nominal concentration **0.30 mg FOE Methylsulfone/L** the measured concentration was **0.29 mg FOE Methylsulfone/L**;
- for the solution having a nominal concentration **0.10 mg FOE Methylsulfone/L** the measured concentration was **0.10 mg FOE Methylsulfone/L**;
- for the solution having a nominal concentration **0.03 mg Flufenacet/L** the measured concentration was **0.03 mg FOE Methylsulfone/L**;
- for the solution having a nominal concentration **0.01 mg Flufenacet/L** the measured concentration was **0.01 mg FOE Methylsulfone/L**.

The results of the determination of the recovery of applied radioactivity are presented below in the table B.8.1.2.1.2._CA-52.

Table B.8.1.2.1.2._CA-52: The results of the determination of the recovery of radioactivity in the **Definitive Test** – after adsorption and desorption steps.

Initial (measured) concentration of FOE Methylsulfone	Replicate	Total radioactivity recovery, expressed in [% AR], in experiment with the test soil:				
		<i>Wurmwiese Loam soil</i>	<i>Höfchen am Hohenseh Silt loam soil</i>	<i>Dollendorf II Clay loam soil</i>	<i>Guadalupe Sandy loam soil</i>	<i>Springfield Silt loam soil</i>
0.99 mg/L	1	100.6	98.6	98.6	99.4	98.6
	2	99.6	96.6	98.9	99.0	98.5
0.29 mg/L	1	100.1	93.3	97.0	99.0	95.8
	2	98.6	98.7	97.0	97.5	96.3
0.10 mg/L	1	97.9	95.8	96.0	99.7	95.7
	2	99.3	97.4	99.5	97.8	92.7
0.03 mg/L	1	98.6	94.7	96.4	98.0	91.6
	2	100.2	95.5	96.6	98.2	83.3
0.01 mg/L	1	103.4	95.1	97.8	96.9	8.61
	2	102.9	96.3	97.2	99.2	90.6

The results of the determination of the pH of supernatants after establishing the adsorption equilibrium in the definitive test are given below in the table B.8.1.2.1.2._CA-53. In the next table – B.8.1.2.1.2._CA-54 are presented the analogical results obtained for the desorption phase of the same test.

Table B.8.1.2.1.2._CA-53: The results of the determination of the pH of solution at equilibrium in the adsorption part of the **Definitive Test**.

Initial concentration of Flufenacet [mg/L]		Replicate	pH of the solution measured in the test system containing the test soil:				
<i>nominal</i>	<i>measured</i>		<i>Wurmwiese Loam soil</i>	<i>Höfchen am Hohenseh Silt loam soil</i>	<i>Dollendorf II Clay loam soil</i>	<i>Guadalupe Sandy loam soil</i>	<i>Springfield Silt loam soil</i>
1.00	0.99	1	5.71	6.76	7.02	6.78	6.57
		2	5.63	6.72	6.98	6.78	6.57
0.30	0.29	1	5.60	6.70	6.97	6.78	6.57
		2	5.62	6.72	6.95	6.75	6.57
0.10	0.10	1	5.62	6.69	6.96	6.74	6.58
		2	5.62	6.74	6.99	6.75	6.58
0.03	0.03	1	5.64	6.69	6.99	6.75	6.69
		2	5.66	6.72	6.98	6.75	6.62
0.01	0.01	1	5.71	6.71	6.97	6.80	6.66
		2	5.79	6.67	6.94	6.85	6.68

Table B.8.1.2.1.2._CA-54: The results of the determination of the pH of solution at equilibrium in the desorption part of the **Definitive Test**.

Initial concentration of Flufenacet [mg/L]		Replicate	pH of the solution measured in the test system containing the test soil:				
<i>nominal</i>	<i>measured</i>		<i>Wurmwiese Loam soil</i>	<i>Höfchen am Hohenseh Silt loam soil</i>	<i>Dollendorf II Clay loam soil</i>	<i>Guadalupe Sandy loam soil</i>	<i>Springfield Silt loam soil</i>
1.0	0.99	1	5.54	6.77	6.89	6.78	6.74
		2	5.52	6.83	6.84	6.79	6.68

The results of the definitive phase – the concentrations of the test item – FOE Methylsulfone, at equilibrium for adsorption and desorption phases, used by the Applicant to determine the Freundlich adsorption and desorption isotherms, are presented below in two tables – B.8.1.2.1.2._CA-55 for adsorption phase and B.8.1.2.1.2._CA-56 for the desorption phase. The Applicant used mean values to determine the isotherms.

Table B.8.1.2.1.2._CA-55: The results of the examination of the adsorption of FOE Methylsulfone onto test soils to determine Freundlich adsorption isotherm.

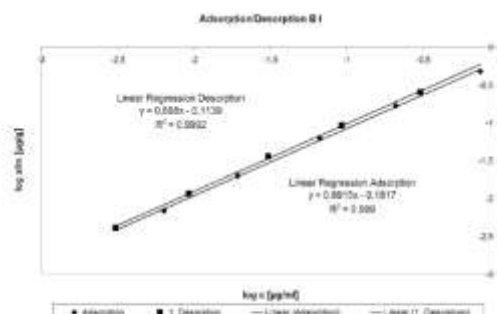
Test soil	Initial concentration of the solution [µg/mL]	Results of the experiment:				
		Concentration at equilibrium				Amount adsorbed onto soil in [%]
		in solution		in soil		
		Ce [µg/mL]	Log Ce	x/m [µg/g]	Log (x/m)	
Wurmweise Loam soil	0.99	0.746	-0.1275	0.479	-0.3195	24.2 ± 0.6
	0.29	0.209	-0.6792	0.168	-0.7740	28.5 ± 0.6
	0.10	0.067	-1.1758	0.062	-1.2057	31.7 ± 0.1
	0.03	0.019	-1.7142	0.020	-1.6987	28.5 ± 0.7
	0.01	0.006	-2.1958	0.007	-2.1635	24.2 ± 2.1
Höfchen am Hohenseh Silt loam soil	0.99	0.593	-0.2269	0.783	-0.1065	39.5 ± 0.1
	0.29	0.164	-0.7860	0.259	-0.5863	44.0 ± 0.4
	0.10	0.051	-1.2956	0.094	-1.253	48.0 ± 1.2
	0.03	0.014	-1.8415	0.030	-1.5256	50.6 ± 0.2
	0.01	0.005	-2.3397	0.010	-1.9808	53.1 ± 0.2
Dollendorf II Clay loam soil	0.99	0.543	-0.2653	0.879	-0.0558	44.4 ± 0.5
	0.29	0.149	-0.8266	0.287	-0.5415	48.8 ± 0.0
	0.10	0.047	-1.3296	0.102	-0.9930	51.7 ± 0.1
	0.03	0.013	-1.8868	0.033	-1.4871	55.3 ± 0.2
	0.01	0.004	-2.3710	0.011	-1.9563	56.2 ± 0.1
Guadalupe Sandy loam soil	0.99	0.642	-0.1927	0.340	-0.4680	34.4 ± 0.0
	0.29	0.180	-0.7444	0.112	-0.9490	38.2 ± 0.7
	0.10	0.057	-1.2410	0.040	-1.3962	40.9± 0.6
	0.03	0.017	-1.7821	0.013	-1.8953	43.2 ± 0.4
	0.01	0.005	-2.2694	0.004	-2.3566	44.7 ± 0.3
Springfield Silt loam soil	0.99	0.759	-0.1195	2.278	0.3575	23.0 ± 0.4
	0.29	0.215	-0.6666	0.785	-0.1050	26.6 ± 0.1
	0.10	0.069	-1.1627	0.293	-0.5337	29.8 ± 0.0
	0.03	0.019	-1.7132	0.100	-0.9993	34.0 ± 0.2
	0.01	0.006	-2.2074	0.036	-1.4417	36.7 ± 0.3

Table B.8.1.2.1.2._CA-55: The results of the examination of the desorption of FOE Methylsulfone from the test soils to determine Freundlich desorption isotherm.

Test soil	Initial concentration of the solution [μg/mL]	Results of the experiment:				
		Concentration at equilibrium				Amount desorbed from soil in [%]
		in solution		in soil		
		Ce [μg/mL]	Log Ce	x/m [μg/g]	Log (x/m)	
Wurmwiese Loam soil	0.99	0.304	-0.5170	0.252	-0.5994	47.5 ± 2.8
	0.29	0.093	-1.0331	0.093	-1.0331	44.9 ± 0.2
	0.10	0.031	-1.5129	0.036	-1.4451	42.4 ± 0.1
	0.03	0.009	-2.0344	0.012	-1.9363	42.2 ± 1.8
	0.01	0.003	-2.5130	0.004	-2.3897	40.7 ± 2.1
Höfchen am Hohenseh Silt loam soil	0.99	0.311	-0.4150	0.503	-0.6937	35.7 ± 1.6
	0.29	0.091	-0.9486	0.174	-1.1925	32.7 ± 0.2
	0.10	0.030	-1.4300	0.065	-1.6671	30.8 ± 0.7
	0.03	0.009	-1.9589	0.021	-2.1440	28.7 ± 0.1
	0.01	0.003	-2.4333	0.008	-2.6225	27.9 ± 0.6
Dollendorf II Clay loam soil	0.99	0.313	-0.5047	0.602	-0.2207	31.6 ± 0.4
	0.29	0.089	-1.0497	0.207	-0.6843	28.0 ± 0.6
	0.10	0.029	-1.5373	0.074	-1.1294	27.0 ± 0.2
	0.03	0.008	-2.0716	0.024	-1.6131	25.2 ± 0.3
	0.01	0.003	-2.5454	0.008	-2.0854	25.7 ± 1.8
Guadalupe Sandy loam soil	0.99	0.369	-0.4332	0.228	-0.6417	33.0 ± 0.6
	0.29	0.108	-0.9657	0.076	-1.1210	32.7 ± 0.3
	0.10	0.035	-1.4553	0.028	-1.5578	31.1 ± 0.2
	0.03	0.010	-1.9904	0.009	-2.0440	29.0 ± 1.1
	0.01	0.003	-2.4769	0.003	-2.4934	27.1 ± 4.1
Springfield Silt loam soil	0.99	0.205	-0.6881	0.917	-0.0377	59.7 ± 0.4
	0.29	0.066	-1.1834	0.317	-0.4995	59.7 ± 0.8
	0.10	0.023	-1.6425	0.123	-0.9040	57.4 ± 0.0
	0.03	0.007	-2.1527	0.047	-1.3271	53.0 ± 0.1
	0.01	0.002	-2.6185	0.017	-1.7576	51.7 ± 0.4

On the basis of the results presented in the tables below the adsorption and desorption isotherms for FOE Methylsulfone in each test soil were determined. They are presented below on figure B.8.1.2.1.2._CA-21. Additionally, in the table B.8.1.2.1.2._CA-56, are presented the Freundlich isotherm parameters obtained for the adsorption and desorption in each test soil.

The adsorption and desorption isotherms obtained in Wurmwiese test soil

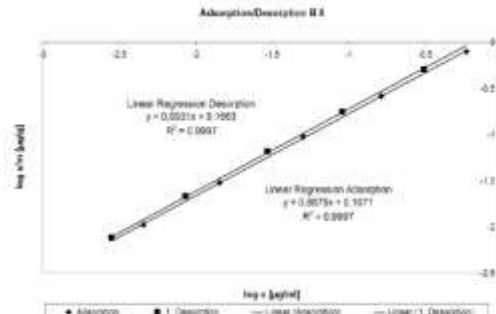


Evaluation of linear regression according to FREUNDLICH:

Regression	R ²	Adsorption	1 st Desorption
Slope	1/n	0.9991	0.9992
Interception	Log K _d	-0.8915	-0.8900
		-0.1817	-0.1139

C: Concentration in water in µg/mL (ppm)
X/m: Concentration in soil in µg/g (ppm)

The adsorption and desorption isotherms obtained in Höfchen am Hohenseh test soil

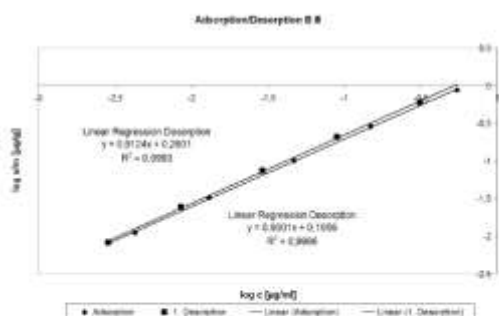


Evaluation of linear regression according to FREUNDLICH:

Regression	R ²	Adsorption	1 st Desorption
Slope	1/n	0.9997	0.9997
Interception	Log K _d	0.9975	0.9971
		-0.1971	-0.1993

C: Concentration in water in µg/mL (ppm)
X/m: Concentration in soil in µg/g (ppm)

The adsorption and desorption isotherms obtained in Dollendorf II test soil

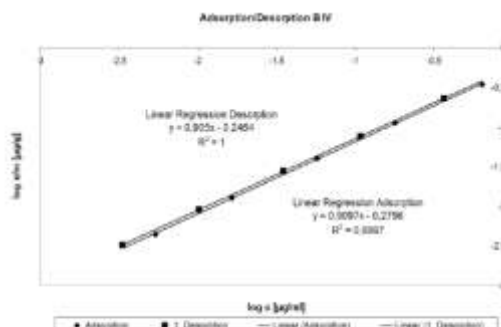


Evaluation of linear regression according to FREUNDLICH:

Regression	R ²	Adsorption	1 st Desorption
Slope	1/n	0.9996	0.9993
Interception	Log K _d	0.9171	0.9124
		0.1996	0.2831

C: Concentration in water in µg/mL (ppm)
X/m: Concentration in soil in µg/g (ppm)

The adsorption and desorption isotherms obtained in Guadelupe test soil

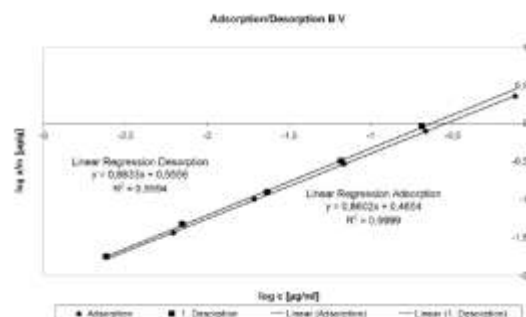


Evaluation of linear regression according to FREUNDLICH:

Regression	R ²	Adsorption	1 st Desorption
Slope	1/n	0.9997	1.0000
Interception	Log K _d	-0.2796	-0.2484

C: Concentration in water in µg/mL (ppm)
X/m: Concentration in soil in µg/g (ppm)

The adsorption and desorption isotherms obtained in Springfield test soil



Evaluation of linear regression according to FREUNDLICH:

Regression	R ²	Adsorption	1 st Desorption
Slope	1/n	0.9999	0.9994
Interception	Log K _d	0.8602	0.8633
		0.4654	0.5556

C: Concentration in water in µg/mL (ppm)
X/m: Concentration in soil in µg/g (ppm)

Figure B.8.1.2.1.2._CA-21: The Freundlich adsorption and desorption isotherms determined for FOE Methylsulfone in each test soil (copied from the study report).

Table B.8.1.2.1.2._CA-56: The key numerical results of the experiment presented in the study report – parameters of Freundlich adsorption and 1st desorption isotherms for FOE Methylsulfone, as reported by the Applicant.

Test soil	Parameters of Freundlich adsorption isotherm					Parameters of Freundlich 1 st desorption isotherm				
	$\text{Log } K_{f\text{ ads}}$	$K_{f\text{ ads}} [\text{mL/g}]$	$1/n$	$K_{f\text{OC ads}} [\text{mL/g}]$	R^2	$\text{Log } K_{f\text{ des}}$	$K_{f\text{ des}} [\text{mL/g}]$	$1/n$	$K_{f\text{OC des}} [\text{mL/g}]$	R^2
Wurmwiese Loam soil	-0.1817	0.6582	0.8915	37.4	0.9990	-0.1139	0.7693	0.8980	43.7	0.9992
Höfchen am Hohenseh Silt loam soil	0.1071	1.2797	0.8875	52.9	0.9997	0.1663	1.4666	0.8931	60.6	0.9997
Dollendorf II Clay loam soil	0.1956	1.5688	0.9001	33.2	0.9996	0.2601	1.8200	0.9124	38.6	0.9993
Guadalupe Sandy loam soil	-0.2796	0.5253	0.9097	75.0	0.9997	-0.2464	0.5671	0.9050	81.0	1.0000
Springfield Silt loam soil	0.4654	2.9201	0.8602	171.8	0.9999	0.5556	3.5944	0.8833	211.4	0.9994

The Applicant also presented the results of the determination of Freundlich isotherms for serial desorption of FOE Methylsulfone from five test soils. The isotherms were determined for the experiment with highest initial concentration tested – 0.99 mg/L. The graphical results – isotherms in their linearised form, are presented below on figure B.8.1.2.1.2.-CA-22. The numerical results of the experiment – the determined Freundlich parameters (K_f , $K_{f\text{OC}}$ and $1/n$ values) are presented in the table B.8.1.2.1.2._CA-57. Analysing the isotherms RMS noticed that they were determined using four experimental points. It may be assumed that while three of them represent the concentrations at equilibrium after each desorption step, the remaining fourth is for concentrations at equilibrium determined during examining the adsorption process.

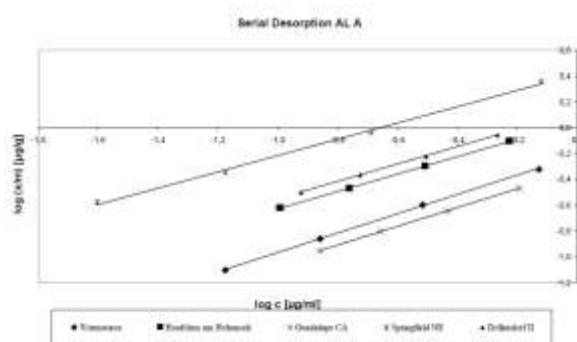


Figure B.8.1.2.1.2._CA-22: Freundlich isotherms for serial desorption of FOE Methylsulfone from the tes soils (copied from the study report)

Table B.8.1.2.1.2._CA-56: The key numerical results of the determination of the Freundlich isotherm for a serial desorption of FOE Methylsulfone from test soils, as reported by the Applicant

Test soil	Parameters of Freundlich serial desorption isotherm			
	$K_{f\text{ des}} [\text{mL/g}]$	$1/n$	$K_{f\text{OC des}} [\text{mL/g}]$	R^2
Wurmwiese Loam soil	0.6027	0.7455	34.2	0.9998
Höfchen am Hohenseh Silt loam soil	1.1029	0.6744	45.8	0.9999
Dollendorf II Clay loam soil	1.3210	0.6723	28.0	0.9999
Guadalupe Sandy loam soil	0.4711	0.7268	67.3	0.9999
Springfield Silt loam soil	2.6021	0.6313	153.1	0.9967

Because of the stated difficulties in the interpretation of the results obtained by the Applicant – the adsorption and desorption isotherms were presented on the same graph, as well as because to determine the isotherms the averaged values were used instead of those for the individual replicates, RMS decided to verify the results of the determination of adsorption and 1st desorption Freundlich isotherms. The results of this exercise, together with input data used in it, are presented below, individually for each test soil. To maintain the consistency with the Applicant's analysis the data used to plot the isotherms were logarithmically transformed to Log₁₀ values. The isotherms were plotted using the CurveExpert Pro 1.0 tool.

a) Results obtained for Wurmwiese Loam soil:

The input data used to determine Freundlich adsorption isotherm are presented below in the table B.8.1.2.1.2._CA-57. The next table – B.8.1.2.1.2._CA-58 presents the input data used to determine Freundlich desorption isotherm. For the purpose of the reporting all values were rounded to the four digits after the decimal point to maintain the consistency with the source data – amounts in soil and in solution at equilibrium, provided in the study report.

The graphical results of the fitting – linearised Freundlich adsorption and desorption isotherms are presented on figure B.8.1.2.1.2._CA-23. Finally, the table B.8.1.2.1.2._CA-59 provides the numerical results of the fitting – the parameters of Freundlich sorption isotherms together with their statistical evaluation.

Table B.8.1.2.1.2._CA-57: The results of the examination of the adsorption of FOE Methylsulfone onto test soil *Wurmwiese (Loam)* used by the RMS to determine Freundlich adsorption isotherm.

Soil mass <i>m</i> , solution volume <i>V</i>	Initial concentration of the solution [μg/mL]	<i>Rep.</i>	Results of the experiment:						<i>Amount adsorbed onto soil in [%]</i>
			<i>In soil at equilibrium</i>			<i>In solution at equilibrium</i>			
			amount [μg]	concentration		amount [μg]	concentration		
				x/m [μg/g]	Log (x/m)		Ce [μg/mL]	Log Ce	
<i>m</i> = 10 g; <i>V</i> = 20.13 mL	0.99	1	4.7025	0.4703	-0.3277	15.0945	0.7499	-0.1250	23.75
		2	4.8805	0.4881	-0.3115	14.9165	0.7410	-0.1302	24.65
	0.29	1	1.7090	0.1709	-0.7673	4.1867	0.2080	-0.6820	28.99
		2	1.6565	0.1657	-0.7808	4.2392	0.2106	-0.6766	28.10
	0.10	1	0.6247	0.0625	-1.2043	1.3406	0.0666	-1.1765	31.79
		2	0.6207	0.0621	-1.2071	1.3445	0.0668	-1.1753	31.58
	0.03	1	0.2029	0.0203	-1.6927	0.3859	0.0192	-1.7174	34.46
		2	0.1973	0.0197	-1.7049	0.3915	0.0194	-1.7111	33.51
	0.01	1	0.0657	0.0066	-2.1824	0.1312	0.0065	-2.1859	33.36
		2	0.0716	0.0072	-2.1451	0.1253	0.0062	-2.2059	36.37

Table B.8.1.2.1.2._CA-58: The results of the examination of the desorption of FOE Methylsulfone from the test soil *Wurmwiese (Loam)* used by the RMS to determine Freundlich adsorption isotherm.

Soil mass <i>m</i> , solution volume <i>V</i>	Initial concentration of the solution [µg/mL]	Rep.	Results of the experiment:						Amount desorbed from soil as [%] of adsorbed
			In soil at equilibrium			In solution at equilibrium			
			amount [µg]	concentration		amount [µg]	concentration		
				x/m [µg/g]	Log (x/m)		Ce [µg/mL]	Log Ce	
<i>m</i> = 10 g; <i>V</i> = 20.13 mL	0.99	1	2.3745	0.2375	-0.6244	6.0981	0.3029	-0.5186	28.03
		2	2.6568	0.2657	-0.5756	6.1420	0.3051	-0.5155	30.19
	0.29	1	0.9390	0.0939	-1.0273	1.8739	0.0931	-1.0311	33.38
		2	0.9143	0.0914	-1.0389	1.8557	0.0922	-1.0353	33.01
	0.10	1	0.3602	0.0360	-1.4435	0.6147	0.0305	-1.5152	36.95
		2	0.3547	0.0357	-1.4468	0.6211	0.0309	-1.5107	36.53
	0.03	1	0.1199	0.0120	-1.9212	0.1867	0.0093	-2.0327	39.12
		2	0.1117	0.0112	-1.9519	0.1852	0.0092	-2.0362	37.61
	0.01	1	0.0380	0.0038	-2.4202	0.0623	0.0031	-2.5094	37.88
		2	0.0435	0.0044	-2.3615	0.0613	0.0030	-2.5164	41.55

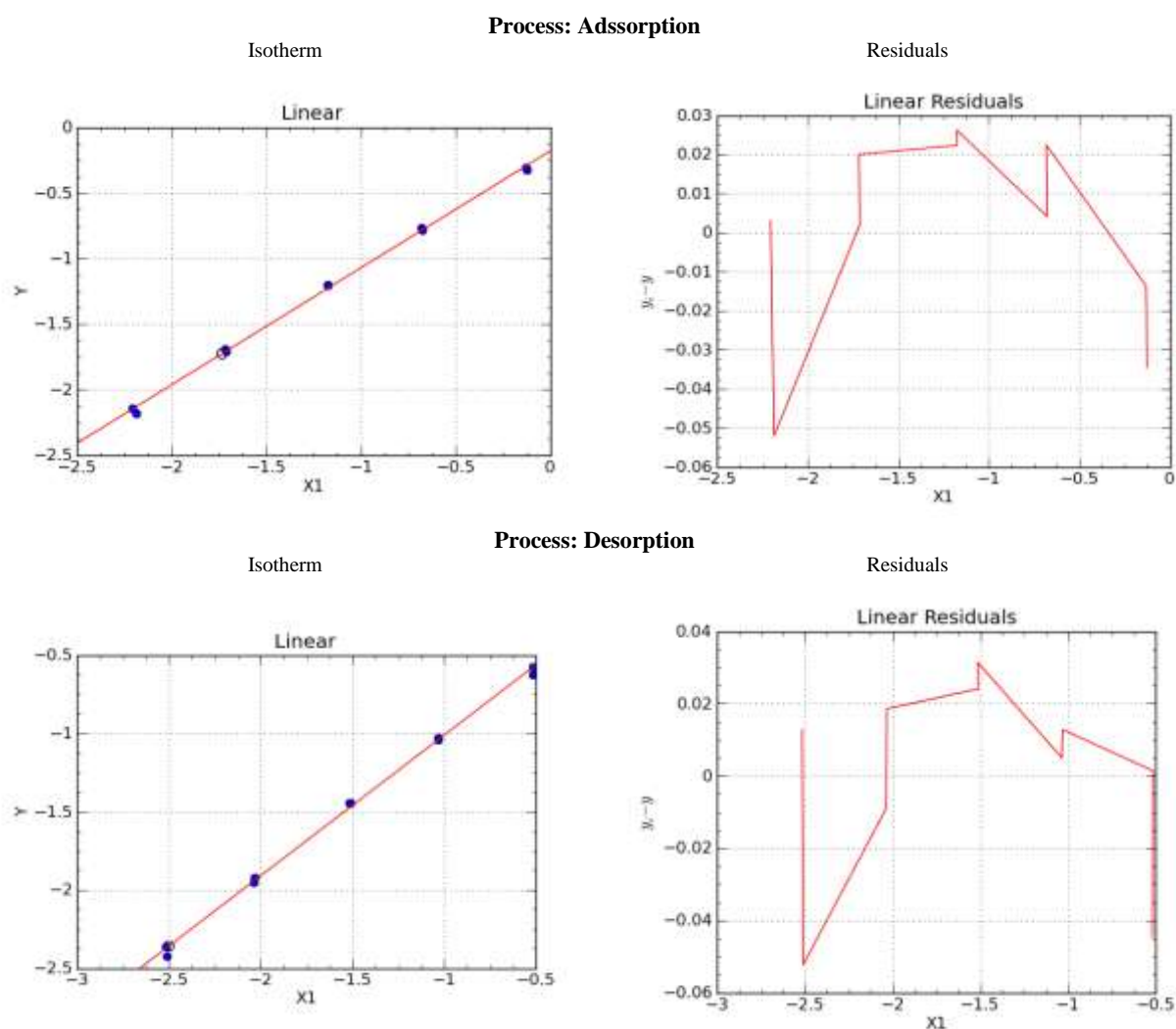


Figure B.8.1.2.1.2._CA-23: The Freundlich adsorption and desorption isotherms for FOE Methylsulfone in Wurmwiese Loam soil determined by the RMS.

Table B.8.1.2.1.2._CA-59: The parameters of the Freundlich adsorption and desorption isotherms determined for FOE Methylsulfone in Wurmwiese Loam soil by the RMS

Test soil	Process	Parameters of isotherm				Statistical evaluation	
		Log K_F	K_F [mL/g]	$K_{F\text{OC}}$ [mL/g]	1/n	SD	Determination coefficient R^2
<i>Wurmwiese, Loam soil</i>	Adsorption	-0.1817	0.6581	37.39	0.8914	0.0279	0.9985
	Desorption	-0.1140	0.7691	43.70	0.8982	0.0297	0.9982

b) Results obtained for Höfchen am Hohenseh Silt loam soil:

The input data used to determine Freundlich adsorption isotherm are presented below in the table B.8.1.2.1.2._CA-60. The next table – B.8.1.2.1.2._CA-61 presents the input data used to determine Freundlich desorption isotherm. For the purpose of the reporting all values were rounded to the four digits after the decimal point to maintain the consistency with the source data – amounts in soil and in solution at equilibrium, provided in the study report.

The graphical results of the fitting – linearised Freundlich adsorption and desorption isotherms are presented on figure B.8.1.2.1.2._CA-24. Finally, the table B.8.1.2.1.2._CA-63 provides the numerical results of the fitting – the parameters of Freundlich sorption isotherms together with their statistical evaluation.

Table B.8.1.2.1.2._CA-60: The results of the examination of the adsorption of FOE Methylsulfone onto test soil *Höfchen am Hohenseh (Silt loam)* used by the RMS to determine Freundlich adsorption isotherm.

Soil mass <i>m</i> , solution volume <i>V</i>	Initial concentration of the solution [µg/mL]	Rep.	Results of the experiment:						Amount adsorbed onto soil in [%]
			In soil at equilibrium			In solution at equilibrium			
			amount [µg]	concentration		amount [µg]	concentration		
				x/m [µg/g]	Log (x/m)		Ce [µg/mL]	Log Ce	
<i>m</i> = 10 g; <i>V</i> = 20.18 mL	0.99	1	7.8457	0.7846	-0.1054	11.9513	0.5922	-0.2275	39.63
		2	7.8066	0.7807	-0.1075	11.9044	0.5899	-0.2292	39.43
	0.29	1	2.6086	0.2609	-0.5836	3.2871	0.1629	-0.7881	44.25
		2	2.5758	0.2576	-0.5891	3.3199	0.1645	-0.7838	43.69
	0.10	1	0.9599	0.0960	-1.0178	1.0053	0.0498	-1.3026	48.84
		2	0.9271	0.0927	-1.0329	1.0381	0.0514	-1.2887	47.17
	0.03	1	0.2991	0.0299	-1.5242	0.2897	0.0144	-1.8430	50.80
		2	0.2971	0.0297	-1.5271	0.2917	0.0145	-1.8400	50.46
	0.01	1	0.1042	0.0104	-1.9821	0.0927	0.0046	-2.3378	52.93
		2	0.1049	0.0105	-1.9792	0.0920	0.0046	-2.3411	53.27

Table B.8.1.2.1.2._CA-61: The results of the examination of the desorption of FOE Methylsulfone from the test soil *Höfchen am Hohenseh (Silt loam)* used by the RMS to determine Freundlich adsorption isotherm.

Soil mass <i>m</i> , solution volume <i>V</i>	Initial concentration of the solution [µg/mL]	<i>Rep.</i>	Results of the experiment:						<i>Amount desorbed from soil as [%] of adsorbed</i>
			<i>In soil at equilibrium</i>			<i>In solution at equilibriun</i>			
			amount [µg]	concentration		amount [µg]	concentration		
				x/m [µg/g]	Log (x/m)		Ce [µg/mL]	Log Ce	
<i>m</i> = 10 g; <i>V</i> = 20.18 mL	0.99	1	4.0684	0.4068	-0.3906	7.8413	0.3886	-0.4105	34.16
		2	4.1911	0.4191	-0.3777	7.8369	0.3883	-0.4108	34.84
	0.29	1	1.3233	0.1323	-0.8783	2.2692	0.1124	-0.9490	36.83
		2	1.2960	0.1296	-0.8874	2.3197	0.1150	-0.9395	35.84
	0.10	1	0.4388	0.0439	-1.3577	0.7607	0.0377	-1.4237	36.58
		2	0.4394	0.0439	-1.3571	0.7540	0.0374	-1.4275	36.82
	0.03	1	0.1464	0.0146	-1.8345	0.2246	0.0111	-1.9535	39.45
		2	0.1465	0.0147	-1.8342	0.2235	0.0111	-1.9556	39.60
	0.01	1	0.0486	0.0049	-2.3134	0.0758	0.0038	-2.4253	39.09
		2	0.0487	0.0049	-2.3125	0.0745	0.0037	-2.4328	39.51

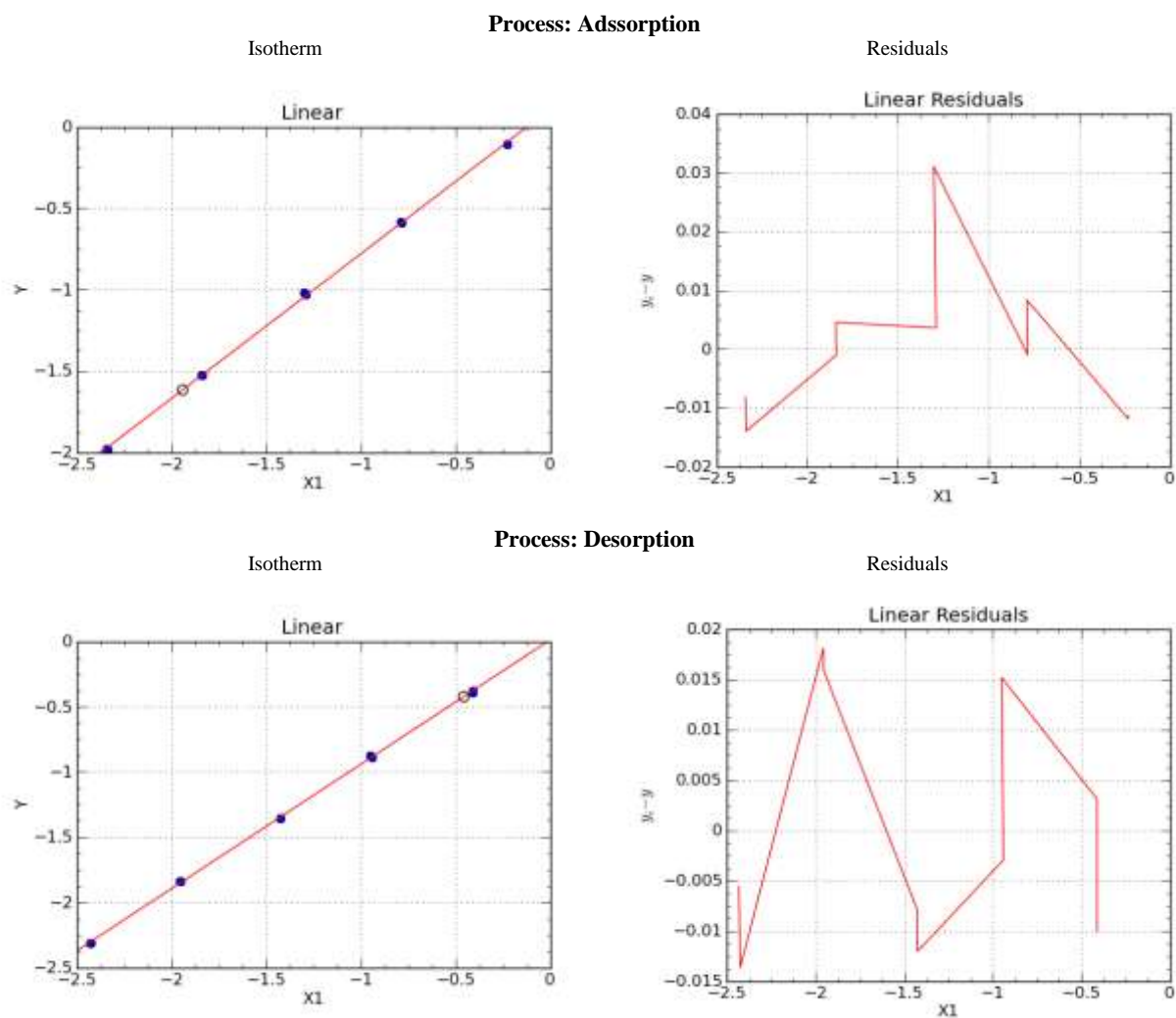


Figure B.8.1.2.1.2._CA-24: The Freundlich adsorption and desorption isotherms for FOE Methylsulfone in Höfchen am Hohenseh Silt loam soil determined by the RMS.

Table B.8.1.2.1.2._CA-62: The parameters of the Freundlich adsorption and desorption isotherms determined for FOE Methylsulfone in Höfchen am Hohenseh Silt loam soil by the RMS

Test soil	Process	Parameters of isotherm				Statistical evaluation	
		Log K_F	K_F [mL/g]	$K_{F\text{OC}}$ [mL/g]	1/n	SD	Determination coefficient R^2
<i>Höfchen am Hohenseh, Silt loam soil</i>	Adsorption	0.1079	1.2820	52.97	0.8880	0.0141	0.9996
	Desorption	0.0105	1.0245	42.33	0.9526	0.0130	0.9997

c) Results obtained for Dollendorf II Clay loam soil:

The input data used to determine Freundlich adsorption isotherm are presented below in the table B.8.1.2.1.2._CA-63. The next table – B.8.1.2.1.2._CA-64 presents the input data used to determine Freundlich desorption isotherm. For the purpose of the reporting all values were rounded to the four digits after the decimal point to maintain the consistency with the source data – amounts in soil and in solution at equilibrium, provided in the study report.

The graphical results of the fitting – linearised Freundlich adsorption and desorption isotherms are presented on figure B.8.1.2.1.2._CA-25. Finally, the table B.8.1.2.1.2._CA-65 provides the numerical results of the fitting – the parameters of Freundlich sorption isotherms together with their statistical evaluation.

Table B.8.1.2.1.2._CA-63: The results of the examination of the adsorption of FOE Methylsulfone onto test soil *Dollendorf II (Clay loam)* used by the RMS to determine Freundlich adsorption isotherm.

Soil mass <i>m</i> , solution volume <i>V</i>	Initial concentration of the solution [μg/mL]	Rep.	Results of the experiment:						Amount adsorbed onto soil in [%]
			In soil at equilibrium			In solution at equilibrium			
			amount [μg]	concentration		amount [μg]	concentration		
				x/m [μg/g]	Log (x/m)		Ce [μg/mL]	Log Ce	
<i>m</i> = 10 g; <i>V</i> = 20.27 mL	0.99	1	8.8608	0.8861	-0.0525	10.9362	0.5395	-0.2680	44.76
		2	8.7263	0.8726	-0.0592	11.0707	0.5462	-0.2627	44.08
	0.29	1	2.8762	0.2876	-0.5412	3.0195	0.1490	-0.8269	48.78
		2	2.8722	0.2872	-0.5418	3.0235	0.1492	-0.8263	48.72
	0.10	1	1.0183	0.1018	-0.9921	0.9470	0.0467	-1.3305	51.81
		2	1.0144	0.1014	-0.9938	0.9508	0.0469	-1.3288	51.62
	0.03	1	0.3268	0.0327	-1.4857	0.2620	0.0129	-1.8886	55.50
		2	0.3248	0.0325	-1.4884	0.2640	0.0130	-1.8852	55.16
	0.01	1	0.1105	0.0111	-1.9566	0.0864	0.0043	-2.3703	56.12
		2	0.1107	0.0111	-1.9559	0.0862	0.0043	-2.3713	56.23

Table B.8.1.2.1.2._CA-64: The results of the examination of the desorption of FOE Methylsulfone from the test soil *Dollendorf II (Clay loam)* used by the RMS to determine Freundlich adsorption isotherm.

Soil mass <i>m</i> , solution volume <i>V</i>	Initial concentration of the solution [µg/mL]	Rep.	Results of the experiment:						Amount desorbed from soil as [%] of adsorbed
			<i>In soil at equilibrium</i>			<i>In solution at equilibrium</i>			
			amount [µg]	concentration		amount [µg]	concentration		
				x/m [µg/g]	Log (x/m)		Ce [µg/mL]	Log Ce	
<i>m</i> = 10 g; <i>V</i> = 20.27 mL	0.99	1	6.0372	0.6037	-0.2192	6.3563	0.3136	-0.5036	48.71
		2	5.9957	0.5996	-0.2222	6.3232	0.3119	-0.5059	48.67
	0.29	1	2.0574	0.2057	-0.6867	1.8359	0.0906	-1.0430	52.84
		2	2.0508	0.2081	-0.6818	1.7789	0.0878	-1.0567	53.91
	0.10	1	0.7421	0.0742	-1.1295	0.5891	0.0291	-1.5367	55.75
		2	0.7427	0.0743	-1.1292	0.5873	0.0290	-1.5380	55.84
	0.03	1	0.2452	0.0245	-1.6105	0.1717	0.0085	-2.0721	58.82
		2	0.2422	0.0242	-1.6158	0.1720	0.0085	-2.0713	58.47
	0.01	1	0.0834	0.0083	-2.0788	0.0559	0.0028	-2.5594	59.89
		2	0.0809	0.0081	-2.0921	0.0596	0.0029	-2.5316	57.57

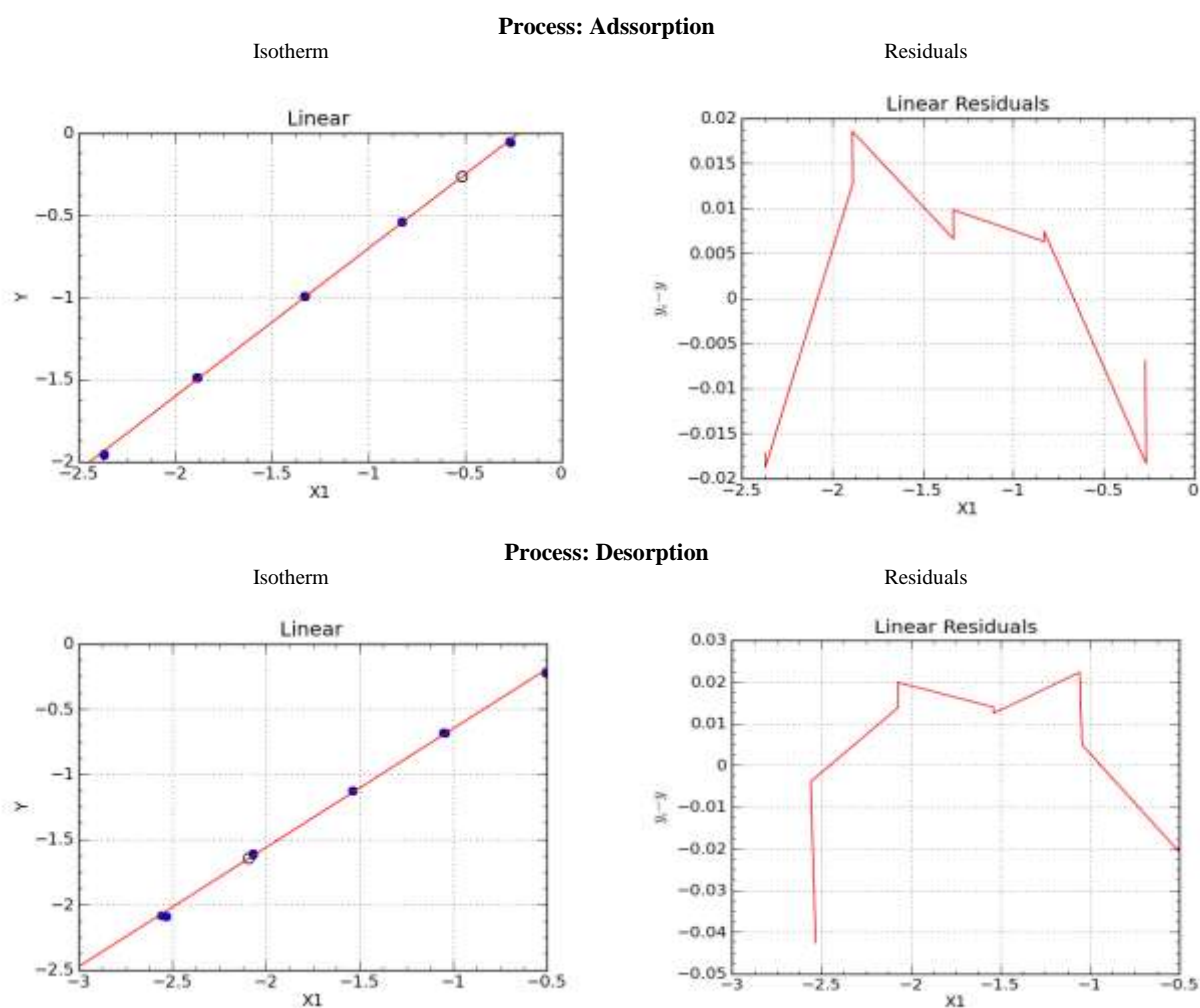


Figure B.8.1.2.1.2._CA-25: The Freundlich adsorption and desorption isotherms for FOE Methylsulfone in Dollendorf II Clay loam soil determined by the RMS.

Table B.8.1.2.1.2._CA-65: The parameters of the Freundlich adsorption and desorption isotherms determined for FOE Methylsulfone in Dollendorf II Clay loam soil by the RMS

Test soil	Process	Parameters of isotherm				Statistical evaluation	
		Log K_F	K_F [mL/g]	$K_{F\text{ oc}}$ [mL/g]	1/n	SD	Determination coefficient R^2
<i>Dollendorf II, Clay loam soil</i>	Adsorption	0.1956	1.5689	33.24	0.9001	0.0149	0.9996
	Desorption	0.2599	1.8193	38.54	0.9122	0.0226	0.9991

d) Results obtained for Guadalupe Sandy loam soil:

The input data used to determine Freundlich adsorption isotherm are presented below in the table B.8.1.2.1.2._CA-66. The next table – B.8.1.2.1.2._CA-67 presents the input data used to determine Freundlich desorption isotherm. For the purpose of the reporting all values were rounded to the four digits after the decimal point to maintain the consistency with the source data – amounts in soil and in solution at equilibrium, provided in the study report.

The graphical results of the fitting – linearised Freundlich adsorption and desorption isotherms are presented on figure B.8.1.2.1.2._CA-26. Finally, the table B.8.1.2.1.2._CA-68 provides the numerical results of the fitting – the parameters of Freundlich sorption isotherms together with their statistical evaluation.

Table B.8.1.2.1.2._CA-66: The results of the examination of the adsorption of FOE Methylsulfone onto test soil *Guadalupe (Sandy loam)* used by the RMS to determine Freundlich adsorption isotherm.

Soil mass <i>m</i> , solution volume <i>V</i>	Initial concentration of the solution [μg/mL]	Rep.	Results of the experiment:						Amount adsorbed onto soil in [%]
			In soil at equilibrium			In solution at equilibriun			
			amount [μg]	concentration		amount [μg]	concentration		
				x/m [μg/g]	Log (x/m)		Ce [μg/mL]	Log Ce	
<i>M</i> = 20 g; <i>V</i> = 20.24 mL	0.99	1	6.8145	0.3407	-0.4676	12.9825	0.6414	-0.1929	34.42
		2	6.8012	0.3401	-0.4684	12.9958	0.6421	-0.1924	34.35
	0.29	1	2.2209	0.1110	-0.9545	3.6748	0.1816	-0.7410	37.67
		2	2.2779	0.1139	-0.9535	3.6178	0.1787	-0.7478	38.64
	0.10	1	0.7945	0.0397	-1.4009	1.1707	0.0578	-1.2378	40.43
		2	0.8119	0.0406	-1.3915	1.1533	0.0570	-1.2443	41.31
	0.03	1	0.2562	0.0128	-1.8925	0.3326	0.0164	-1.7843	43.51
		2	0.2528	0.0126	-1.8983	0.3360	0.0166	-1.7799	42.94
	0.01	1	0.0884	0.0044	-2.3546	0.1084	0.0054	-2.2712	44.92
		2	0.0875	0.0044	-2.3590	0.1093	0.0054	-2.2676	44.47

Table B.8.1.2.1.2._CA-67: The results of the examination of the desorption of FOE Methylsulfone from the test soil *Guadalupe (Sandy loam)* used by the RMS to determine Freundlich adsorption isotherm.

Soil mass <i>m</i> , solution volume <i>V</i>	Initial concentration of the solution [μg/mL]	Rep.	Results of the experiment:						Amount desorbed from soil as [%] of adsorbed
			In soil at equilibrium			In solution at equilibriun			
			amount [μg]	concentration		amount [μg]	concentration		
				x/m [μg/g]	Log (x/m)		Ce [μg/mL]	Log Ce	
<i>m</i> = 20 g; <i>V</i> = 20.24 mL	0.99	1	4.5965	0.2298	-0.6386	7.3951	0.3654	-0.4373	38.,33
		2	4.5320	0.2266	-0.6447	7.5350	0.3723	-0.4291	37.56
	0.29	1	1.4896	0.0745	-1.1280	2.2039	0.1089	-0.9630	40.33
		2	1.5378	0.0769	-1.1141	2.1775	0.1076	-0.9683	41.39
	0.10	1	0.5489	0.0274	-1.5615	0.7136	0.0353	-1.4528	43.48
		2	0.5589	0.0279	-1.5542	0.7055	0.0349	-1.4577	44.18
	0.03	1	0.1838	0.0092	-2.0367	0.2037	0.0101	-1.9972	47.44
		2	0.1776	0.0089	-2.0516	0.2102	0.0104	-1.9836	45.79
	0.01	1	0.0671	0.0034	-2.4743	0.0650	0.0032	-2.4933	50.79
		2	0.0613	0.0031	-2.5136	0.0700	0.0035	-2.4611	46.69

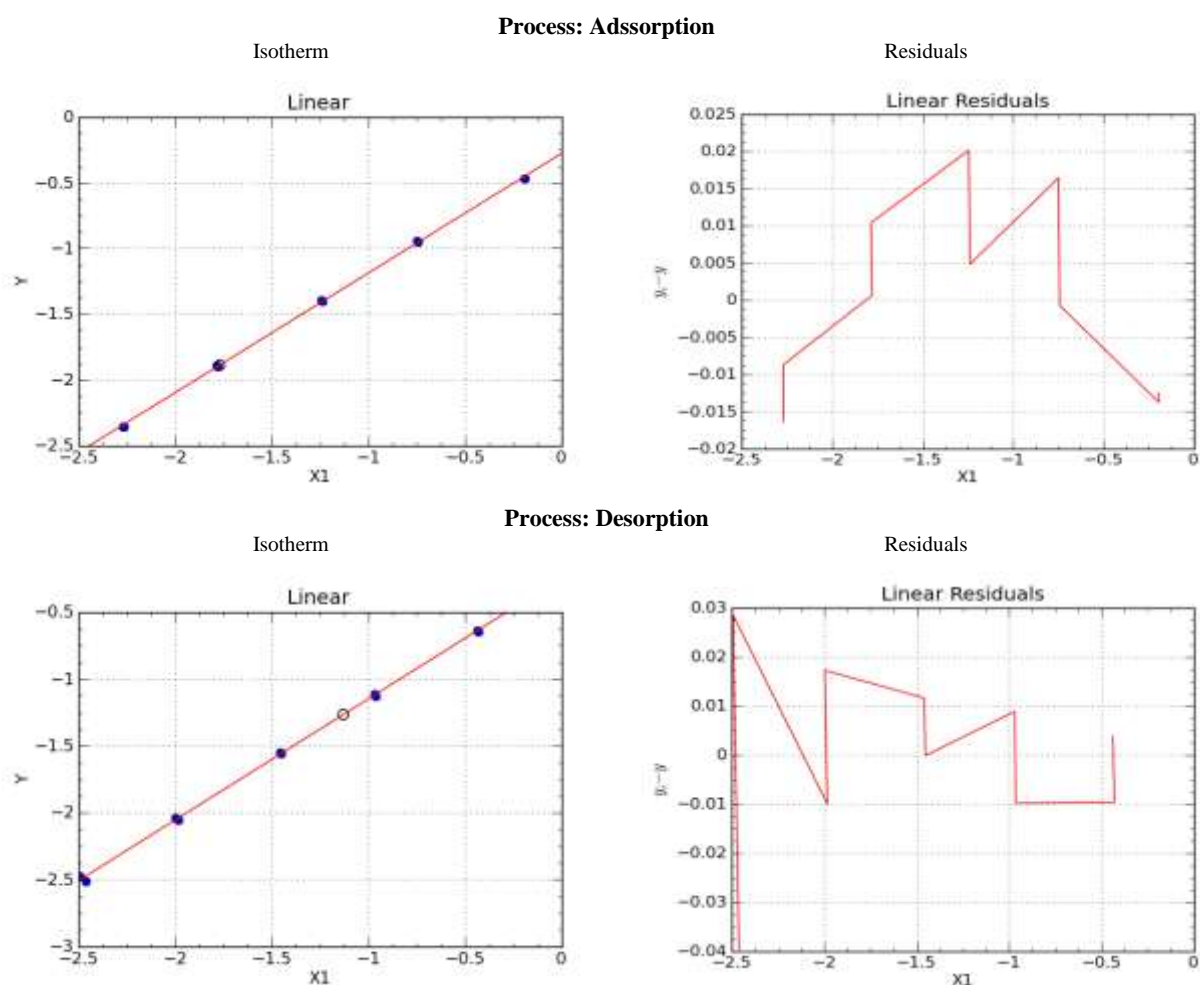


Figure B.8.1.2.1.2._CA-26: The Freundlich adsorption and desorption isotherms for FOE Methylsulfone in Guadalupe Clay loam soil determined by the RMS.

Table B.8.1.2.1.2._CA-69 The parameters of the Freundlich adsorption and desorption isotherms determined for FOE Methylsulfone in Guadalupe Clay loam soil by the RMS

Test soil	Process	Parameters of isotherm				Statistical evaluation	
		Log K_F	K_F [mL/g]	$K_{F OC}$ [mL/g]	1/n	SD	Determination coefficient R^2
<i>Wurmwiese, Loam soil</i>	Adsorption	-0.2796	0.5253	75.04	0.9098	0.0137	0.9997
	Desorption	-0.2467	0.5666	80.94	0.9048	0.0201	0.9992

e) Results obtained for Springfield Silt loam soil:

The input data used to determine Freundlich adsorption isotherm are presented below in the table B.8.1.2.1.2._CA-70. The next table – B.8.1.2.1.2._CA-71 presents the input data used to determine Freundlich desorption isotherm. For the purpose of the reporting all values were rounded to the four digits after the decimal point to maintain the consistency with the source data – amounts in soil and in solution at equilibrium, provided in the study report.

The graphical results of the fitting – linearised Freundlich adsorption and desorption isotherms are presented on figure B.8.1.2.1.2._CA-27. Finally, the table B.8.1.2.1.2._CA-72 provides the numerical results of the fitting – the parameters of Freundlich sorption isotherms together with their statistical evaluation.

Table B.8.1.2.1.2._CA-70: The results of the examination of the adsorption of FOE Methylsulfone onto test soil *Springfield (Silt loam)* used by the RMS to determine Freundlich adsorption isotherm.

Soil mass <i>m</i> , solution volume <i>V</i>	Initial concentration of the solution [μg/mL]	Rep.	Results of the experiment:						Amount adsorbed onto soil in [%]
			In soil at equilibrium			In solution at equilibrium			
			amount [μg]	concentration		amount [μg]	concentration		
				x/m [μg/g]	Log (x/m)		Ce [μg/mL]	Log Ce	
<i>m</i> = 2 g; <i>V</i> = 20.07 mL	0.99	1	4.4991	2.2496	0.3521	15.2978	0.7622	-0.1179	22.73
		2	4.6112	2.3056	0.3628	15.1858	0.7566	-0.1211	23.29
	0.29	1	1.5664	0.7832	-0.1061	4.3294	0.2157	-0.6661	26.57
		2	1.5749	0.7875	-0.1038	4.3208	0.2153	-0.6670	26.71
	0.10	1	0.5857	0.2929	-0.5334	1.3796	0.0687	-1.1628	29.80
		2	0.5848	0.2924	-0.5340	1.3804	0.0688	-1.1625	29.76
	0.03	1	0.1994	0.0997	-1.0013	0.3894	0.0194	-1.7122	33.86
		2	0.2013	0.1007	-0.9972	0.3876	0.0193	-1.7142	34.18
	0.01	1	0.0727	0.0364	-1.4395	0.1242	0.0062	-2.2084	36.92
		2	0.0720	0.0360	-1.4437	0.1249	0.0062	-2.2060	36.56

Table B.8.1.2.1.2._CA-71: The results of the examination of the desorption of FOE Methylsulfone from the test soil *Springfield (Silt loam)* used by the RMS to determine Freundlich adsorption isotherm.

Soil mass <i>m</i> , solution volume <i>V</i>	Initial concentration of the solution [µg/mL]	Rep.	Results of the experiment:						Amount desorbed from soil as [%] of adsorbed
			In soil at equilibrium			In solution at equilibrium			
			amount [µg]	concentration		amount [µg]	concentration		
				x/m [µg/g]	Log (x/m)		Ce [µg/mL]	Log Ce	
<i>m</i> = 2 g; <i>V</i> = 20.07 mL	0.99	1	1.8225	0.9113	-0.0404	4.0497	0.2018	-0.6951	31.04
		2	1.8447	0.9224	-0.0351	4.1824	0.2084	-0.6811	30.61
	0.29	1	0.6309	0.3155	-0.5011	1.3154	0.0655	-1.1835	32.41
		2	0.6356	0.3178	-0.4978	1.3163	0.0656	-1.1832	32.56
	0.10	1	0.2461	0.1231	-0.9099	0.4668	0.0233	-1.6334	34.52
		2	0.2529	0.1265	-0.8981	0.4475	0.0223	-1.6518	36.11
	0.03	1	0.0926	0.0463	-1.3344	0.1417	0.0071	-2.1512	39.52
		2	0.0957	0.0479	-1.3201	0.1407	0.0070	-2.1543	40.49
	0.01	1	0.0349	0.0175	-1.7582	0.0483	0.0024	-2.6186	41.96
		2	0.0350	0.0175	-1.7570	0.0483	0.0024	-2.6186	41.99

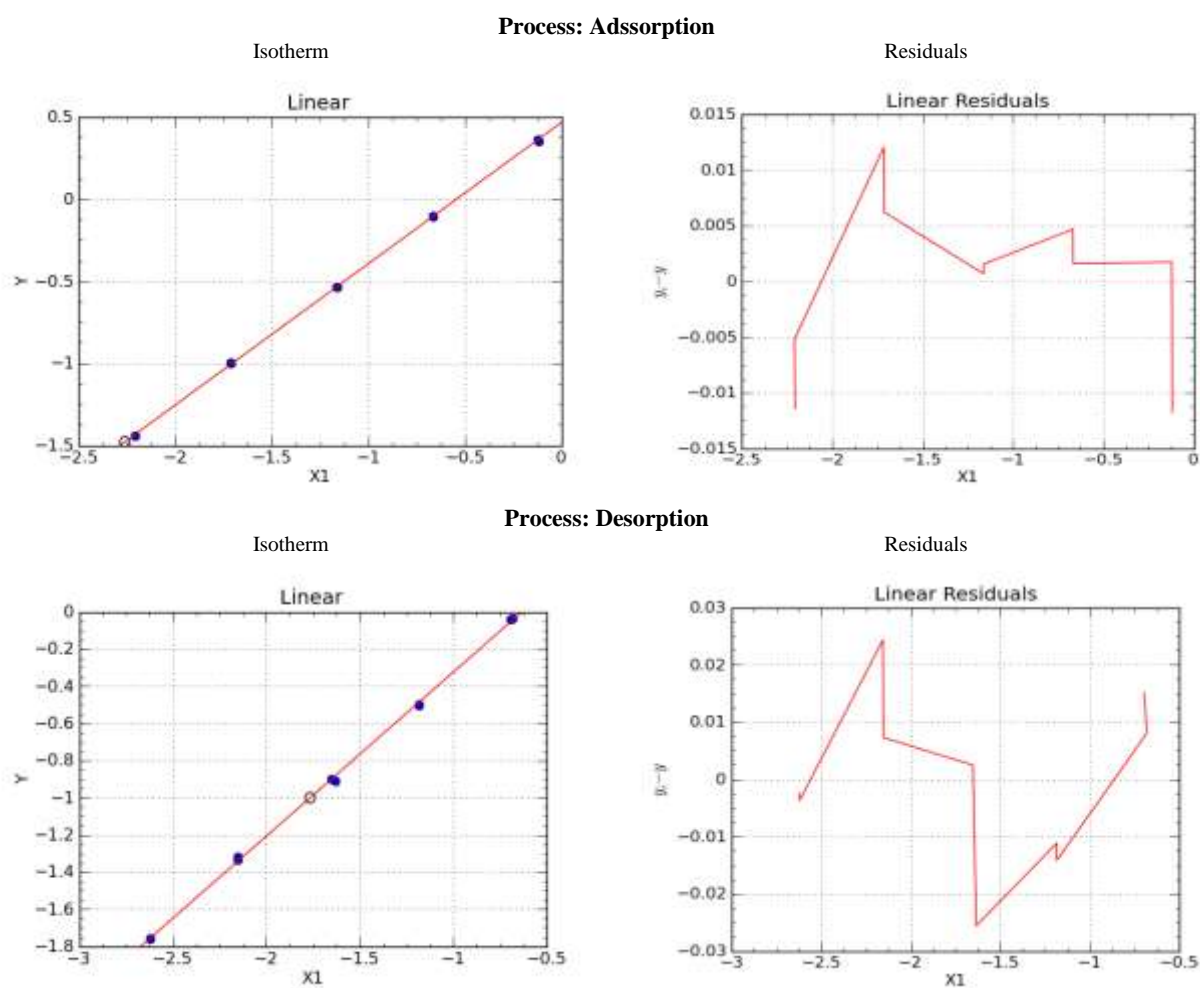


Figure B.8.1.2.1.2._CA-27: The Freundlich adsorption and desorption isotherms for FOE Methylsulfone in Springfield Silt loam soil determined by the RMS.

Table B.8.1.2.1.2._CA-72: The parameters of the Freundlich adsorption and desorption isotherms determined for FOE Methylsulfone in Springfield Silt loam soil by the RMS.

Test soil	Process	Parameters of isotherm				Statistical evaluation	
		Log K_F	K_F [mL/g]	$K_{F\text{OC}}$ [mL/g]	1/n	SD	Determination coefficient R^2
<i>Wurmwiese, Loam soil</i>	Adsorption	0.4652	2.9188	171.69	0.8601	0.0080	0.9999
	Desorption	0.5585	3.6183	212.84	0.8833	0.0156	0.9995

As a next step RMS compared the results obtained by the Applicant with presented above own results of the repeated analysis. That comparison is presented below in two separate tables – B.8.1.2.1.2._CA-73 for adsorption endpoints and B.8.1.2.1.2._CA-74 for desorption endpoints.

Table B.8.1.2.1.2._CA-73: The comparison of the key parameters of the Freundlich adsorption isotherms obtained by the Applicant and RMS for FOE Methylsulfone in five test soils.

Test soil	Parameters of Freundlich adsorption isotherm determined by the Applicant					Parameters of Freundlich adsorption isotherm determined by the RMS				
	$\text{Log } K_{f \text{ ads}}$	$K_{f \text{ ads}} [\text{mL/g}]$	$1/n$	$K_{fOC \text{ ads}} [\text{mL/g}]$	R^2	$\text{Log } K_{f \text{ des}}$	$K_{f \text{ des}} [\text{mL/g}]$	$1/n$	$K_{fOC \text{ des}} [\text{mL/g}]$	R^2
Wurmwiese Loam soil	-0.1817	0.6582	0.8915	37.4	0.9990	-0.1817	0.6581	0.8914	37.39	0.9985
Höfchen am Hohenseh Silt loam soil	0.1071	1.2797	0.8875	52.9	0.9997	0.1079	1.2820	0.8880	52.97	0.9996
Dollendorf II Clay loam soil	0.1956	1.5688	0.9001	33.2	0.9996	0.1956	1.5689	0.9001	33.24	0.9996
Guadalupe Sandy loam soil	-0.2796	0.5253	0.9097	75.0	0.9997	-0.2796	0.5253	0.9098	75.04	0.9997
Springfield Silt loam soil	0.4654	2.9201	0.8602	171.8	0.9999	0.4652	2.9188	0.8601	171.69	0.9999

Table B.8.1.2.1.2._CA-74: The comparison of the key parameters of the Freundlich adsorption isotherms obtained by the Applicant and RMS for FOE Methylsulfone in five test soils.

Test soil	Parameters of Freundlich 1 st desorption isotherm determined by the Applicant					Parameters of Freundlich 1 st desorption isotherm determined by the RMS				
	$\text{Log } K_{f \text{ des}}$	$K_{f \text{ des}} [\text{mL/g}]$	$1/n$	$K_{fOC \text{ ads}} [\text{mL/g}]$	R^2	$\text{Log } K_{f \text{ des}}$	$K_{f \text{ des}} [\text{mL/g}]$	$1/n$	$K_{fOC \text{ des}} [\text{mL/g}]$	R^2
Wurmwiese Loam soil	-0.1139	0.7693	0.8980	43.7	0.9992	-0.1140	0.7691	0.8982	43.70	0.9982
Höfchen am Hohenseh Silt loam soil	0.1663	1.4666	0.8931	60.6	0.9997	0.0105	1.0245	0.9526	42.33	0.9997
Dollendorf II Clay loam soil	0.2601	1.8200	0.9124	38.6	0.9993	0.2599	1.8193	0.9122	38.54	0.9991
Guadalupe Sandy loam soil	-0.2464	0.5671	0.9050	81.0	1.0000	-0.2467	0.5666	0.9048	80.94	0.9992
Springfield Silt loam soil	0.5556	3.5944	0.8833	211.4	0.9994	0.5585	3.6183	0.8833	212.84	0.9995

The comparative analysis of the results presented above showed that the differences between K_f and K_{fOC} calculated by the Applicant and RMS for the adsorption process were not significant. Also not very substantial were the differences between calculated $1/n$ values.

In case of the desorption parameters the significant difference was found in case of the constants obtained in Höfchen am Hohenseh test soil. The possible reason for that was not identified, as the raw data used by the RMS and the Applicant were the same.

Final conclusion:

The Freundlich adsorption parameters obtained by the Applicant can be considered fully reliable to be reported in the EU List of Endpoints and to be used in GW and SW model exposure assessment. They are presented below, in form recommended for reporting the EU-agreed endpoints.

Soil adsorption transformation products (Regulation (EU) N° 283/2013, Annex Part A, point 7.1.3.1.2 and Regulation (EU) N° 284/2013, Annex Part A, point 9.1.2.1)

FOE Methylsulfone							
Soil Type (USDA)	OC %	Soil pH ^{a)}	K _d (mL/g)	K _{doc} (mL/g)	K _F (mL/g)	K _{Foc} (mL/g)	1/n
Loam	1.8	5.5	----	----	0.6582	37.4	0.892
Silt loam	2.4	6.8	----	----	1.2797	52.9	0.888
Clay loam	4.6	7.4	----	----	1.5688	33.2	0.900
Sandy loam	0.7	6.8	----	----	0.5253	75.0	0.910
Silt loam	1.7	7.2	----	----	2.9201	171.8	0.860
Geometric mean (if not pH dependent)					1.1518	61.03	----
Arithmetic mean (if not pH dependent)					----	----	0.860
pH dependence, <i>Yes or No</i>			No				

^{a)} All values measured in water;

Study 3:

Report: Moendel M., Hein W., (2011): “[1-¹⁴C] BCS-AZ56567: Adsorption/Desorption in Five Different Soils.”; RLP AgroScience GmbH, Breitenweg 71, 67435 Neustadt a. d. Weinstrasse, Germany (performing laboratory) for Bayer CropScience Aktiengesellschaft, Development, Environmental Safety Metabolism/ADME and Environmental Fate, Alfred Nobel Str. 50, D-40789 Monheim, Germany; Study number (RLP AgroSciences GmbH) AS155; Bayer Report No. M-406740-01-1; 07 April 2011; study reference number: M-406740-01-1.

Guidelines: The study was performed to comply with the following Guidelines:

- OECD Guideline for Testing of Chemicals No 106 “Adsorption/Desorption”, Jan. 21, 2000;
- US. EPA Fate, Transport and Transformation Test Guidelines OPPTS 835. 1220 Sediment and Soil Adsorption/Desorption Isotherm;
- Canada Pest Management Regulatory Agency (PMRA), Environmental Chemistry and Fate, Guidelines for Registration of Pesticides in Canada, 1987.

GLP: Yes;

RMS comments: This is a newly submitted study, aimed on the examination of the soil sorption of Trifluoroacetic acid (TFA) – one of the major soil degradation products of Flufenacet. For the purpose of the current assessment it was evaluated for compliance with the following Guidelines:

- OECD Guideline for Testing of Chemicals No 106, Adsorption – Desorption Using a Batch Equilibrium Method, adopted 21st January 2000;
- US. EPA Fate, Transport and Transformation Test Guidelines OPPTS 835.1220, Sediment and Soil Adsorption/Desorption Isotherm, January 1998;
- US. EPA Fate, Transport and Transformation Test Guidelines OPPTS 835.1230, Adsorption/Desorption (Batch Equilibrium), October 2000;

It was stated that the study complied with the provisions of the evoked Guidelines. As a result, it was found acceptable and is summarised below.

Summary:

The aim of the study was to examine the adsorption and desorption in soil of Trifluoroacetic acid - TFA (for the purpose of this study bearing a codename BCS-AZ565697), a major soil degradation product of Flufenacet. The examination was performed using five test soils – three EU and two US soils. Their characteristic is provided below in the table B.8.1.2.1.2._CA-75.

Table B.8.1.2.1.2._CA-75: The characteristic of soils used in the study.

Parameter		Soil				
		<i>Wurmwiese</i>	<i>Höfchen am Hohenseh 4a</i>	<i>Dollendorf II</i>	<i>Guadalupe CA</i>	<i>Springfield NE</i>
Soil origin		Monheim am Rhein, Northrhine-Westfalia, Germany	Burscheid, Northrhine-Westfalia, Germany	Blankenheim, Northrhine-Westfalia, Germany	Guadalupe, CA, USA	Springfield, NE, USA
Soil type (USDA)		Loam	Silt loam	Clay loam	Sandy loam	Silt loam
Particle size distribution	Sand [%]	51	27	31	56.0	12.7
	Silt [%]	28	54	38	32.6	60.8
	Clay [%]	21	19	31	11.4	26.5
Soil pH	in CaCl ₂	5.3	6.6	7.3	6.7	6.6
	in water	5.5	6.8	7.4	6.8	7.2
Organic matter content (OM) [%]		3.03	4.17	8.14	1.1	2.9
Organic carbon content (OC) [%]		1.76	2.42	4.72	0.7	1.7
CEC [meq/100 g]		10.8	13.9	21.9	16.1	16.1

The test soils were sampled from the agriculturally used areas. In case of the EU soils, they were sampled from fields on which no pesticides were used for at least 5 years prior to the sampling. They were collected from the 0-20 cm layer using the shovel. The soil samples were air-dried and sieved through 2-mm sieve before being

delivered to the test facility. There they were stored first in ambient conditions and then at $T = 0-10^{\circ}\text{C}$ until being used.

One of the US soils was sampled from the field on which different pesticides used on cabbage, broccoli and lettuce were applied until December 2007. After that, until sampling in march 2009 (for approx. 15 consecutive months), no use of any plant protection products was recorded. The second US soil was sampled from the field on which no pesticides were used for at least three consecutive years before sampling. Soil samples were collected by shovel from the top 6- to 8-inch layer (corresponding to the soil depth of 0-15 cm or 0-20 cm). The soil samples were air-dried and sieved through 2-mm sieve before being delivered to the test facility. There they were stored first in ambient conditions and then at $T = 0-10^{\circ}\text{C}$ until being used.

The storage period was following:

- for the EU soils: 587 days after delivery to the test facility;
- for the US soils: 565 days after delivery to the test facility.

The test compound used in the experiment was the ^{14}C -TFA (Trifluoroacetic acid), shown below on figure B.8.1.2.1.2._CA-27.

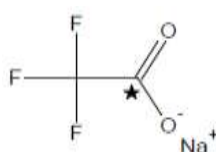


Figure B.8.1.2.1.2._CA-27: The structural formula of the radiolabelled TFA (BCS-AZ56567) used in the experiment; the asterisk (*) indicates radiolabelling position (copied from the study report).

The test compound had specific activity of 3.48 MBq/mg (94.04 $\mu\text{Ci/mg}$) and radiochemical purity, determined by HPLC, > 98%. It was delivered to the test facility as a colourless, vacuum-dried solid. It was stored in the test facility in cold until being used.

The delivered sample was used to prepare the **Standard Stock Solution I**, bearing the code-name **SSL I**. That was done by dissolving 5.66 mg of the radiolabelled test with 5 mL of bi-distilled water. The so prepared stock solution was analysed for its concentration of the test item by LSC. That was done using two 0.1-mL aliquots of the stock solution diluted 50 times before being analysed.

The so determined concentration of the test item in the standard solution was 0.566 mg/mL. The radiopurity of the solution, determined using radio-HPLC, was > 99%.

Additionally, as a reference compound for chromatography, the non-radiolabelled TFA was used in the experiment. It was delivered to the test facility as a colourless liquid, having a chemical purity of 99.9%. It was used to prepare the **Standard Stock Solution II** by dissolving 6.5 mg of it in 6.5 mL CH_3CN .

The whole experiment was carried out using 0.01M CaCl_2 _{aq} solution, prepared by dissolving 2.94 g $\text{CaCl}_2 \times 2 \text{H}_2\text{O}$ in 2 litres of distilled water. The so prepared solutions were used throughout the whole study. Their pH was in range 6.92 – 6.96. It was generally labelled **Stock Solution I_{Bio}** (**SL I_{Bio}**) and as such used to prepare the treatment solutions used in the experiment.

The whole study consisted of three steps, further called experiments:

- the **Preliminary Test I**, aimed on the determination of the appropriate soil:solution ratio for each test soil, stability of the test item in 0.01M CaCl_2 _{aq} solution and its potential adsorption to the test vessels; the experiment was performed using a single initial concentration of the test item – 1.00 mg/L (highest concentration of Trifluoroacetic acid – TFA, used in the study);
- the **Preliminary Test II**, in which was determined the appropriate equilibration time and parental mass balance in order to demonstrate the stability of the test compound during incubation for determining sorption isotherms; the experiment was performed using a single initial concentration of the test item – 1.00 mg/L (highest concentration of Trifluoroacetic acid – TFA, used in the study);
- the **Definitive Test**, aimed on the determination of the Freundlich adsorption and desorption isotherm and calculation of their parameters - K_F and $1/n$ values; at this stage five different nominal initial concentrations of the test compound – Trifluoroacetic acid (TFA), were used: 0.01 mg/L, 0.03 mg/L, 0.10 mg/L, 0.30 mg/L and 1.00 mg/L (**N. b.** RMS noticed that due to the low level of adsorption determined in both **Preliminary tests** only the experiment aimed on the determination of adsorption isotherm was carried out.

The test compound was administered in form of the application solutions prepared from the **Standard Stock Solution I (SSL I)** as aqueous solutions in 0.01M CaCl_2 aq.

In case of the **Preliminary Test I** the application solution was prepared by transferring 0.883 mL of the solution **SSL I** into the appropriate flask. The solution was brought to volume by addition of 50 mL **SL I_{Bio}** solution. The so prepared solution was then analysed by LSC for concentration of the test item and by radio-HPLC for its radiopurity.

In case of the **Preliminary Test II** the application solution was prepared by transferring 3.54 mL of the solution **SSL I** into the appropriate flask. The solution was then brought to volume by addition of 200 mL of **SL I_{Bio}** solution. The so prepared solution was then analysed by LSC for concentration of the test item and by radio-HPLC for its radiopurity.

The application solutions for the **Definitive Test** were prepared by a serial dilution of the solution **SSL I**. As a first step the **Solution A**, having a nominal concentration 10 mg/L was prepared from a solution **SSL I**. That was done by transferring 0.883 mL of the solution **SSL I** into the appropriate flask. The solution was then brought to volume with 50 mL of **SL I_{Bio}** solution. The so prepared solution was analysed by LSC for concentration of the test item and by radio-HPLC for its radiopurity. Next the four remaining application solutions, marked **B**, **C**, **D** and **E** were prepared by diluting the **Solution A** with the **SL I_{Bio}** solution. The procedure looked as follows:

- the **Solution B**, having a nominal concentration of 3.0 mg/L, was prepared by transferring 7.50 mL of the **Solution A** into 25-mL volumetric flask and filling it to the volume with **SL I_{Bio}** solution;
- the **Solution C**, having a nominal concentration of 1.0 mg/L, was prepared by transferring 2.50 mL of the **Solution A** into 25-mL volumetric flask and filling it to the volume with **SL I_{Bio}** solution;
- the **Solution D**, having a nominal concentration of 0.30 mg/L, was prepared by transferring 0.75 mL of the **Solution A** into 25-mL volumetric flask and filling it to the volume with **SL I_{Bio}** solution;
- the **Solution E**, having a nominal concentration of 0.10 mg/L, was prepared by transferring 0.25 mL of the **Solution A** into 25-mL volumetric flask and filling it to the volume with **SL I_{Bio}** solution.

The so prepared solutions were then analysed by LSC for concentration of the test item and by radio-HPLC for their radiopurity.

The measured concentrations of the so prepared application solutions were following:

- **Solution A** (nominal concentration 10.0 mg/L): 10.38 mg/L;
- **Solution B** (nominal concentration 3.00 mg/L): 3.10 mg/L;
- **Solution C** (nominal concentration 1.00 mg/L): 1.04 mg/L;
- **Solution D** (nominal concentration 0.30 mg/L): 0.31 mg/L;
- **Solution E** (nominal concentration 0.10 mg/L): 0.10 mg/L;

Their radiopurity was > 99%.

The study was performed using the following general conditions:

- all experiments were performed in the darkness and at constant temperature $T = 20 \pm 2^\circ\text{C}$;
- test vessels were borosilicate glass centrifuge tubes with Teflon lined screw caps;
- the **Preliminary Test I** and the **Definitive Test** were carried out in 42-mL test vessels using the total volume of solution (not corrected for the soil residual moisture content) of 20 mL;
- the **Preliminary Test II** was performed in 83-mL test vessels using the total volume of solution (not corrected for the soil residual moisture content) of 50 mL;
- equilibration was performed by shaking the test vessels for the pre-defined amount of time on the horizontal overhead shaker at ~20 rpm;
- at the end of equilibration samples containing soil were centrifuged for about 10 minutes at ~5000 rpm (~4200 g) to separate liquid and solid phases;
- in all experiments with the test soils the samples were preequilibrated for at least 16 hours before introduction of the test compound; the pre-equilibration procedure is characterised in details for each experiment, as they differed due to the different amounts of solution used.

The **Preliminary Test I** was aimed on the determination of the appropriate soil:solution ratio for each test soil and the stability of the test compound in 0.01M CaCl_2 aq solution.

The examination of the stability of Trifluoroacetic acid (TFA) in 0.01M CaCl_2 aq solution was carried out in soilless systems. First, two 42-mL test vessels were filled each with 18 mL of **SL I_{Bio}** solution. Next, to each of them 2 mL of the **Solution A** were added to obtain the final volume of 20 mL and the concentration of the test

item (nominal) 1.0 mg/L. So prepared test vessels were capped and equilibrated for up to 96 hours. At pre-defined time points – 24 hours, 48 hours, 72 hours and 96 hours of shaking, aliquots of each test solution were analysed by LSC and HPLC. In this experiment the measured initial concentration of the test item in solution was 0.994 mg/L.

The experiment aimed on the determination of the appropriate soil:solution ratio began by weighing 2-g, 10-g and 20-g portions of each test soil into 42-mL test vessels. All samples were prepared in duplicate. Next, to each test vessel 18 mL of **SL I_{Bio}** solution were added, test vessels capped and so prepared samples pre-equilibrated overnight (for ≥ 16 hours). After pre-equilibration samples were centrifuged for 5 minutes at 1000 rpm and 2 mL of the **Solution A** were added to obtain the final volume of 20 mL and the concentration of the test item (nominal) 1.0 mg/L. So prepared samples were then equilibrated, by shaking on horizontal shaker, for 24 hours. After that period samples were centrifuged and radioactivity content in supernatants determined by LSC. Additionally, for each test soil and each tested soil:solution ratio, pH of the supernatants was determined using one of the replicates.

The appropriate soil:solution ratio was determined on the basis of the results of LSC analysis of supernatants after equilibration and in comparison to the initial measured concentration of the test item in solution, which was 0.989 mg/L.

The **Preliminary Test II** was aimed on the determination of the appropriate equilibration time and the stability of the test compound in the test system.

The experiment was performed using 83-mL test vessels and the total volume of the solution (not corrected for residual soil moisture content) of 50 mL. It was carried out using the soil:solution ratio determined at preceding step.

The experiment was initiated by weighing the appropriate amount of the test soil into the test vessels. For each test soil five replicates were prepared. Next, to each test vessel 45 mL of **SL I_{Bio}** solution were added, test vessels capped and so prepared samples pre-equilibrated overnight (for ≥ 16 hours). After pre-equilibration 5 mL of the **Solution A** were added to obtain the final volume of 50 mL and the concentration of the test item (nominal) 1.0 mg/L. So prepared samples were then equilibrated, by shaking on horizontal shaker, for up to 120 hours. At pre-defined time points – after 2 hours, 4 hours, 6 hours 24 hours, 30 hours, 48 hours, 72 hours 96 hours and 120 hours of shaking, samples were taken for analysis. The sampling procedure, as characterised in the study report, is presented below on figure B.8.1.2.1.2._CA-28.

Sampling Procedure for the Determination of Adsorption Equilibrium Times and Matrix Stability Analysis per Soil:

Time	2 h	4 h	6 h	24 h	30 h	48 h	72 h	96 h	120 h
Rep 1		X		O					
Rep 2			X	X		O			
Rep 3	X		X			X	O		
Rep 4	X				X		X	O	
Rep 5		X			X			X	O

X = 1) Removed from shaker
2) Centrifuged, 10 min, 5000 rpm = 4200^g, 20°C
3) An aliquot of the supernatant was taken and afterwards analysed by LSC
4) Return to shaker

O = 1) Centrifuged (Conditions see above)
2) Complete removal of supernatant
3) LSC and HPLC supernatant
4) Extracted soil and analyzed by HPLC
5) Combustion of soil residue and LSC-measurement

At each sampling interval the mentioned test vessels were centrifuged and aliquots of 100 μ L were taken from the supernatants for LSC.

Figure B.8.1.2.1.2._CA-28: The sampling procedure used in the **Preliminary Test II** (copied from the study report).

The soil extraction was a 5-step cold-extraction process. At each step soil was extracted for 30 minutes with 40 mL of distilled H₂O. The extracts were combined and analysed by LSC for radioactivity content and by radio-HPLC to determine the nature of the extracted radioactivity.

The **Definitive Test** was carried out using the the procedure presented below on figure B.8.1.2.1.2._CA-29. The experiment was performed in 42-mL test vessels and using 20 mL of the test solution. The nominal initial concentrations of the test item – Trifluoroacetic acid (TFA), used in the experiment were following: 1.00 mg/L, 0.30 mg/L, 0.10 mg/L, 0.03 mg/L and 0.01 mg/L. The measured initial concentrations of the test item in solution were calculated using the actual volume of the solution, corrected by addition of the residual soil moisture content.

The resulting total volume of the solution in the test system were:

- **20.25 mL** for Wurmwiese Loam soil (the determined residual soil moisture content was 0.25 mL);
- **20.36 mL** for Höfchen am Hohenseh Silt loam soil (the determined residual soil moisture content was 0.36 mL);
- **20.56 mL** for Dollendorf II Clay loam soil (the determined residual soil moisture content was 0.56 mL);
- **20.27 mL** for Guadalupe Sandy loam soil (the determined residual soil moisture content was 0.27 mL);
- **20.80 mL** for Springfield Silt loam soil (the determined residual soil moisture content was 0.80 mL).

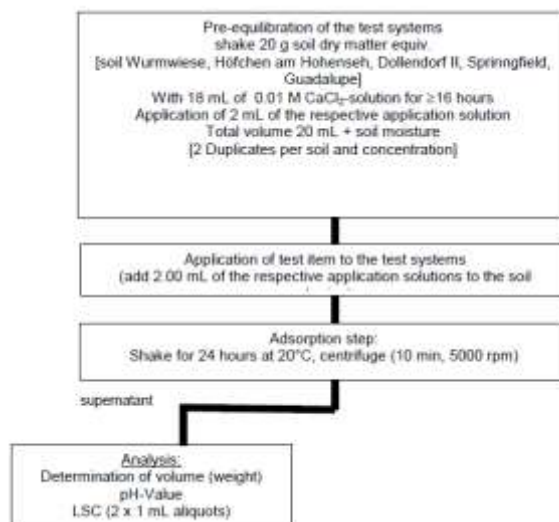


Figure B.8.1.2.1.2._CA-29: The conceptual scheme of the experimental procedure used in the **Definitive Test** (copied from the study report).

The examination of the 1st step of desorption was carried out for all five nominal concentrations of the test item, in order to determine the Freundlich desorption isotherms. The next steps – 2nd and 3rd, were examined using the samples with the highest initial (nominal) concentration of the test item – 1.00 mg/L.

In all samples left after the examination of the desorption the mass balance was established. That was done by mixing the remaining soil sample with cellulose added in amount 0.4 g/g soil. So prepared samples were air-dried, homogenised and their four 300-mg aliquots (for each test soil) were analysed after combustion by LSC.

All liquid samples were analysed for their radioactivity content using LSC method. The analysis was carried out using TRI-CARB 2800 TR or TRI-CARB 2300 TR liquid scintillation counters. Samples were analysed in Ultima Gold LS cocktail. The counting time was usually 10 minutes. The background was determined using blank samples and automatically subtracted from the analysed samples during the LSC analysis. Also automatically, by the instrument, was performed quench and counting efficiency correction for transformation of gross count (cpm) into dmp.

The solid samples used to determine the mass balance were oxidised using Sample Oxidiser OX 500. Generated ¹⁴CO₂ was absorbed in Oxisolve C-400 and analysed using TRI-CARB 2800 TR or TRI-CARB 2300 TR liquid scintillation counters.

The chromatographic analysis was performed in a gradient mode using Jasco HPLC system equipped with radio-HPLC detector and conductivity detector. The chromatographic separation was carried out on Sequant ZIC-HILIC (150 x 4.6 mm; 5 µm) chromatographic column. The elution was performed in a gradient mode characterised below in the table B.8.1.2.1.2._CA-76. The solvent system used in elution consisted of:

- **Solvent A:** Water + 0.2% H₃PO₄ (85%),
- **Solvent B:** CH₃CN.

The flow rate was set to 1.0 mL/min. The retention time of the test item – [¹⁴C] Trifluoroacetic acid (TFA) was R_t = approx 11 min.

Table B.8.1.2.1.2._CA-76: The gradient mode used in the HPLC analysis of samples collected during the study.

Time [minutes]	Solvent system	
	% Solvent A	% Solvent B
0	0	100
5	0	100
10	100	0
15	0	100
20	0	100

The calculations of the Freundlich sorption parameters were performed using the equations presented below on figure B.8.1.2.1.2._CA-30.

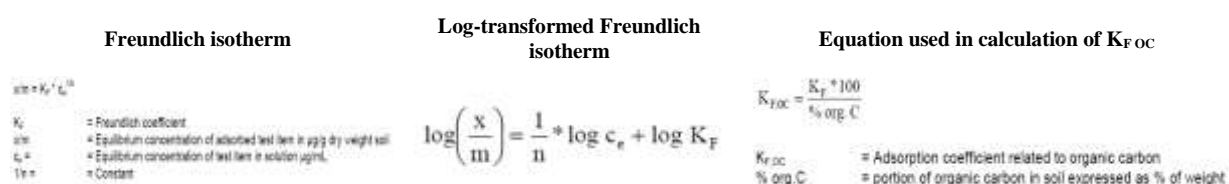


Figure B.8.1.2.1.2._CA-30: The equations used in the calculations of the Freundlich sorption parameters (copied from the study report).

The results of the study are presented and discussed below.

Results and their discussion:

The characteristic of the test soils used in the study has been presented at the beginning of this summary in the table B.8.1.2.1.2._CA-75. On their basis it may be stated that all test soils fully meet the acceptability criteria set by the OECD 106 Guideline.

The results of the monitoring of the temperature during the definitive test are presented below on figure B.8.1.2.1.2._CA-31. On their basis it was stated that the mean $T = 20.4^{\circ}\text{C}$ and its range $20.3 - 21.0^{\circ}\text{C}$. It was therefore within the pre-defined limits of $T = 20 \pm 2^{\circ}\text{C}$.

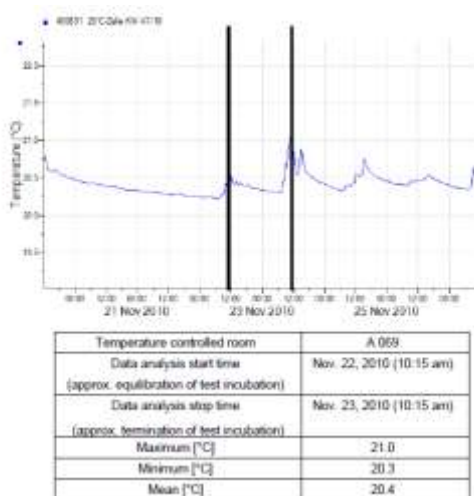


Figure B.8.1.2.1.2._CA-31: The graphical results of the monitoring of the temperature during the study (copied from the study report).

The numerical results of the examination of stability of the test item – Trifluoroacetic acid (TFA) in 0.01M CaCl_2 aq solution, are presented below in the table B.8.1.2.1.2._CA-77. On their basis it was stated that the compound was stable.

Table B.8.1.2.1.2._CA-77: The results of the examination of the stability of the test item in the test solution.

I) Experimental conditions				
Amount of soil:		Test system without soil		
Amount of test solution in test vessel:		20 mL		
Concentration of the test item:		0.994 mg/L (measured highest concentration used in experiment)		
Equilibration time:		0 – 96 h		
II) Results				
Equilibraion time [Hours]	Replicate	Obtained results		
		Total radioactivity in the test vessel in [Bq/20 mL]	Total radioactivity in the test vessel [%AR]	Amount of the test item [%]
0		69175.3	100.0	100.0
24	1	66356.4	95.9	95.9
	2	67603.9	97.7	97.7
48	1	64363.4	93.0	93.0
	2	64464.8	93.2	93.2
72	1	67089.2	97.0	97.0
	2	64608.1	93.4	93.4
96	1	67132.1	97.0	97.0
	2	67740.1	97.9	97.9

The results of the determination of the appropriate soil:solution ratio are presented below, in numerical form in the table B.8.1.2.1.2._CA-78 and in graphical form on figure B.8.1.2.1.2._CA-32. The symbols used on that graph to denominate test soils were following:

- I for Wurmwiese test soil;
- II for Höfchen am Hohenseh test soil;
- III for Dollendorf II test soil;
- IV for Guadalupe test soil;
- V for Springfield test soil.

Table B.8.1.2.1.2._CA-78: The numerical results of the determination of the appropriate soil:solution ratio.

Test soil	Soil solution ratio		Amount of Trifluoroacetic acid (TFA) remaining in solution [% AR]	Amount of Trifluoroacetic acid (TFA) sorbed onto soil [% AR]
	in g soil/mL solution	as ratio		
<i>Wurmwiese Loam soil</i>	2/20	1:10	100.5	-0.5
	10/20	1:2	101.8	-1.8
	20/20	1:1	106.0	-6.0
<i>Höfchen am Hohenseh Silt loam soil</i>	2/20	1:10	101.2	-1.2
	10/20	1:2	101.2	-1.2
	20/20	1:1	103.3	-3.3
<i>Dollendorf II Clay loam soil</i>	2/20	1:10	100.3	-0.3
	10/20	1:2	102.1	-2.1
	20/20	1:1	106.1	-6.1
<i>Guadalupe Sandy loam soil</i>	2/20	1:10	100.4	-0.4
	10/20	1:2	100.6	-0.6
	20/20	1:1	101.5	-1.5
<i>Springfield Silt loam soil</i>	2/20	1:10	100.6	-0.6
	10/20	1:2	101.9	-1.9
	20/20	1:1	105.0	-5.0



Figure B.8.1.2.1.2._CA-32: The graphical results of the determination of the appropriate soil:solution ratio – amount of Trifluoroacetic acid (TFA) adsorbed onto soil (copied from the study report).

On the basis of the obtained results the soil:solution ratio selected to be used in further tests was 1:1.

The results obtained during the **Preliminary Test II** are presented below in numerical and graphical form. In the tables B.8.1.2.1.2._CA-79 and B.8.1.2.1.2._CA-80 are provided the numerical results of the determination of the the appropriate equilibration time. These results are also given in graphical form on figure B.8.1.2.1.2._CA-33. On the basis of the obtained results the selected appropriate equilibration time was 24 hours. It was also stated that the recovery of radioactivity and the test item was > 90% during the whole incubation period, indicating that Trifluoroacetic acid was stable in the test system for up to 120 hours. The declared initial concentration of the test item was 0.994 mg/L

Table B.8.1.2.1.1._CA-79: The numerical results of the determination of the appropriate equilibration time.

Equilibration time [hours]	Results									
	Concentration of applied radioactivity in the solution of the test system with soil Wurmwiese, expressed as:		Concentration of applied radioactivity in the solution of the test system with soil Höfchen am Hohenseh, expressed as:		Concentration of applied radioactivity in the solution of the test system with soil Dollenroff II, expressed as:		Concentration of applied radioactivity in the solution of the test system with soil Guadalupe, expressed as:		Concentration of applied radioactivity in the solution of the test system with soil Springfield, expressed as:	
	Test item equivalents [mg/L]	Test item [mg/L]	Test item equivalents [mg/L]	Test item [mg/L]	Test item equivalents [mg/L]	Test item [mg/L]	Test item equivalents [mg/L]	Test item [mg/L]	Test item equivalents [mg/L]	Test item [mg/L]
2	1.00	----	0.98	----	1.03	----	0.98	----	1.00	----
4	0.99	----	1.00	----	1.04	----	0.95	----	0.98	----
6	0.99	----	1.00	----	1.05	----	0.98	----	0.50	----
24	0.99	0.99	0.99	0.99	1.03	1.03	0.97	0.97	0.98	0.98
30	0.97	----	1.00	----	0.99	----	0.95	----	0.95	----
48	1.00	1.00	1.00	1.00	1.02	1.02	0.96	0.96	n. a. ¹⁾	n. a. ¹⁾
72	0.99	0.99	1.02	1.02	1.04	1.04	0.91	0.91	n. a. ¹⁾	n. a. ¹⁾
96	1.00	1.00	1.01	1.01	1.03	1.03	0.97	0.97	1.00	1.00
120	1.01	1.01	1.03	1.03	1.02	1.02	0.94	0.94	0.97	0.97

Footnotes to the table:

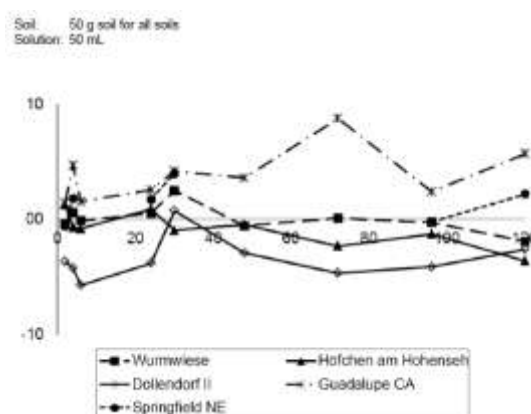
1) n. a. = not available - no reliable data due to the breakage of the test vessels;

Table B.8.1.2.1.1._CA-80: The numerical results of the determination of the appropriate equilibration time.

Equili- bration time [hours]	Results: radioactivity adsorbed onto soil									
	Wurmwiese, expressed as:		Höfchen am Hohenseh, expressed as:		Dollenroff II, expressed as:		Guadalupe, expressed as:		Springfield, expressed as:	
	%AR	% test item adsorbed	%AR	% test item adsorbed	%AR	% test item adsorbed	%AR	% test item adsorbed	%AR	% test item adsorbed
2	-0.5	----	1.3	----	-3.7	----	1.5	----	-0.6	----
4	0.6	----	-0.7	----	-4.2	----	4.7	----	1.8	----
6	-0.1	----	-0.8	----	-5.7	----	1.6	----	----	----
24	0.6	100	0.9	100	-3.8	100	2.6	100	1.8	100
30	2.5	----	-1.0	----	0.8	----	4.2	----	4.0	----
48	-0.6	100	-0.5	100	-2.9	100	3.6	100	n. a. ¹⁾	n. a. ¹⁾
72	0.1	100	-2.3	100	-4.7	100	8.8	100	n. a. ¹⁾	n. a. ¹⁾
96	-0.3	100	-1.3	100	-4.1	100	2.4	100	-0.2	100
120	-1.9	100	-3.6	100	-2.6	100	5.7	100	2.2	100

Footnotes to the table:

1) n. a. = not available - no reliable data due to the breakage of the test vessels;

**Figure B.8.1.2.1.2._CA-33:** The graphical results of the determination of the appropriate equilibration time (copied from the study report).

The results of the **Definitive Test** are presented below. The verification of the application rate of Trifluoroacetic acid (TFA) in the **Definitive Test** gave the following results:

- for the solution having a nominal concentration **1.0 mg TFA/L** the measured concentration was **1.04 mg TFA/L** and the applied amount of radioactivity was 72248.0 Bq/test vessel;
- for the solution having a nominal concentration **0.30 mg TFA/L** the measured concentration was **0.31 mg TFA/L** and the applied amount of radioactivity was 21602.5 Bq/test vessel;
- for the solution having a nominal concentration **0.10 mg TFA/L** the measured concentration was **0.10 mg TFA/L** and the applied amount of radioactivity was 7213.7 Bq/test vessel;
- for the solution having a nominal concentration **0.03 mg TFA/L** the measured concentration was **0.03 mg TFA/L** and the applied amount of radioactivity was 2161.5 Bq/test vessel;
- for the solution having a nominal concentration **0.01 mg TFA/L** the measured concentration was **0.01 mg TFA/L** and the applied amount of radioactivity was 711.1 Bq/test vessel.

The results of the determination of the recovery of applied radioactivity are presented below in the table B.8.1.2.1.2._CA-81.

Table B.8.1.2.1.2._CA-81: The results of the determination of the recovery of radioactivity in the **Definitive Test**.

Initial (measured) concentration of Trifluoroacetic acid (TFA)	Replicate	Total radioactivity recovery, expressed in [% AR], in experiment with the test soil:				
		<i>Wurmwiese Loam soil</i>	<i>Höfchen am Hohenseh Silt loam soil</i>	<i>Dollendorf II Clay loam soil</i>	<i>Guadalupe Sandy loam soil</i>	<i>Springfield Silt loam soil</i>
1.04 mg/L	1	97.7	97.2	98.7	98.4	97.7
	2	97.2	97.5	97.5	98.1	98.2
0.31 mg/L	1	89.9	98.2	98.1	98.7	97.8
	2	97.9	97.7	98.2	98.9	97.4
0.10 mg/L	1	97.4	96.6	97.4	98.0	97.4
	2	98.0	97.2	97.6	98.4	96.5
0.03 mg/L	1	96.7	96.6	98.6	97.9	96.6
	2	98.5	96.2	98.5	97.8	96.1
0.01 mg/L	1	98.0	97.4	100.4	100.5	98.7
	2	98.7	97.9	103.1	99.8	98.9

The results of the determination of the pH of supernatants after establishing the adsorption equilibrium in the definitive test are given below in the table B.8.1.2.1.2._CA-82.

Table B.8.1.2.1.2._CA-82: The results of the determination of the pH of solution at equilibrium in the adsorption part of the **Definitive Test**.

Initial concentration of Flufenacet [mg/L]		Replicate	pH of the solution measured in the test system containing the test soil:				
<i>nominal</i>	<i>measured</i>		<i>Wurmwiese Loam soil</i>	<i>Höfchen am Hohenseh Silt loam soil</i>	<i>Dollendorf II Clay loam soil</i>	<i>Guadalupe Sandy loam soil</i>	<i>Springfield Silt loam soil</i>
1.00	1.04 mg/L	1	5.81	6.95	7.24	6.80	6.45
		2	5.77	6.92	7.23	6.77	6.43
0.30	0.31 mg/L	1	5.78	6.96	7.24	6.75	6.45
		2	5.75	6.92	7.19	6.75	6.44
0.10	0.10 mg/L	1	5.83	6.86	7.21	6.75	6.47
		2	5.77	6.84	7.27	6.71	6.47
0.03	0.03 mg/L	1	5.81	6.86	7.17	6.72	6.46
		2	5.82	6.84	7.10	6.73	6.48
0.01	0.01 mg/L	1	5.77	6.86	7.19	6.70	6.44
		2	5.76	6.90	7.08	6.75	6.51

The results of the definitive phase – the concentrations of the test item – Trifluoroacetic acid (TFA), at equilibrium for adsorption phase are presented below in the table B.8.1.2.1.2._CA-83. The mean values for the two replicates are provided.

Table B.8.1.2.1.2._CA-83: The results of the examination of the adsorption of Trifluoroacetic acid (TFA) onto test soils to determine Freundlich adsorption isotherm.

Test soil	Initial concentration of the solution [µg/mL]	Results of the experiment:				
		Concentration at equilibrium				Amount adsorbed onto soil in [%]
		in solution		in soil		
		Ce [µg/mL]	Log Ce	x/m [µg/g]	Log (x/m)	
Wurmweise Loam soil	1.025	1.042	0.0180	----	----	-1.7 ± 1.0
	0.306	0.309	-0.5101	----	----	-0.8 ± 0.7
	0.102	0.102	-0.9921	----	----	0.5 ± 0.8
	0.031	0.030	-1.5173	----	----	0.9 ± 0.3
	0.010	0.010	-1.9913	----	----	-1.1 ± 0.2
Höfchen am Hohenseh Silt loam soil	1.020	1.055	0.0233	----	----	-3.4 ± 0.4
	0.305	0.318	-0.4974	----	----	-4.3 ± 1.0
	0.102	0.105	-0.9802	----	----	-2.8 ± 0.3
	0.031	0.031	-1.5035	----	----	-2.8 ± 0.5
	0.010	0.010	-1.9818	----	----	-3.9 ± 1.2
Dollendorf II Clay loam soil	1.009	1.093	0.0387	----	----	-8.2 ± 0.2
	0.302	0.328	-0.4846	----	----	-8.5 ± 0.3
	0.101	0.109	-0.9609	----	----	-8.5 ± 0.1
	0.030	0.033	-1.4828	----	----	-8.9 ± 1.1
	0.010	0.011	-1.9628	----	----	-9.6 ± 0.6
Guadalupe Sandy loam soil	1.024	1.038	0.0164	----	----	-1.4 ± 0.7
	0.306	0.312	-0.5054	----	----	-2.0 ± 0.6
	0.102	0.104	-0.9847	----	----	-1.3± 0.7
	0.031	0.031	-1.5078	----	----	-1.4 ± 0.1
	0.010	0.010	-1.9830	----	----	-3.2 ± 1.2
Springfield Silt loam soil	0.997	1.061	0.0257	----	----	-6.3 ± 0.4
	0.298	0.316	-0.4999	----	----	-6.0 ± 0.3
	0.100	0.104	-0.9814	----	----	-4.7 ± 0.3
	0.030	0.031	-1.5034	----	----	-5.1 ± 0.1
	0.010	0.010	-1.9843	----	----	-5.5 ± 0.3

On the basis of the results presented above it was stated that there was no adsorption of the test item – Trifluoroacetic acid, on any test soil. It was indicated that the negative level of adsorption was recorded in majority of cases, but without any attempt to explain that phenomenon. As a result it was stated that it was not possible to determine the adsorption isotherms.

In the study report it was stated that the experiment examining 1st desorption step was carried out, but its results were the same as for adsorption, therefore the results were not presented in the study report.

The final outcome of the study – the proposed parameters for adsorption and desorption (RMS's) proposal, are presented below in table B.8.1.2.1.2._CA-84. The proposed K_{fOC} and $1/n$ values are defaults presented with aim to be used as recommended in GW and SW modelling assessment.

Table B.8.1.2.1.2._CA-84: The key numerical results of the experiment – parameters of Freundlich adsorption and desorption isotherms for Trifluoroacetic acid (TFA); RMS's proposal.

Test soil	Parameters of Freundlich adsorption isotherm					Parameters of Freundlich desorption isotherm				
	Log $K_{f ads}$	$K_{f ads}$ [mL/g]	1/n	$K_{fOC ads}$ [mL/g]	R^2	Log $K_{f des}$	$K_{f des}$ [mL/g]	1/n	$K_{fOC des}$ [mL/g]	R^2
Wurmwiese Loam soil	n. d. ¹⁾	0.0	1.0	0.0001 ²⁾	n. d. ¹⁾	n. d. ¹⁾	0.0	1.0	0.0	n. d. ¹⁾
Höfchen am Hohenseh Silt loam soil	n. d. ¹⁾	0.0	1.0	0.0001 ²⁾	n. d. ¹⁾	n. d. ¹⁾	0.0	1.0	0.0	n. d. ¹⁾
Dollendorf II Clay loam soil	n. d. ¹⁾	0.0	1.0	0.0001 ²⁾	n. d. ¹⁾	n. d. ¹⁾	0.0	1.0	0.0	n. d. ¹⁾
Guadalupe Sandy loam soil	n. d. ¹⁾	0.0	1.0	0.0001 ²⁾	n. d. ¹⁾	n. d. ¹⁾	0.0	1.0	0.0	n. d. ¹⁾
Springfield Silt loam soil	n. d. ¹⁾	0.0	1.0	0.0001 ²⁾	n. d. ¹⁾	n. d. ¹⁾	0.0	1.0	0.0	n. d. ¹⁾

Footnotes to the table:

1) n. d. = not determined as it was not possible to determine the isotherm;

2) default value proposed to be used in GW and SW modelling;

Final conclusion:

The examination of the adsorption of Trifluoroacetic acid (TFA) onto soil at equilibrium showed that the test compound did not sorb onto soil to any extent (in most cases adsorption at equilibrium was shown to be negative). Therefore it was proposed to use for TFA the value of $K_f = 0$ mg/L and consider the adsorption process as fully linear, hence $1/n = 1.0$. The proposed outcome of the study – reliable endpoint values for the adsorption process, are presented below, in form recommended for reporting the EU-agreed endpoints.

Soil adsorption transformation products (Regulation (EU) N° 283/2013, Annex Part A, point 7.1.3.1.2 and Regulation (EU) N° 284/2013, Annex Part A, point 9.1.2.1)

Trifluoroacetic acid (TFA)							
Soil Type (USDA)	OC %	Soil pH ^{a)}	K_d (mL/g)	K_{doc} (mL/g)	K_F (mL/g)	K_{Foc} (mL/g)	1/n
Loam	1.76	5.5	----	----	0.0	0.0001	1.0
Silt loam	2.42	6.8	----	----	0.0	0.0001	1.0
Clay loam	4.72	7.4	----	----	0.0	0.0001	1.0
Sandy loam	0.7	6.8	----	----	0.0	0.0001	1.0
Silt loam	1.7	7.2	----	----	0.0	0.0001	1.0
Geometric mean (if not pH dependent)					0.0	0.0001	----
Arithmetic mean (if not pH dependent)					----	----	1.0
pH dependence, <i>Yes or No</i>			No				

^{a)} All values measured in water;

Study 4:

Report: Traub M., (2013): “Determination of the Adsorption/Desorption behaviour of FOE 5043-trifluoroethanesulfonic acid in five Soils.”; Eurofins Agrosience Services EcoChem GmbH, Eutinger Strasse 24, 75223 Niefern-Öschelbronn, Germany (performing laboratory) for Bayer CropScience AG, 40789 Monheim, Germany; Study number (Eurofins) S11-03923; Report No. MEFOP017; 18. 02. 2013; study reference number (Bayer): M-449893-01-1.

Guidelines: The study was performed to comply with the following Guidelines:

- OECD Guideline for Testing of Chemicals No 106 “Adsorption/Desorption”, Jan. 21, 2000;
- US. EPA Fate, Transport and Transformation Test Guidelines OPPTS 835.1230, Adsorption/Desorption (Batch Equilibrium), October 2000.

GLP: Yes;

RMS comments: This is a newly submitted study, aimed on the examination of the soil sorption of Trifluoroacetic acid (TFA) – one of the major soil degradation products of Flufenacet. For the purpose of the current assessment it was evaluated for compliance with the following Guidelines:

- OECD Guideline for Testing of Chemicals No 106, Adsorption – Desorption Using a Batch Equilibrium Method, adopted 21st January 2000;
- US. EPA Fate, Transport and Transformation Test Guidelines OPPTS 835.1220, Sediment and Soil Adsorption/Desorption Isotherm, January 1998;
- US. EPA Fate, Transport and Transformation Test Guidelines OPPTS 835.1230, Adsorption/Desorption (Batch Equilibrium), October 2000;

It was stated that the study complied with the provisions of the evoked Guidelines. As a result, it was found acceptable and is summarised below.

Summary:

The aim of the study was to examine the adsorption and desorption in soil of FOE 5043-Trifluoroethanesulfonic acid - TFESA (for the purpose of this study bearing a codename BCS-CU62474), a major soil degradation product of Flufenacet. The examination was performed using five EU test soils. Their characteristic is provided below in the table B.8.1.2.1.2._CA-85.

Table B.8.1.2.1.2._CA-85: The characteristic of soils used in the study.

Parameter		Soil				
		<i>Laacher Hof AXXa (AX)</i>	<i>Höfchen am Hohenseh 4a (HaH)</i>	<i>Hansheider Hof (HH)</i>	<i>Dollendorf II (DD)</i>	<i>Wurmwiese (WW)</i>
Soil origin		Monheim, North Rhine- Westphalia, Germany	Burscheid, North Rhein- Westphalia, Germany	Burscheid, North Rhein- Westphalia, Germany	Blankenheim, North Rhein- Westphalia, Germany	Monheim, North Rhine- Westphalia, Germany
Soil type (USDA)		Loamy sand	Silt loam	Silt loam	Loam	Sandy loam
Particle size distribution	Sand [%]	79	19	27	35	55
	Silt [%]	16	66	56	38	30
	Clay [%]	5	15	17	27	15
Soil pH	in 0.01M CaCl ₂ (1:2)	6.4	6.5	5.0	7.4	5.2
	in water (1:1)	6.6	6.7	5.3	7.5	5.4
	in 1M KCl (1:1)	6.1	6.1	4.7	7.1	4.8
Water holding capacity	maximum, [g H ₂ O/100 g soil]	43.4	54.3	63.7	84.6	57.4
	at 0.1 bar [%]	15.2	27.9	29.1	43.1	21.2
	at 0.33 bar [%]	10.6	20.6	22.9	33.5	17.0
Organic matter content (OM) [%]		3.1	2.9	4.8	8.6	3.3
Organic carbon content (OC) [%]		1.8	1.7	2.8	5.0	1.9
CEC [meq/100 g]		9.6	11.5	10.1	21.5	11.0
Bulk density [g/cm ³]		1.27	1.10	1.04	1.00	1.13

The test soils were sampled from the agriculturally used areas, from fields covered with grass, on which no pesticides were used for at least 5 years prior to the sampling. They were collected from the 0-20 cm layer using the shovel. The soil samples were air-dried, sieved through 2-mm sieve and stored at $T = 20^{\circ}\text{C}$ until being used.

The test compound used in the experiment was the non-radiolabelled FOE 5043-Trifluoroethanesulfonic acid – TFESA, in form of its sodium salt, shown below on figure B.8.1.2.1.2._CA-34.



Figure B.8.1.2.1.2._CA-34: The structural formula of the test compound – FOE Trifluoroethanesulfonic acid (FOE TFESA; BCS-CU62474), used in the experiment (copied from the study report).

The test compound, having a chemical purity of 99.4%, was delivered to the test facility as a white solid. It was stored in the test facility at $T = 10 - 30^{\circ}\text{C}$ until being used.

The delivered sample was used to prepare the **Stock Solution**, bearing the code-name **S1000**. That was done by dissolving the appropriate amount of the TFESA in acetonitrile to obtain a solution having a concentration of 1000 mg/L. That solution was subsequently used to prepare set of application solutions, having concentration of the test item in range 0.1 mg/L – 10 mg/L, in 0.01 M CaCl_2 aq.

The whole experiment was carried out using 0.01M CaCl_2 aq solution, prepared by dissolving 2.94 g $\text{CaCl}_2 \times 2 \text{H}_2\text{O}$ in 2 litres of distilled water. The so prepared solutions were used throughout the whole study.

The whole study consisted of two sets of experiments:

b) the **Preliminary Tests** aimed on:

- determination of the stability of the test item in matrix solution;
- examination of the potential of adsorption of the test item onto the test vessels;
- determination of the optimal soil:solution ratio for each test soil;
- determination of the appropriate equilibration time for adsorption;
- determination of the appropriate equilibration time for desorption;
- determination of the parental mass balance;

c) the **Definitive Test**, aimed on the determination of the Freundlich adsorption and desorption isotherm and calculation of their parameters - K_F and $1/n$ values; at this stage five different nominal initial concentrations of the test compound – FOE 5043-Trifluoroethanesulfonic acid (TFESA), were used: 0.01 mg/L, 0.03 mg/L, 0.10 mg/L, 0.30 mg/L and 1.00 mg/L;

The test compound was administered in form of the application solutions prepared from the **Stock Solution S1000** as aqueous solutions in 0.01M CaCl_2 aq. This was done using the procedure of serial dilution aimed on obtaining the solutions having the concentrations presented above in the paragraph characterising the stages of the experiment (characterisation of the definitive study). The whole procedure is characterised below in the table B.8.1.2.1.2._CA-86. Within that procedure an additional application solution, having the concentration 0.01 mg/L was prepared to examine the recoveries at the LOQ level. The application solutions were prepared freshly before application of the test item.

Table B.8.1.2.1.2._CA-86: The characterisation of the prepared application solutions.

Application solution ID	Nominal concentration of the test item [mg/L]	Final volume of the solution [mL]	Main solvent	Application solution prepared from solution:			Application solution used in/for:
				ID of the solution	Nominal concentration of the test item [mg/L]	Volume used [mL]	
S10	10	250	0.01M CaCl ₂ aq	S1000	1000	2.5	Preliminary and Definitive Tests
S3	3	250	0.01M CaCl ₂ aq	S1000	1000	0.75	Definitive Tests
S1	1	250	0.01M CaCl ₂ aq	S1000	1000	0.25	Definitive Tests
S0.3	0.3	250	0.01M CaCl ₂ aq	S3	3	25	Definitive Tests
S0.1	0.1	250	0.01M CaCl ₂ aq	S10	10	2.5	Definitive Tests
S0.01	0.01	----	0.01M CaCl ₂ aq	----	----	----	Examination of recoveries at LOQ

The **Stock Solution S1000** was also used to prepare a series of **Calibration Standard Solutions**, used in analysis of the samples. These were prepared by diluting the appropriate amounts of the **S1000** solution with 0.01M CaCl₂ aq. These, freshly prepared solutions were used to construct the calibration curve covering the concentrations range (nominal) 0.02 ng/mL – 100 ng/mL. Eight **Calibration Standard Solutions** were prepared, having the following concentrations of the test item: 0.02 ng/mL, 0.1 ng/mL, 0.5 ng/mL, 1.0 ng/mL, 5 ng/mL, 10 ng/mL, 50 ng/mL and 100 ng/mL.

Finally, the 0.01M CaCl₂ aq solution was used to prepare **Soil Blank Matrix** solutions for each test soil. For that purpose 1 kg of the given test soil was agitated overnight – for at least 12 hours, on a flat bed shaker with 1 L of 0.01M CaCl₂ aq solution (soil:solution ratio was 1:1). After that time soil suspension was centrifuged at 1295g and the supernatant collected to be used as the soil matrix for the given soil. The solutions were stored at $T = 20 \pm 2^{\circ}\text{C}$.

The study was performed using the following general conditions:

- all experiments were performed in the darkness and at constant temperature $T = 20 \pm 2^{\circ}\text{C}$;
- test vessels were glass vessels with PTFE screw caps, having a volume of 100 mL;
- the final volume of liquid used throughout the study was constant – 50 mL;
- equilibration was performed by shaking the test vessels for the pre-defined amount of time on the horizontal overhead shaker at ~130 rpm;
- at the end of equilibration samples containing soil were centrifuged for about 4 minutes at 1295 g to separate liquid and solid phases;
- in all experiments with the test soils the samples were preequilibrated for at least 12 hours before introduction of the test compound using the appropriate soil sample and the constant volume of blank CaCl₂ aq solution – 45 mL;
- the volume of application solutions introduced to each sample at the beginning of each test was also constant – 5 mL;
- all tests were carried out in duplicate for each kind of samples;
- all samples were analysed using HPLC-MS/MS method characterised further down the summary.

All **Preliminary Tests** were carried out using the highest nominal concentration of the test item in solution – 1 mg/L, applied as application solution **S10**.

The examination of the stability of the test item – FOE 5043-Trifluoroethanesulfonic acid (TFESA), in solution and its affinity to the test vessels was carried out using soil blank matrix solutions of each test soil. For that purpose to the vessels containing 45 mL of the given soil blank matrix solution 5 mL of the solution **S10** were introduced and so prepared samples equilibrated by agitating for 96 hours. After that period the supernatants were analysed for the content of the test item using HPLC-MS/MS method.

The determination of the appropriate soil:solution ratio was carried out using all five test soils. The examined soil:solution ratios were:

- 1:1 – the test vessels contained 50 g of the given test soil and 50 mL of the solution (final volume);
- 1:2 – the test vessels contained 25 g of the given test soil and 50 mL of the solution (final volume);
- 1:5 – the test vessels contained 10 g of the given test soil and 50 mL of the solution (final volume).

The experiment was performed in the following way: after pre-equilibration of the test vessels containing the appropriate amount of the test soil and 45 mL of blank 0.01M CaCl_2 _{aq} solutions, to each test vessel 5mL of **S10** solution were added to obtain the final volume of 50 mL. So prepared samples were equilibrated for 24 hours. After that period liquid phase was separated from solid by centrifugation, supernatants collected and analysed by HPLC-MS/MS.

The determination of the appropriate equilibration time for the adsorption process was carried out for all test soils using the appropriate soil:solution ratio determined in the test characterised above. After pre-equilibration the solution in each test vessels was brought to the final volume of 50 mL by addition of 5 mL of the application solution **S10**. So prepared test vessels were equilibrated for up to 96 hours. The concentration of the test item in solution was measured at pre-defined time points: 0, 6 24, 48, 72 and 96 hours after initiation of the experiment, as described above.

The determination of the appropriate equilibration time for desorption process was not performed as the results of the previous experiments demonstrated that virtually no adsorption of the test item onto soil occurred.

The **Definitive Test** aimed on the determination of the Freundlich adsorption isotherm and its parameters was carried out in the same manner as characterised above for preliminary test. The soil:solution ratio used in this experiment was 1:1 and the equilibration time was 96 hours. To the pre-equilibrated samples containing the appropriate amount of the test soil and 45 mL of blank 0.01M CaCl_2 _{aq} solution, 5 mL of the appropriate application solution – **S10**, **S3**, **S1**, **S0.3**, or **S0.1**, were added to obtain the final volume of the solution of 50 mL and the nominal concentration of the test item 1 mg/L, 0.3 mg/L, 0.1 mg/L 0.03 mg/L or 0.01 mg/L respectively. After application of the test item test vessels were sealed, placed on the horizontal shaker and equilibrated by agitation for the appropriate amount of time.

Because it was stated that virtually no adsorption onto any test soil was observed in this experiment the desorption at equilibrium was not examined.

All samples containing soil were after the end of equilibration period processed in the manner presented below on figure B.8.1.2.1.2._CA-35.

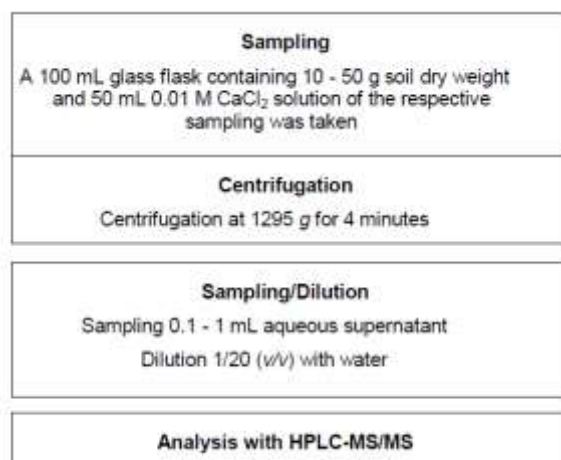


Figure B.8.1.2.1.2._CA-35: The scheme of the sample processing used in the study (copied from the study report).

The chromatographic analysis was performed in a gradient mode using Agilent HPLC system with autosampler coupled with Sciex API5000 MS/MS detector. The chromatographic separation was carried out on Phenomenex Synergi 4 μ Hydro-RP 80A (150 x 3 mm; 4 μ m) chromatographic column preceded by 4-mm guard column. The chromatographic column was kept in chromatographic oven set to constant temperature $T = 40^\circ\text{C}$. The elution was performed in a gradient mode presented below in the table B.8.1.2.1.2._CA-87. The solvent system used in elution consisted of:

- **Solvent A:** Water + 0.1% CH_3COOH ,
- **Solvent B:** CH_3CN + 0.1% CH_3COOH .

The flow rate was set to 0.5 mL/min. The retention time of the test item – FOE 5043-Trifluoroethanesulfonic acid (TFESA) was R_t = approx 2.5 min.

Table B.8.1.2.1.2._CA-87: The gradient mode used in the HPLC analysis of samples collected during the study.

Time [minutes]	Solvent system	
	% Solvent A	% Solvent B
0.00	90	10
4.00	35	65
4.01	10	90
5.00	10	90
5.01	90	10
6.00	90	10

The MS/MS detector used in the study was Sciex API5000 device, working in ESI ionisation mode with negative polarity of the source and at $T = 400^{\circ}\text{C}$.

Identification and quantitation of the test compound – FOE 5043-Trifluoroethanesulfonic acid (TFESA) was performed using the following signals:

- $m/z = 162.9$ – signal of parent compound;
- $m/z = 142.8$ – quantifier;
- $m/z = 122.8$ – qualifier 1;
- $m/z = 79.8$ – qualifier 2.

The example mass spectrum of the test item – FOE 5043-Trifluoroethanesulfonic acid (TFESA), is shown below on figure B.8.1.2.1.2._CA-36

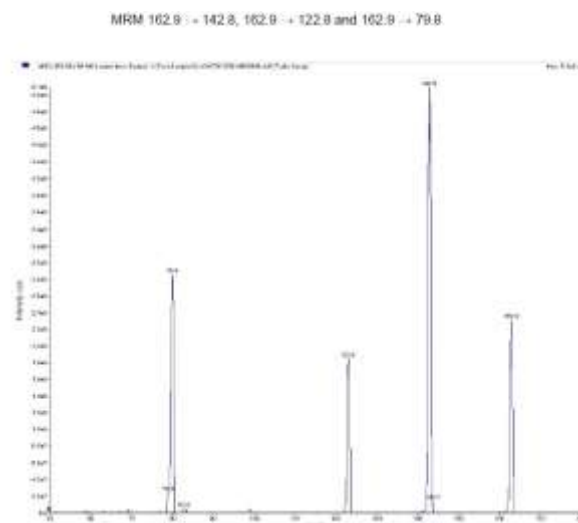


Figure B.8.1.2.1.2._CA-36: The example mass spectrum of FOE 5043-Trifluoroethanesulfonic acid (copied from the study report).

The quantitative analysis was carried out by means of calibration curve.

The whole analytical method was validated by determining the following parameters:

- LOD (Limit Of Detection) and LOQ (Limit Of Quantitation) of the method and its linearity;
- accuracy and repeatability of the analytical method;
- effect of the soil matrix on the linearity of the calibration curve;
- recovery levels of the test item.

The linearity of the whole method was determined on the basis of the calibration curve. The effect of the soil matrix on the calibration curve was examined by comparison of the mass spectra of pure 0.01M $\text{CaCl}_{2\text{aq}}$ solution and **Soil Blank Matrix** solutions, both diluted 10 times with water.

The LOD and LOQ of the method were determined when the calibration curve was constructed. The principle used here was that the LOD was the lowest measurable concentration for which signal:noise ratio was ≥ 3 . The linearity range of the calibration curve and of the method was determined analysing the constructed curve.

To determine the recovery level of the test substance – FOE 5043-Trifluoroethanesulfonic acid (TFESA), as well as the accuracy and repeatability of the analytical method, **Soil Blank Matrix** solutions for each test soil were fortified at two levels: LOQ and 1000-fold LOQ and then analysed by HPLC-MS/MS.

The results of the validation of analytical method are presented in section “Results and their discussion”.

The calculations of the Freundlich sorption parameters were performed using the equations presented below on figure B.8.1.2.1.2._CA-37.

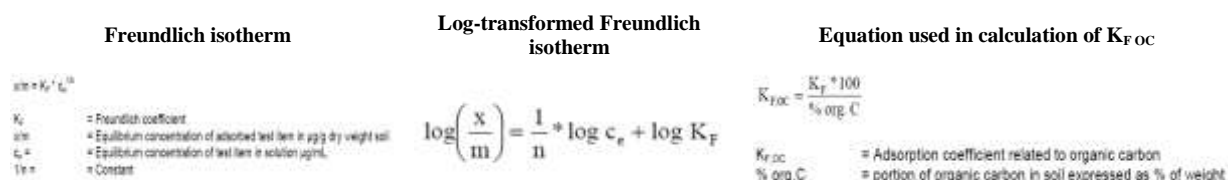


Figure B.8.1.2.1.2._CA-37: The equations used in the calculations of the Freundlich sorption parameters (copied from the study report).

The results of the study are presented and discussed below.

Results and their discussion:

The characteristic of the test soils used in the study has been presented at the beginning of this summary in table B.8.1.2.1.2._CA-85. On their basis it may be stated that all test soils fully meet the acceptability criteria set by the OECD 106 Guideline.

The results of the monitoring of the temperature during the preliminary and definitive tests are presented below on figure B.8.1.2.1.2._CA-38. On their basis it was stated that:

- during the preliminary tests the mean $T = 20.3^{\circ}\text{C}$ and its range $19.1 - 20.9^{\circ}\text{C}$;
- during the definitive tests the mean $T = 20.2^{\circ}\text{C}$ and its range $19.3 - 20.9^{\circ}\text{C}$.

It was therefore during the whole experiment within the pre-defined limits of $T = 20 \pm 2^{\circ}\text{C}$.

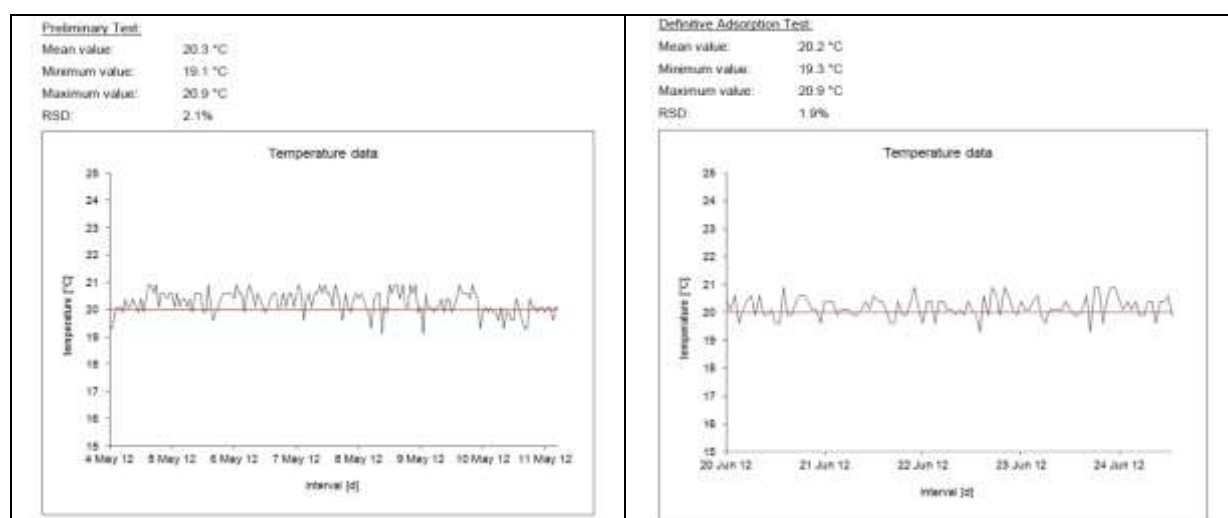


Figure B.8.1.2.1.2._CA-37: The graphical results of the monitoring of the temperature during the study (copied from the study report).

The results of the determination of linearity of analytical method and its LOD and LOQ are presented below on figure B.8.1.2.1.2._CA-38. On their basis it was stated that the method was linear in concentration range 0.02 ng/mL – 100.0 ng/mL. The determined LOQ = 0.1 ng/mL and the LOD was set to $\frac{1}{5}$ LOQ – LOQ = 0.02 ng/mL. That concentration was declared to be two orders of magnitude lower than the lowest nominal concentration of the test item used in the definitive test – 0.01 mg/L (equal to 10 ng/mL). Also at LOD level the signal to noise ratio was ≥ 3 .

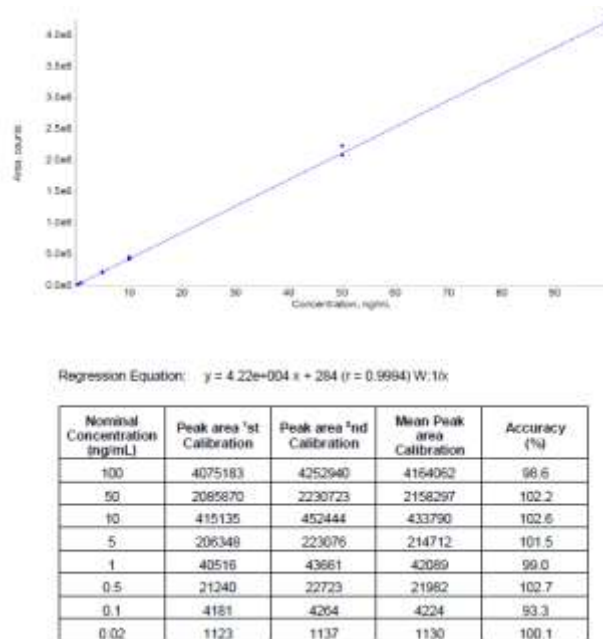


Figure B.8.1.2.1.2._CA-38: The results of the determination of linearity of analytical method (copied from the study report).

The analysis of the matrix effect on the calibration curve showed that:

- for Laacher Hof AXXa soil the matrix effect was 4%;
- for Dollendorf II soil the matrix effect was 8%;
- for Höfchen am Hohenseh 4a soil the matrix effect was 1%;
- for Hansheider Hof soil the matrix effect was 10%;
- for Wurmweise soil the matrix effect was 9%.

On that basis it was stated that there was no need to take the matrix effect into account constructing calibration curves and all calibration curves were constructed using the solutions of the test compound in pure 0.01M CaCl_2 aq.

The results of the determination of the recovery, accuracy and precision of the analytical method were following:

- for Laacher Hof AXXa soil the mean recovery at LOQ level (0.001 mg/L) was 100% (range 85 – 110%; $n = 5$) with RSD = 9%, at 1000 LOQ (1.00 mg/L) it was 108% (range 106 – 110%, $n = 5$) with RSD = 1%; the overall mean recovery was 104% with RSD = 7%;
- for Dollendorf II soil the mean recovery at LOQ level (0.001 mg/L) was 106% (range 96 – 114%; $n = 5$) with RSD = 7%, at 1000 LOQ (1.00 mg/L) it was 110% (range 108 – 113%, $n = 5$) with RSD = 2%; the overall mean recovery was 108% with RSD = 5%;
- for Höfchen am Hohenseh 4a soil the mean recovery at LOQ level (0.001 mg/L) was 95% (range 87 – 100%; $n = 5$) with RSD = 6%, at 1000 LOQ (1.00 mg/L) it was 103% (range 100 – 106%, $n = 5$) with RSD = 2%; the overall mean recovery was 99% with RSD = 6%;
- for Hansheider Hof soil the mean recovery at LOQ level (0.001 mg/L) was 109% (range 108 – 111%; $n = 5$) with RSD = 1%, at 1000 LOQ (1.00 mg/L) it was 110% (range 109 – 111%, $n = 5$) with RSD = 1%; the overall mean recovery was 110% with RSD = 1%;

- for Wurmwiese soil the mean recovery at LOQ level (0.001 mg/L) was 109% (range 103 – 116%; n = 5) with RSD = 5%, at 1000 LOQ (1.00 mg/L) it was 109% (range 107 – 112%, n = 5) with RSD = 2%; the overall mean recovery was 109% with RSD = 3%.

On the basis of these results it was stated that because the mean recoveries were in range 70-110% and RSD below 20%, therefore in line with the requirements of SANCO/3029/00, the accuracy and precision of the analytical method were considered acceptable.

Additionally the values of the blank samples were <20% LOQ in all five soils.

As a result the developed analytical method was considered suitable and specific for the test item – FOE 5043-Trifluoroethanesulfonic acid (TFESA).

The results of the determination of the initial concentration of the test item during the Preliminary Test are presented below in the table B.8.1.2.1.2._CA-88. These values were subsequently referred to as 100% AA (Applied Amount) throughout the Preliminary Test.

Table B.8.1.2.1.2._CA-88: The measured initial concentrations of the test item in the Preliminary Test.

Nominal concentration of TFESA [mg/L]	Replicate	Measured concentration of the test item – TFESA, [mg/L] in samples containing the test soil:				
		<i>Laacher Hof AXXa (AX)</i>	<i>Dollendorf II (DD)</i>	<i>Höfchen am Hohenseh 4a (HaH)</i>	<i>Hansheider Hof (HH)</i>	<i>Wurmwiese (WW)</i>
1.0	1	0.992	0.992	1.082	0.958	1.022
	2	0.960	0.988	1.066	0.930	0.992
	<i>Mean value</i>	<i>0.976</i>	<i>0.990</i>	<i>1.074</i>	<i>0.944</i>	<i>0.972</i>

The examination of the stability of the test item – FOE 5043-Trifluoroethanesulfonic acid (TFESA) in soil blank matrices showed lack of degradation during 96-hours lasting incubation. Therefore the test item was considered to be stable in the test systems for at least 96 hours.

The results of the determination of the adsorption of the test item to the test vessels, obtained for each type of the blank soil matrix, are presented below in the table B.8.1.2.1.2._CA-89. On their basis it was stated that the test compound did not display significant potential of the adsorption/adhesion onto the test vessels.

Table B.8.1.2.1.2._CA-89: The results of the determination of the adsorption/adhesion potential of the test item onto the test vessels.

Nominal concentration of TFESA [mg/L]	Replicate	% Adsorption of the test item onto the test vessels in samples containing blank control matrix of the test soil:				
		<i>Laacher Hof AXXa (AX)</i>	<i>Dollendorf II (DD)</i>	<i>Höfchen am Hohenseh 4a (HaH)</i>	<i>Hansheider Hof (HH)</i>	<i>Wurmwiese (WW)</i>
1.0	1	-1.4	2.4	2.6	3.8	4.1
	2	-5.9	0.2	8.0	-4.2	3.3
	<i>Mean value</i>	<i>-3.7</i>	<i>1.3</i>	<i>5.3</i>	<i>-0.2</i>	<i>3.7</i>

The results of the determination of the appropriate soil:solution ratio are presented below in the table B.8.1.2.1.2._CA-90. The incubation time used in that experiment was 24 hours.

Table B.8.1.2.1.2._CA-90: The numerical results of the determination of the appropriate soil:solution ratio.

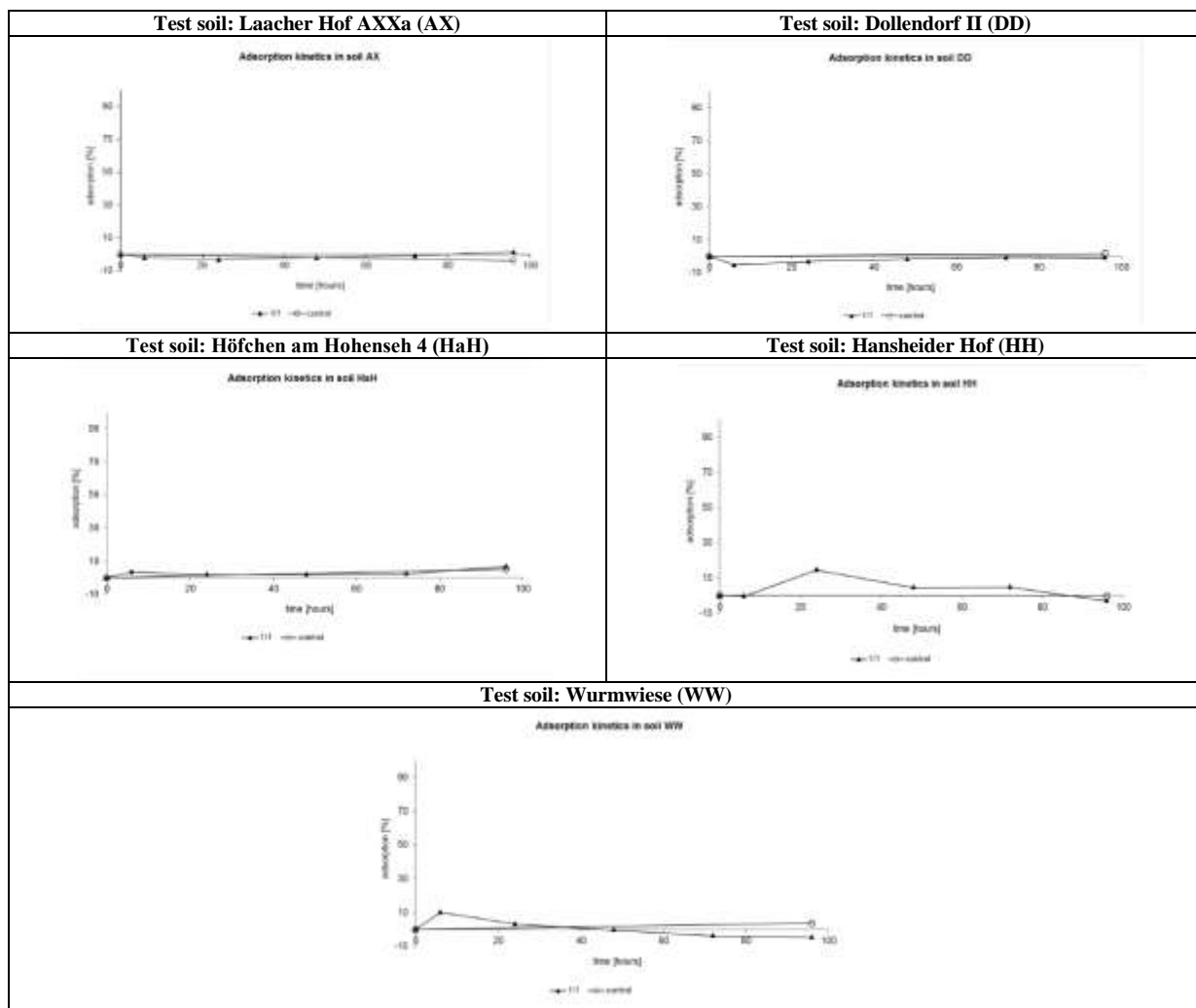
Test soil	Soil solution ratio		Replicate	Adsorption of FOE Trifluoroethanesulfonic acid (TFESA) onto soil [% AA]
	in g soil/mL solution	as ratio		
<i>Laacher Hof AXxXa (AX)</i>	50/50	1:1	1	-1.2
			2	-4.3
			mean	-2.8
	25/50	1:2	1	1.6
			2	1.4
			mean	1.5
	10/50	1:5	1	-0.8
			2	11.9
			mean	5.6
<i>Dollendorf II (DD)</i>	50/50	1:1	1	-2.4
			2	-4.0
			mean	-3.2
	25/50	1:2	1	13.9
			2	-6.3
			mean	3.8
	10/50	1:5	1	1.4
			2	-1.8
			mean	-0.2
<i>Höfchen am Hohenseh 4a (HaH)</i>	50/50	1:1	1	1.5
			2	2.1
			mean	1.8
	25/50	1:2	1	10.4
			2	6.9
			mean	8.7
	10/50	1:5	1	8.9
			2	4.3
			mean	6.6
<i>Hansheider Hof (HH)</i>	50/50	1:1	1	16.7
			2	12.5
			mean	14.6
	25/50	1:2	1	-4.9
			2	-6.6
			mean	-5.8
	10/50	1:5	1	-4.4
			2	-11.9
			mean	----
<i>Wurmwiese (WW)</i>	50/50	1:1	1	8.9
			2	-2.5
			mean	3.2
	25/50	1:2	1	1.0
			2	-5.6
			mean	-2.3
	10/50	1:5	1	-2.7
			2	-1.9
			mean	-2.3

On the basis of the obtained results the soil:solution ratio selected to be used in further tests was 1:1.

The results obtained during the determination of the appropriate equilibration time are presented below in numerical form in the table B.8.1.2.1.2_CA-91 and in graphical form on figure B.8.1.2.1.2_CA-39. On their basis the selected appropriate equilibration time was 96 hours.

Table B.8.1.2.1.1._CA-91: The numerical results of the determination of the appropriate equilibration time.

Equilibration time [hours]	Replicate	% Adsorption of the test item onto the test soil:				
		<i>Laacher Hof AXXa (AX)</i>	<i>Dollendorf II (DD)</i>	<i>Höfchen am Hohenseh 4a (HaH)</i>	<i>Hansheider Hof (HH)</i>	<i>Wurmwiese (WW)</i>
6	1	-3.9	-4.4	-5.2	0.6	15.3
	2	0.8	-6.3	12.1	-1.3	4.9
	Mean value	-1.6	-5.4	3.5	-0.4	10.1
24	1	-1.2	-2.4	1.5	16.7	8.9
	2	-4.3	-4.0	2.1	12.5	-2.5
	Mean value	-2.8	-3.2	1.8	14.6	3.2
48	1	-2.0	-0.3	0.9	13.1	-1.2
	2	-1.4	-3.0	2.8	-4.2	0.6
	Mean value	-1.7	-1.7	1.9	4.5	-0.3
72	1	1.4	1.1	-2.4	19.6	-1.8
	2	-2.5	-3.4	7.1	-10.1	-5.8
	Mean value	-0.6	-1.2	2.4	4.8	-3.8
96	1	1.8	-25.	7.4	-0.7	-2.4
	2	1.6	-2.2	6.4	-5.3	-6.8
	Mean value	1.7	-2.4	6.9	-3.0	-4.6

**Figure B.8.1.2.1.2._CA-39:** The graphical results of the determination of the appropriate equilibration time (copied from the study report).

The results of the **Definitive Test** are presented below, in tabularised form (tables B.8.1.2.1.2._CA-92 – B.8.1.2.1.2._CA-96), separately for each test soil. Presenting the results of the examination of adsorption at equilibrium – the amounts of the TFESA in supernatant expressed in % of Applied Amount ([%AA]), the Applicant provided an explanation that they were presented in relation to the corresponding mean values in matrix control samples, defined as 100% AA. The values were verified by the RMS and corrected when necessary. In case the values were corrected, those provided in the study report are given in brackets after the correct values calculated by the RMS. Calculating the values expressed as [%AA], in case of the mean values RMS calculated those values from the corresponding mean concentrations and not as a mean of calculated [%AA] for the two replicates.

Additionally the Applicant stated that although some mean values (RMS noticed that that concerned also the individual replicates) determined in supernatants at equilibrium were higher than 110% when referred to the respective application rate in control samples, that did not influence the validity of the experiment. It was explained that these exceedances were due, most probably, to the analytical variation, possibly also increased by low to no adsorption onto soil.

RMS, in principle agreeing with the explanation provided by the Applicant concerning the validity of the study, is of the opinion, that such phenomenon may indicate that systematic error occurred during application. Therefore the control of the amount applied should have been, rather, carried out in test samples immediately after application, using the small amounts of the solution, in order to limit the uncertainty related to the obtained results.

Table B.8.1.2.1.2._CA-92: The results of the **Definitive Test** – amounts of the test item (TFESA) in supernatant at equilibrium (after 96-hours equilibration) obtained in test soil **Laacher Hof AXXa**.

Nominal concentration of the test item [mg/L]	Replicate	Measured concentration of the test item – amount in the Matrix Control Samples		Amount in solution (supernatant) at equilibrium (after 96 hours)	
		[mg/L]	[%AA]	[mg/L]	[%AA]
1.00	1	0.957	-----	0.987	103.6
	2	0.949	-----	1.008	105.8
	Mean	0.953	100.0	0.998	104.7
0.30	1	0.295	-----	0.300	99.0
	2	0.311	-----	0.293	96.7
	Mean	0.303	100.0	0.297	98.0 (97.9)
0.10	1	0.102	-----	0.107	105.9 (106.1)
	2	0.099	-----	0.107	105.9 (106.5)
	Mean	0.101	100.0	0.107	105.9 (106.3)
0.03	1	0.0287	-----	0.0302	106.7
	2	0.0279	-----	0.0289	102.1
	Mean	0.0283	100.0	0.0296	104.6 (104.4)
0.01	1	0.0087	-----	0.0103	115.7 (116.4)
	2	0.0091	-----	0.0101	113.5 (113.4)
	Mean	0.0089	100.0	0.0102	114.6 (114.9)

Table B.8.1.2.1.2._CA-93: The results of the **Definitive Test** – amounts of the test item (TFESA) in supernatant at equilibrium (after 96-hours equilibration) obtained in test soil **Dollendorf II**.

Nominal concentration of the test item [mg/L]	Replicate	Measured concentration of the test item – amount in the Matrix Control Samples		Amount in solution (supernatant) at equilibrium (after 96 hours)	
		[mg/L]	[%AA]	[mg/L]	[%AA]
1.00	1	0.940	-----	1.081	117.0 (117.1)
	2	0.907	-----	1.085	117.4 (117.5)
	Mean	0.924	100.0	1.083	117.2 (117.3)
0.30	1	0.297	-----	0.311	108.0
	2	0.279	-----	0.313	108.7
	Mean	0.288	100.0	0.312	108.3
0.10	1	0.093	-----	0.109	118.5 (118.6)
	2	0.090	-----	0.110	119.6 (119.7)
	Mean	0.092	100.0	0.109	118.5 (119.1)
0.03	1	0.0272	-----	0.0315	113.7
	2	0.0282	-----	0.0342	123.5
	Mean	0.0277	100.0	0.0329	118.8 (118.6)
0.01	1	0.0089	-----	0.0101	111.0
	2	0.0093	-----	0.0108	118.7 (118.6)
	Mean	0.0091	100.0	0.0104	114.3 (114.8)

Table B.8.1.2.1.2._CA-94: The results of the **Definitive Test** – amounts of the test item (TFESA) in supernatant at equilibrium (after 96-hours equilibration) obtained in test soil **Höfchen am Hohenseh 4a**.

Nominal concentration of the test item [mg/L]	Replicate	Measured concentration of the test item – amount in the Matrix Control Samples		Amount in solution (supernatant) at equilibrium (after 96 hours)	
		[mg/L]	[%AA]	[mg/L]	[%AA]
1.00	1	0.971	-----	0.989	101.2 (99.2)
	2	1.022	-----	0.975	99.8 (97.8)
	Mean	0.977	100.0	0.982	100.5 (98.5)
0.30	1	0.297	-----	0.296	98.0 (98.2)
	2	0.306	-----	0.285	94.4 (94.5)
	Mean	0.302	100.0	0.291	96.4
0.10	1	0.101	-----	0.105	106.1 (106.3)
	2	0.096	-----	0.105	106.1 (106.2)
	Mean	0.099	100.0	0.105	106.1 (106.2)
0.03	1	0.0277	-----	0.0292	103.9
	2	0.0285	-----	0.0285	101.4
	Mean	0.0281	100.0	0.0289	102.8 (102.7)
0.01	1	0.0097	-----	0.0099	100.0 (99.8)
	2	0.0101	-----	0.0098	99.0 (98.9)
	Mean	0.0099	100.0	0.0098	99.0 (99.3)

Table B.8.1.2.1.2._CA-95: The results of the **Definitive Test** – amounts of the test item (TFESA) in supernatant at equilibrium (after 96-hours equilibration) obtained in test soil **Hanscheider Hof**.

Nominal concentration of the test item [mg/L]	Replicate	Measured concentration of the test item – amount in the Matrix Control Samples		Amount in solution (supernatant) at equilibrium (after 96 hours)	
		[mg/L]	[%AA]	[mg/L]	[%AA]
1.00	1	0.974	-----	1.008	103.8 (103.9)
	2	0.967	-----	1.063	109.5
	Mean	0.971	100.0	1.036	106.7
0.30	1	0.307	-----	0.326	107.9
	2	0.297	-----	0.182	60.3 (60.4)
	Mean	0.302	100.0	0.254	84.1 (84.2)
0.10	1	0.099	-----	0.105	105.0 (104.4)
	2	0.102	-----	0.104	104.0 (103.4)
	Mean	0.100	100.0	0.104	104.0 (103.9)
0.03	1	0.0278	-----	0.0300	106.4
	2	0.0286	-----	0.0298	105.7
	Mean	0.0282	100.0	0.0299	106.0
0.01	1	0.0101	-----	0.0096	98.0 (107.1)
	2	0.0096	-----	0.0095	96.3 (108.3)
	Mean	0.0098	100.0	0.0095	96.3 (107.7)

Table B.8.1.2.1.2._CA-96: The results of the **Definitive Test** – amounts of the test item (TFESA) in supernatant at equilibrium (after 96-hours equilibration) obtained in test soil **Wurmweise**.

Nominal concentration of the test item [mg/L]	Replicate	Measured concentration of the test item – amount in the Matrix Control Samples		Amount in solution (supernatant) at equilibrium (after 96 hours)	
		[mg/L]	[%AA]	[mg/L]	[%AA]
1.00	1	0.955	-----	1.057	111.3
	2	0.944	-----	1.045	110.0 (110.1)
	Mean	0.950	100.0	105.1	110.6 (110.7)
0.30	1	0.300	-----	0.305	102.7 (102.9)
	2	0.293	-----	0.323	108.7 (108.9)
	Mean	0.297	100.0	0.314	105.7 (105.9)
0.10	1	0.101	-----	0.102	103.0 (102.7)
	2	0.098	-----	0.108	109.1 (108.6)
	Mean	0.099	100.0	0.105	106.1 (105.6)
0.03	1	0.0260	-----	0.0267	101.1 (101.3)
	2	0.0267	-----	0.0288	109.1 (109.3)
	Mean	0.0264	100.0	0.0278	105.3
0.01	1	0.0097	-----	0.0106	107.1
	2	0.0101	-----	0.0107	108.1 (108.3)
	Mean	0.0099	100.0	0.0107	108.1 (107.7)

On the basis of the results presented above it was stated that there was no adsorption of the test item – FOE 5043-Trifluoroethanesulfonic acid, on any test soil. It was indicated that the negative level of adsorption was recorded in majority of cases. As a result it was stated that it was not possible to determine the adsorption isotherms.

In the study report it was stated that the experiment examining the desorption was not carried out because the level adsorption was low or not it was not observed.

The final outcome of the study – the proposed parameters for adsorption and desorption (RMS's) proposal, are presented below in table B.8.1.2.1.2._CA-97. The proposed K_{fOC} and $1/n$ values are defaults presented with aim to be used as recommended in GW and SW modelling assessment.

Table B.8.1.2.1.2. CA-97: The key numerical results of the experiment – parameters of Freundlich adsorption isotherm for Trifluoroethanesulfonic acid (TFESA); RMS's proposal.

Test soil	Parameters of Freundlich adsorption isotherm				
	$\log K_{fads}$	$K_{fads} [mL/g]$	$1/n$	$K_{fOCads} [mL/g]$	R^2
Laacher Hof AXXa; Loamy sand	n. d. ¹⁾	0.0	1.0	0.0001 ²⁾	n. d. ¹⁾
Dollendorf II; Loam	n. d. ¹⁾	0.0	1.0	0.0001 ²⁾	n. d. ¹⁾
Höfchen am Hohenseh 4a; Silt loam	n. d. ¹⁾	0.0	1.0	0.0001 ²⁾	n. d. ¹⁾
Hanscheider Hof; Silt loam	n. d. ¹⁾	0.0	1.0	0.0001 ²⁾	n. d. ¹⁾
Wurmweise; Sandy loam	n. d. ¹⁾	0.0	1.0	0.0001 ²⁾	n. d. ¹⁾

Footnotes to the table:

- 1) n. d. = not determined as it was not possible to determine the isotherm;
 2) default value proposed to be used in GW and SW modelling;

Final conclusion:

The examination of the adsorption of FOE 5043-Trifluoroethanesulfonic acid (TFESA) onto soil at equilibrium showed that the test compound did not sorb onto soil to any extent (in most cases adsorption at equilibrium was shown to be negative). Therefore it was proposed to use for TFESA the value of $K_f = 0$ mg/L and consider the adsorption process as fully linear, hence $1/n = 1.0$. The proposed outcome of the study – reliable endpoint values for the adsorption process, are presented below, in form recommended for reporting the EU-agreed endpoints.

Soil adsorption transformation products (Regulation (EU) N° 283/2013, Annex Part A, point 7.1.3.1.2 and Regulation (EU) N° 284/2013, Annex Part A, point 9.1.2.1)

FOE 5043-Trifluoroethanesulfonic acid (TFESA)							
Soil Type (USDA)	OC %	Soil pH ^{a)}	K_d (mL/g)	K_{doc} (mL/g)	K_F (mL/g)	K_{Foc} (mL/g)	$1/n$
Loamy sand	1.8	6.6	----	----	0.0	0.0001	1.0
Loam	5.0	7.5	----	----	0.0	0.0001	1.0
Silt loam	1.7	6.7	----	----	0.0	0.0001	1.0
Silt loam	2.8	5.3	----	----	0.0	0.0001	1.0
Sandy loam	1.9	5.4	----	----	0.0	0.0001	1.0
Geometric mean (if not pH dependent)					0.0	0.0001	----
Arithmetic mean (if not pH dependent)					----	----	1.0
pH dependence, <i>Yes or No</i>			No				

^{a)} All values measured in water;

The Applicant also submitted the study examining the time-dependent sorption of FOE Sulfonic acid onto soil. The study has already been used to derive the kinetic endpoints for the process of degradation of that compound in aerobic soil and as such summarized in this Renewal Assessment Report as **Study 10** under the point B.8.1.1.2.1.1. – Aerobic degradation (on pages 290 – 301). Analysing the study report RMS noticed that it contained the data enabling to determine the Freundlich sorption isotherms for FOE Sulfonic acid in soil. Due to the specific design of the study, it is not possible to precisely define the would-be isotherms, but in RMS's opinion they may be representative rather for adsorption than desorption process. However, due to that uncertainty RMS is of the opinion that they should be considered only as supplementary and the resulting Freundlich isotherm parameters should not be included into the set of EU-agreed endpoints for FOE Sulfonic acid in the area of the soil sorption for that compound.

The study was presently evaluated for its compliance with OECD 106 Guideline. It is summarised below.

Study 5:

Report: Hellpointner E., (2003): "Time-Dependent Sorption of FOE5043-Sulfonic Acid in Soil."; Bayer Crop Science AG, Development – Global Regulatory Affairs, D-40789 Monheim, Germany; unpublished study Report No. MEF-229/03; 2003-10-13; study reference number: M-111445-01-1;

Guidelines: Due to the aims of the study – examination of the time-dependent sorption of FOE Sulfonic acid, it was declared to be performed in such way, to comply with the following Guidelines:

- examination of soil sorption of the test compound: OECD Guideline for Testing of Chemicals No. 106, Adsorption and Desorption;
- in the area of incubation of the test flasks – ageing and processing of test soils:
 - BBA Guidelines for the Official Testing of Plant Protectants, Part IV, 4-1 (1986);
 - SETAC-Europe Procedures for Assessing the Environmental Fate and Ecotoxicology of Pesticides (*ed.* Mark Lynch), March 1995;
 - US. EPA Guideline 162-1 Aerobic Soil Metabolism (supplemental);

GLP: Yes

RMS comments: This is a newly submitted study. Its was to examine the time-dependent sorption of FOE Sulfonic acid in soil. The study had already been evaluated, and found acceptable, with regard to its aspects aimed on the examination of the rate of degradation of the test compound in aerobic soils. At present the study was evaluated for its compliance with the following guideline:

- OECD Guideline for Testing of Chemicals No. 106, Adsorption and Desorption; to determine its suitability for the determination of Freundlich sorption isotherm for FOE Sulfonic acid in each test soil.

It was verified by the RMS and found acceptable in the area of the examination of the equilibrium sorption of FOE Sulfonic acid onto soil. It is summarised below. The summary is extended summary of that presented on pp. 290-301 as **Study 10**, containing elements strictly related to the examination of the soil sorption at equilibrium. The numbering of the figures and graphs is continuous in relation to this section of the Assessment Report.

Summary:

The aim of the study was to examine the phenomenon of the time-dependent sorption, i.e. increase with time of the K_{OC} value, of FOE Sulfonic acid onto soil. That was done in order to clarify the reasons for the observed discrepancies of the results of different studies, namely:

- high mobility and leaching potential of FOE Sulfonic acid in soil, demonstrated by the results of the batch equilibrium sorption studies – average K_{OC} = 12.5 mL/g, and modelling GW exposure assessment, with PEC_{GW} for cereals in range of 3.1 – 9.2 µg/L;
- moderate concentrations of the compound in lysimeter studies – up to 1.69 µg/L in the average 1st year leachates when the compound was applied twice in the same year;
- the fact stated in the regulatory study by Hellpointner [1999], examining the degradation of FOE Sulfonic acid in soil (summarised under the point B.8.1.1.2.1.1. as **Study 9**), that the compound was not as easily extracted from soil, especially at later time points, as it might be suggested by its K_{OC} value.

The experiment was performed using the [Phenyl-U-¹⁴C] FOE Sulfonic acid in form of ammonium salt. Its structural formula is presented below on figure B.8.1.2.1.2._CA-40. The specific activity of the test compound was 2.66 MBq/mg (21.0 mCi/mMole) and its radiochemical purity was 98%.

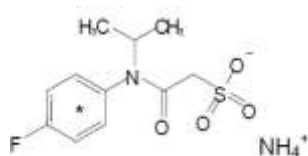


Figure B.8.1.2.1.2._CA-40: The structural formula of the test compound (copied from the study report).

The test compound was used to prepare the **Stock solution**, subsequently used in the experiment to treat the test soil. That solution was prepared by dissolving the whole delivered amount of radiolabelled FOE Sulfonic acid in 1 mL of CH₃CN and 19 mL of H₂O. Next, the concentration of the test compound in the solution was determined. For that purpose five 50-μL aliquots of the **Stock solution** were radioassayed. The concentration of the test compound, expressed as radioactivity, was determined to be 9706.3 kBq/20 mL (9.7063 MBq/20 mL), corresponding to 0.1824 mg FOE Sulfonic acid/mL. The radiochemical purity of the solution, determined by TLC, was ~98%. The **Stock solution** was used directly to treat the test soils.

Two test soils were used in the study. The soil were freshly sampled, shortly before the beginning of the experiment, from the 0-20 cm layer. Their characteristic is presented below in the table B.8.1.2.1.2._CA-98.

Table B.8.1.2.1.2._CA-98: The characteristic of soils used in the study.

Parameter		Soil	
		<i>Laacherhof AXXa</i>	<i>Laacherhof AIII</i>
Soil origin		Monheim, Germany	Monheim, Germany
Soil type (USDA)		Sandy loam	Silt loam
Particle size distribution	Sand (50 μm – 2 mm) [%]	72.4	36.9
	Silt (2 – 50 μm) [%]	22.6	51.1
	Clay (< 2 μm) [%]	5.0	12.0
pH value in CaCl ₂		6.3	6.8
pH value in H ₂ O		6.9	7.6
pH value in KCl		6.3	7.2
Organic carbon content (OC) [%]		1.47	0.88
Organic matter content (OM) [%]		2.53	1.51
Cation Exchange Capacity – CEC [mEq/100g]		10.3	9.8
Water holding capacity	Max. [g H ₂ O/100 g soil]	34.42	36.40
	In air-dried and sieved soil [%]	8.62	7.22
Bulk density [g/cm ³]		2.5	2.55
Soil microbial biomass [mg microbial C/kg soil]	At start of incubation period – DAT 0	242	275
	At the end of incubation period – DAT 100	209	195
Soil microbial biomass [% OC] ¹⁾	At start of incubation period – DAT 0	1.65	3.13
	At the end of incubation period – DAT 100	1.42	2.22

Footnotes to the table:

1) Value calculated by the RMS.

In the laboratory the test soils were air-dried and sieved to a particle size ≤ 2 mm. Then the soil moisture content was measured in sieved soil by drying it at 105°C and determining the loss of weight.

Next, 100-g (d.w.) portions of air-dried and sieved test soils (109.43 g in case of Laacherhof AXXa soil and 107.78 g in case of Laacherhof AIII soil) were weighed into 1000-mL centrifuge tubes and brought to 40% MWHC by the addition of the appropriate amount of distilled water – 4.33 g/vessel for Laacherhof AXXa soil and 6.78 g/vessel for Laacherhof AIII. The test vessels were then closed with cotton-wool plugs and pre-incubated for about one week in the darkness and at constant T = 20°C.

At the beginning of the whole experiment the soils in the test vessels were treated with the test compound applied as already described **Stock Solution** in amount 73 μL/vessel, using a 100- μL Eppendorf pipette. That gave the treatment dose of 35.5 kBq/vessel when expressed in terms of radioactivity, corresponding to the application dose of 13 μg FOE Sulfonic acid/100 g soil. It was declared in the study report that such application dose corresponded to the lowest concentration of the test compound – 0.13 μg/g soil, used in the study examining adsorption of FOE Sulfonic acid onto soil.

RMS recalculated that application dose to obtain the theoretic application rate expressed in g/ha. Standard assumptions were used: soil density $d = 1.5 \text{ g/cm}^3$ and the depth of the soil layer $l = 5 \text{ cm}$. The resulting application rate was **A = 99.70 g FOE Sulfonic acid/ha**. It corresponds to ~41% highest application rate of Flufenacet proposed in the current EU-representative GAP – 240 g/ha.

When the experimentally determined soil bulk density values were used, the calculated theoretic application rates were as follows:

- in Laacherhof AXXa soil (bulk density $d = 2.5 \text{ g/cm}^3$) application rate **A = 162.50 g FOE Sulfonic acid/ha**;
- in Laacherhof AIII soil (bulk density $d = 2.55 \text{ g/cm}^3$) application rate **A = 165.75 g FOE Sulfonic acid/ha**.

After treatment of the test soils with the test compound several test were performed, aimed on the determination of adsorption parameters. All they were performed in the same way as typical batch sorption tests described in OECD 106 Guidance document. The main test was performed with treated soil aged for the determined amount of days before the adsorption was examined. All test are briefly characterised, in form of a table copied from the study report, on figure B.8.1.2.1.2._CA-41 below.

Table 2 Applications with each approx. 35.5 kBq of test item

Test	Tubes/soil	Investigations
a) DAT-0: Soil treated prior to shaking	1	Samples taken after 1, 3, 7 and 24 hrs of shaking with 100 mL of 0.01 M CaCl_2 solution LSC and TLC of supernatant
b) DAT-0: Solution treated prior to shaking	1	Samples taken after 1, 3, 7 and 24 hrs of shaking with 100 mL of 0.01 M CaCl_2 solution LSC and TLC of supernatant
c) DAT-0: Reference solution: soil not treated during shaking	1	Processing after 24 hrs of shaking with 100 mL of 0.01 M CaCl_2 solution, then treatment of decanted aqueous 0.01 M CaCl_2 filled into a new empty tube and shaking for 24 hrs, LSC and TLC of solution and LSC of tube extract ^{a)}
d) DAT-0: soil treated prior to shaking	1	Processing after 24 hrs of shaking with 333 mL of 0.01 M CaCl_2 solution LSC and TLC of supernatant and soil extract combustion of soil solids
e) DAT-0: Control without soil Solution treated prior to shaking	1	Samples taken after 1, 3, 7 and 24 hrs of shaking with 100 mL of 0.01 M CaCl_2 solution LSC and TLC of supernatant and LSC of tube extract ^{a)}
Main Test: DAT-X: soil treated then aged prior to shaking	14	Processing after 24 hrs of shaking with 100 mL of 0.01 M CaCl_2 solution, LSC and TLC of supernatant and soil extract, combustion of soil solids

^{a)}: In order to get information on the sorption of radioactivity onto the walls of the testing tubes. The tube was washed (extracted) as it is described for test a or d.

Figure B.8.1.2.1.2._CA-41: The table listing and briefly characterising tests performed in the experiment (copied from the study report).

The tests a) – e) are the equivalents of the preliminary tests in the typical experiment on the batch sorption equilibrium performed in line with OECD 106 Guideline.

All they were carried out using the 0.01M CaCl_2 _{aq} solution prepared by dissolving 2.94 g of $\text{CaCl}_2 \times \text{H}_2\text{O}$, pre-weighed into measuring flask, in 2 L of Milli-Q water. The pH of so prepared solutions was in range of 5.5 – 6.2.

The **test a)** was performed in order to establish the equilibration time for the soil:solution system in case when the test item was introduced by direct application to the soil surface, before the addition of the solution. For that purpose single vessels containing 100-g (d. w.) portions of each test soil were treated with 73 μL of characterised above **Stock Solution**, applied to the soil surface. The soil moisture of each test soil was then adjusted to 40% MWHC, 100 mL of blank 0.01M CaCl_2 _{aq} solution added to obtain the soil:solution ratio 1:1. So prepared samples were incubated for up to 24 hours, by shaking, in the darkness at constant temperature $T = 20^\circ\text{C}$. At pre-designated time points – after 1, 3 and 7 hours of shaking, 1-mL aliquots of clarified supernatant (obtained by 10-min centrifugation) were taken to analysis by LSC. At the last time point – after 24 hours of shaking, the whole test vessels were centrifuged for 15 min, clarified supernatants decanted and weighed in order to determine their volume. Then 1-mL aliquots were analysed by LSC for radioactivity content.

The **test b)** was performed in order to establish the equilibration time for the soil:solution system in case when the test item was introduced the with the 0.01M CaCl_2 _{aq} solution. For that purpose to the single vessels containing 100-g (d.w.) portions of each pre-equilibrated test soils (100 g d.w.) were added 100-mL portions of 0.01M CaCl_2 _{aq} solution treated with 73 μL of characterised above **Stock Solution**, to obtain the soil:solution ratio 1:1. The so prepared samples incubated for up to 24 hours, by shaking, in the darkness at constant

temperature $T = 20^{\circ}\text{C}$. At pre-designated time points – after 1, 3 and 7 hours of shaking, 1-mL aliquots of clarified supernatant (obtained by 10-min centrifugation) were taken to analysis by LSC. At the last time point – after 24 hours of shaking, the whole test vessels were centrifuged for 15 min, clarified supernatants decanted and weighed in order to determine their volume. Then 1-mL aliquots were analysed by LSC for radioactivity content.

The **test c)** was performed in order to determine the affinity of the test item to the test vessel. For that purpose the in single vessels 100-g (d. w.) portions of each pre-equilibrated test soil were shaken for 24 hours with 100 mL of blank 0.01M CaCl_2 aq solution (soil:solution ratio was 1:1). After that period samples were centrifuged for 15 minutes, clear supernatants decanted to empty test vessels and treated with 73 μL of characterised above **Stock Solution**. So prepared samples were then equilibrated, by shaking in the darkness at $T = 20^{\circ}\text{C}$, for another 24 hours. After that time vessels were centrifuged, supernatants collected and weighed in order to determine their amount, and 1-mL aliquots analysed by LSC to determine the radioactivity content. The empty test vessels remaining after centrifugation were washed with organic solvents in the same manner as was used in the main test in organic extraction step of test soils.

The **test d)** was performed in order to establish the equilibration time for the soil:solution system in case when the test item was introduced by direct application to the soil surface, before the addition of the solution. Therefore it looked similarly to characterised above **test a)**, except that the tested soil:solution ratio was 1:3 – the amount of blank 0.01M CaCl_2 aq solution was 333 mL.

The last of the preliminary experiments – **test e)**, had the same aim as **test b)**. The main difference between the two consisted in that it was performed in soilless system, therefore the preliminary step – equilibration of blank 0.01M CaCl_2 aq solution with 100-g portions of test soil, was omitted.

The procedure used in the **main test** is characterised below.

For each test soil 14 pre-incubated test vessels were treated with the test compound applied to the soil surface as **Stock solution** in amount 73 μL /vessel, to obtain the application dose of 0.13 mg/kg, corresponding to the theoretic application rate **A = 99.7 g/ha**. Then the test vessels were closed with cotton-wool plugs and all, except DAT-0 samples were placed in the darkness in the temperature-controlled room and incubated for up to 100 days at $T = 20^{\circ}\text{C}$.

For each test soil duplicate samples were removed for further processing at the following time points: DAT 0, DAT 3, DAT 7, DAT 14, DAT 28, DAT 56 and DAT 100. The samples removed from the incubation room were further processed following their procedure presented below on figure B.8.1.2.1.2._CA-42.

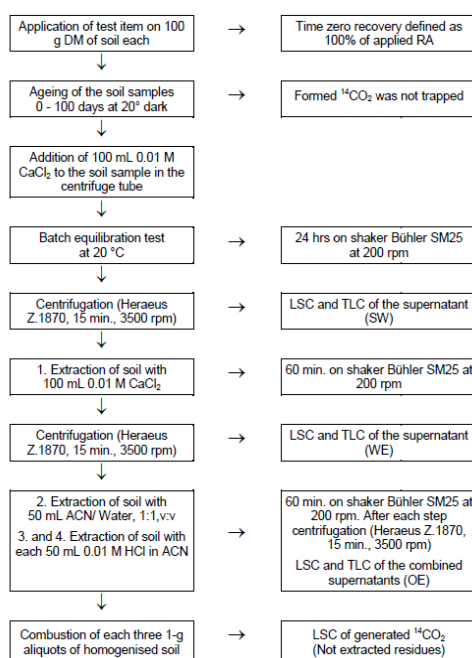


Figure B.8.1.2.1.2._CA-42: The flow chart of the processing of samples during the main test of the experiment (copied from the study report).

The 0.01M CaCl_2 solution used at the first stage of extraction, named on the flow chart “batch equilibration test”, was prepared by dissolving 2.94 g of $\text{CaCl}_2 \times \text{H}_2\text{O}$ in 2 L of deionised (Milli-Q) water. Three such solutions were prepared for the purpose of the experiment, having a pH ranging from 5.5 to 6.2. The same solution was also used at 1st step of extraction.

The clear supernatants obtained at each step after centrifugation were collected and their volume determined by weighing. The acetonitrile extracts ($\text{CH}_3\text{CN}/\text{H}_2\text{O}$ and 0.01N $\text{HCl}_{\text{aq}}/\text{CH}_3\text{CN}$ extracts) were combined.

The supernatant obtained during batch equilibration test was further called **Supernatant**, that obtained after extraction with 100 mL of 0.01 M CaCl_2 – **water extract**, while combined supernatants obtained after extraction with solutions containing CH_3CN – **organic extract**.

The extracts were not further processed but their three 200- μL aliquots analysed for radioactivity content using LSC.

The extracts were also analysed using radio-TLC. For that purpose the following amounts of each fraction were used:

- in case of **Supernatant** one 100- μL aliquot;
- in case of **Water extract** one 200- μL aliquot;
- in case of **Organic extract** one 500- μL aliquot

The extracted soil pellets were air-dried, homogenised and analysed for the content of NER fraction. For that purpose their three 1-g aliquots were combusted in oxidiser and generated $^{14}\text{CO}_2$ quantified using LSC.

The LSC analysis of the liquid samples (200- μL aliquots) was performed in 2-mL Quicksafe-A scintillation liquid containing 5% of water. The measurements were done on LS 6500 or LS 6000LL counters. Sample counting time was 10 minutes, average counting efficiency ~91% and the background 14-16 cpm.

The $^{14}\text{CO}_2$ generated during the oxidative combustion of the extracted soil pellets was absorbed in Oxysolve C-400 scintillation cocktail and analysed by LSC.

The TLC analysis was performed on crude solutions of each extract in order to determine the concentration of the test compound in each of the fractions. The analysed samples were not enriched or preconditioned prior to the analysis.

The TLC analysis was performed on 200 x 200 mm silica gel Si60 TLC plates. Chromatograms were developed in glass chamber using the following solvent system: $\text{CH}_3\text{CN}/\text{CH}_3\text{CHOHCH}_3/\text{CH}_3\text{COOC}_2\text{H}_5/\text{H}_2\text{O}$ 60:9:6:3 (v/v/v/v) solution ($\text{CH}_3\text{CHOHCH}_3$ stands for 2-propanol and $\text{CH}_3\text{COOC}_2\text{H}_5$ for ethyl acetate).

The identification of the test compound was performed by means of the comparison of the R_f values for the analysed samples with those of the known standards.

The quantitative analysis – radioactivity counting, was performed using BIO imaging analyser (Fuji Co.). The LOD (determination limit) for a single peak was 0.5% AR. That value however significantly depended on the volume of sample introduced on the plate.

Results and their discussion:

The characteristic of the test soils used in the study has been presented at the beginning of this summary in table B.8.1.2.1.2._CA-98. On that basis it may be stated that both test soils fully meet the acceptability criteria set by the OECD 106 Guideline.

The temperature in incubation chamber was demonstrated to be constant during the whole incubation period, and maintained at the designated level $T = 20 \pm 1^\circ\text{C}$. The mean temperature during incubation was $T = 19.9^\circ\text{C}$ ranging from 19.8°C to 20.35°C .

The graphical presentation of the changes of incubation temperature are presented below on figure B.8.1.2.1.2._CA-44.

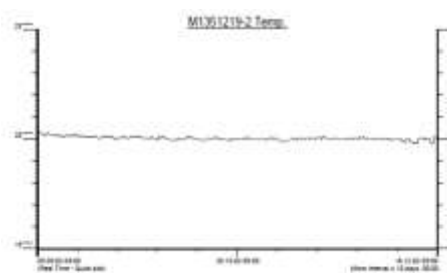


Figure B.8.1.2.1.2._CA-44: Temperature recorded in incubation chamber during the experiment (copied from the study report).

The results of the primary tests – **test a)** – **test e)**, are presented below, in tabularised form in tables B.8.1.2.1.2._CA-99 for **test a)** and **test b)**, table B.8.1.2.1.2._CA-100 for **test c)** and table B.8.1.2.1.2._CA-101 for **test e)**. The Applicant decided not to present the results of the **test d)**, as they were declared to be similar to those obtained in **test a)**.

Table B.8.1.2.1.2._CA-99: The numerical results of the **test a)** and **test b)**, aimed on the determination of the appropriate equilibration time.

Equilibration time [hours]	Radioactivity (RA) [Bq] in supernatants in vessels with the test soil: Laacher Hof AXXa, Sandy loam				Radioactivity (RA) [Bq] in supernatants in vessels with the test soil: Laacher Hof AIII, Silt loam			
	<i>test a)</i>		<i>test b)</i>		<i>test a)</i>		<i>test b)</i>	
	RA in 0.2-mL aliquots	RA in 1.0-mL samples	RA in 0.2-mL aliquots	RA in 1.0-mL samples	RA in 0.2-mL aliquots	RA in 1.0-mL samples	RA in 0.2-mL aliquots	RA in 1.0-mL samples
1	61.80	309	60.75	304	62.31	312	62.25	311
3	62.11	311	61.17	306	61.52	308	61.41	307
7	60.63	303	60.67	303	61.43	307	59.91	300
24	60.74	304	60.90	305	60.17	301	58.89	299

Table B.8.1.2.1.2._CA-100: The numerical results of the **test c)**, aimed on the determination of the affinity of the test item to test vessels in solution containing soil matrix.

Test soil matrix	Volume of supernatant [mL]	Radioactivity in 0.2-mL aliquots [Bq]	Radioactivity in supernatant	
			total ^{14}C [Bq]	as FOE Sulfonic acid [% radioactivity]
<i>Laacher Hof AXXa, Sandy loam</i>	74.7	93.73 (92.86 – 94.24)	35010	98.90
<i>Laacher Hof AIII, Silt loam</i>	74.6	95.27 (94.31 – 95.78)	35540	98.85

Table B.8.1.2.1.2._CA-101: The numerical results of the **test e)**, aimed on the determination of the affinity of the test item to test vessels in soilless test system.

Equilibration time [hours]	Radioactivity in 0.2-mL aliquots [Bq]			Radioactivity in 1.0-mL samples [Bq]		
	Replicate 1	Replicate 2	Average	Replicate 1	Replicate 2	Average
1	71.12	71.37	71.25	356	357	356
3	70.78	70.90	70.84	354	355	354
7	71.38	70.98	71.18	357	355	356
24	71.19	71.17	71.118	356	356	356

The total amount of radioactivity recovered in supernatants was 34312 Bq for Replicate 1, 34445 Bq for Replicate 2 and 34379 Bq on average. The amount of radioactivity washed from vessels with organic extrahents was 1763 Bq for Replicate 1, 1661 Bq for Replicate 2 and 1712 Bq on average. Given that the total radioactivity applied was 36090 Bq (100%) the average amount of radioactivity in supernatants was 95.26% and that adhered/adsorbed to the test vessels – 4.74%.

On the basis of the results presented above it was stated that the most appropriate equilibration time was 24 hours. Analysing the results presented in the table B.8.1.2.1.2._CA-99 RMS noticed that there was little difference in the radioactivity content in supernatants obtained from systems with treated soil and treated solution. That may indicate that in the definitive test the results of the batch equilibration test may be representative rather for adsorption than the desorption process.

The results of the **test c)** and **test e)** clearly demonstrated that the level of adsorption of the test item to the test vessels was very low. Additionally the results of the **test c)** demonstrated that the test item – FOE Sulfonic acid, was stable in the test system during the equilibration period.

Below are presented the results obtained during the main test.

The total recoveries of Applied Radioactivity in DAT-0 samples were as follows:

- for Laacherhof AXXa soil: **34.152 kBq**, subsequently used as a reference 100% AR value; it corresponded to 12.23 µg FOE Sulfonic acid/100 g soil;
- for Laacherhof AIII soil: **34.840 kBq**, subsequently used as a reference 100% AR value; it corresponded to 12.40 µg FOE Sulfonic acid/100 g soil.

In the study report it was stated that both soils were microbiologically viable and that the microbial biomass was within the usual range expected for soils sampled from agricultural fields.

RMS stated that the microbial biomass was above the minimal level recommended by OECD 307 Guideline – 1% OC throughout the whole study duration. It was also noted that, as expected, higher decrease in microbial biomass was observed in soil having lower OC content, but that parameter at the end of the study was still on such level that the test soil may be considered fully viable.

The results of the qualitative and quantitative analysis of the radioactivity in both test systems are presented below. Because of the design of the incubation vessels – the traps for the volatile compounds were not set, it was not possible to determine the level of mineralisation and hence it was also not possible to determine the mass balance.

RMS also noticed that the way the results were reported in the study report made them not fully transparent with regard to their further use in kinetic analysis. In particular, the results of the determination of radioactivity in each fraction was given in [Bq] for individual replicates. When transformed to % AR the values were given as averages of the two replicates.

The concentrations of FOE Sulfonic acid in different fractions at each time point determined by TLC, were expressed as % radioactivity in analysed sample. Only for extracts obtained in Laacherhof AIII soil were given the values for %AR in given fraction, enabling the calculation of the concentration of FOE Sulfonic acid expressed as % AR.

As a result, RMS decided to recalculate all the results provided in the study report in order to:

- a) obtain the results of the quantitation of radioactivity in each fraction, on each time point and for each replicate, expressed as %AR;
- b) obtain the concentrations of FOE Sulfonic acid in each replicate at each time point expressed as %AR.

The repeated calculations were carried out using the raw results presented in the study report. These are shown below, as tables copied from the study report, on figures B.8.1.2.1.2._CA-45 and B.8.1.2.1.2._CA-46. On figure B.8.1.2.1.2._CA-45 are reproduced the results of the determination of radioactivity in each fraction. For calculations were used the values marked bold – amount of radioactivity in the whole sample expressed in [Bq]. The reference value, defined as 100% AR, was “Avg. DAT-0” value reported at the bottom of each table.

On the next figure – B.8.1.2.1.2._CA-46 are presented the raw results of the analysis of each fraction by TLC. The following abbreviations were used by the Applicant in the reproduced tables to characterise fractions:

- SW for **Supernatant**;
- WE for **Water extract**;
- OE for **Organic extract**.

The numerical, re-formatted results of the experiment are given in two tables – B.8.1.2.1.2._CA-102 for Laacherhof AXXa soil and B.8.1.2.1.2._CA-103 for Laacherhof AIII soil. Presenting them the RMS decided to provide the average values for concentration of radioactivity in fractions at each sampling point as they were given in the study report. Also the concentrations of the test compound – FOE Sulfonic acid, expressed in [µg/100 g soil] are taken from the study report.

To maintain the coherence of the reported results RMS decided to present them all in format of a single digit after the decimal point. The only exception was made when the average concentrations of FOE Sulfonic acid in [µg/100 g soil], reproduced from the study report, were reported – the format used in the study report was kept.

Such approach may possibly result in small discrepancies between the averages reported by the Applicant and those calculated by the RMS, but such differences are estimated to be negligible.

In addition to numerical results RMS presented the graphical results of the determination of the distribution of radioactivity between extractable and non-extractable phases, reproduced from the study report (figure B.8.1.2.1.2._CA-47).

Finally RMS decided to provide the estimates of the mineralisation level. That was done assuming the theoretical total recovery level of AR at each time point and for each replicate equal to 100% and subtracting from that value the experimentally determined total radioactivity recovered. The resulting value was considered to represent the approximate level of mineralisation. RMS noticed that the obtained values were in line with those obtained in the study by [Hellpointner; 1999] (Study 9, point B.8.1.1.2.1.1.).

Raw results obtained in Laacherhof AXXa soil (LSC analysis)																	
Days	Sample ID DH25	Supernatant after 24h shaking (SW)				Water extract (WE)				organic extract (OE)				Soil not extracted			Recovery Total Bq Total
		V _T [mL]	V _A [mL]	LS [Bq]	Subtotal [Bq]	V _T [mL]	V _A [mL]	LS [Bq]	Subtotal [Bq]	V _T [mL]	V _A [mL]	LS [Bq]	Subtotal [Bq]	M _T [g]	LS [Bq/g]	Subtotal [Bq]	
0	A1T1	76.0	0.2	59.36	22,557	92.4	0.2	16.30	7,531	152	0.2	4.46	3,390	100.3	7.12	714	34,191
	A2T1	77.5	0.2	58.61	22,711	93.4	0.2	15.94	7,444	156	0.2	4.18	3,260	100.6	6.94	698	34,114
3	A1T2	77.1	0.2	56.94	21,950	95.7	0.2	16.02	7,666	152	0.2	4.71	3,580	100.4	10.24	1,028	34,224
	A2T2	75.0	0.2	57.26	21,473	97.1	0.2	15.84	7,690	154	0.2	4.95	3,812	100.4	10.07	1,011	33,985
7	A1T3	76.5	0.2	55.42	21,198	96.6	0.2	15.14	7,313	152	0.2	4.59	3,488	100.4	16.33	1,640	33,639
	A2T3	76.4	0.2	55.22	21,094	96.0	0.2	15.05	7,224	152	0.2	4.58	3,481	100.6	17.61	1,772	33,570
14	A1T4	77.4	0.2	50.73	19,633	94.4	0.2	13.83	6,528	162	0.2	4.59	3,718	100.5	24.27	2,439	32,317
	A2T4	75.9	0.2	51.12	19,400	94.1	0.2	13.85	6,516	156	0.2	4.85	3,783	100.5	24.41	2,453	32,153
28	A1T5	77.4	0.2	41.34	15,999	97.2	0.2	11.68	5,676	156	0.2	4.49	3,502	100.3	49.01	4,916	30,093
	A2T5	77.8	0.2	43.32	16,851	94.4	0.2	11.84	5,588	156	0.2	4.27	3,331	100.3	43.12	4,325	30,095
56	A1T6	76.8	0.2	32.12	12,334	95.1	0.2	8.93	4,246	156	0.2	3.79	2,956	100.5	70.68	7,103	26,640
	A2T6	76.9	0.2	34.20	13,150	93.4	0.2	9.27	4,329	156	0.2	3.90	3,042	100.3	66.61	6,681	27,202
100	A1T7	68.5	0.2	15.68	5,370	100.3	0.2	5.23	2,623	156	0.2	2.62	2,044	101.4	102.22	10,365	20,402
	A2T7	68.5	0.2	15.38	5,268	102.2	0.2	5.24	2,678	156	0.2	2.70	2,106	102.4	103.54	10,602	20,654
Avg. DAT-0:																	34,153
Raw results obtained in Laacherhof AIII soil (LSC analysis)																	
Days	Sample ID DH25	Supernatant after 24h shaking (SW)				Water extract (WE)				organic extract (OE)				Soil not extracted			Recovery Total Bq Total
		V _T [mL]	V _A [mL]	LS [Bq]	Subtotal [Bq]	V _T [mL]	V _A [mL]	LS [Bq]	Subtotal [Bq]	V _T [mL]	V _A [mL]	LS [Bq]	Subtotal [Bq]	M _T [g]	LS [Bq/g]	Subtotal [Bq]	
0	B1T1	78.3	0.2	61.55	24,097	92.9	0.2	16.10	7,478	160	0.2	3.61	2,888	100.0	8.39	839	35,302
	B2T1	79.3	0.2	59.40	23,552	94.5	0.2	15.40	7,277	160	0.2	3.57	2,856	100.3	6.92	694	34,379
3	B1T2	76.1	0.2	58.43	22,233	97.0	0.2	15.93	7,726	158	0.2	4.08	3,223	100.1	11.78	1,179	34,361
	B2T2	76.3	0.2	57.44	21,913	95.2	0.2	15.93	7,583	158	0.2	3.96	3,128	100.0	11.98	1,198	33,822
7	B1T3	78.3	0.2	56.03	21,936	96.1	0.2	14.35	6,895	158	0.2	3.94	3,113	100.1	15.14	1,516	33,459
	B2T3	77.9	0.2	54.48	21,220	96.4	0.2	14.17	6,830	158	0.2	3.95	3,121	100.1	20.88	2,090	33,260
14	B1T4	77.5	0.2	53.08	20,569	93.8	0.2	13.90	6,519	160	0.2	3.96	3,168	100.4	21.64	2,173	32,428
	B2T4	77.9	0.2	51.03	19,876	95.7	0.2	13.68	6,546	160	0.2	4.11	3,288	100.0	23.68	2,368	32,078
28	B1T5	78.6	0.2	45.14	17,740	96.9	0.2	11.52	5,581	160	0.2	3.64	2,912	100.3	39.28	3,940	30,173
	B2T5	77.4	0.2	43.81	16,954	95.7	0.2	11.71	5,603	160	0.2	3.57	2,856	100.1	43.79	4,383	29,797
56	B1T6	78.4	0.2	33.54	13,148	93.7	0.2	8.92	4,179	162	0.2	3.05	2,471	100.1	62.03	6,209	26,006
	B2T6	76.6	0.2	32.30	12,371	97.7	0.2	8.75	4,274	158	0.2	3.14	2,481	100.2	66.23	6,636	25,762
100	B1T7	71.9	0.2	14.51	5,216	108.6	0.2	4.99	2,710	158	0.2	2.18	1,722	97.0	101.61	9,856	19,504
	B2T7	70.8	0.2	16.96	6,004	99.7	0.2	4.29	2,139	158	0.2	2.04	1,612	95.3	104.25	9,935	19,689
Avg. DAT-0:																	34,840
108.6 10 mL of solvent had to be added in addition																	

Figure B.8.1.2.1.2._CA-45: Raw results of the LSC quantitation of radioactivity in extracts and extracted soil (copied from the study report).

Raw results of the TLC analysis of extracts obtained in Laacherhof AXXa soil							Raw results of the TLC analysis of extracts obtained in Laacherhof AIII soil							
Analytical Investigation - TLC Distribution of the Spotted Radioactivity - Values in % PSL-BKG Soil: Laacher Hof AXXa							Analytical Investigation - TLC Distribution of the Spotted Radioactivity - Values in % PSL-BKG Soil: Laacher Hof AIII							
Incubation time [d] (Replicate)	Extract	DH25 TLC-No./ Trace	Origin	FOE5043 SA	Diffuse radioact.	Total	Incubation time [d] (Replicate)	Extract	Radioact. (% of applied)	DH25 TLC-No./ Trace	Origin	FOE5043 SA	Diffuse radioact.	Total
0 (A1)	SW	d007/1	0.18	98.40	1.42	100.00	0 (B1)	SW	69.16	d007/3	0.34	97.86	1.80	100.00
	WE	d004/1	0.49	94.47	5.04	100.00		WE	21.46	d004/3	0.67	96.04	3.29	100.00
	OE	d010/1	0.80	90.68	8.32	100.00		OE	8.20	d010/3	2.09	93.15	4.78	100.00
0 (A2)	SW	d007/2	0.26	98.31	1.43	100.00	0 (B2)	SW	67.60	d007/4	0.37	97.26	2.37	100.00
	WE	d004/2	0.56	97.00	2.44	100.00		WE	20.89	d004/4	0.46	95.69	3.85	100.00
	OE	d010/2	0.56	95.70	3.74	100.00		OE	8.20	d010/4	0.58	93.15	6.27	100.00
3 (A1)	SW	d011/1	1.05	97.44	1.51	100.00	3 (B1)	SW	63.81	d011/3	0.94	97.69	1.37	100.00
	WE	d013/1	0.21	98.49	1.30	100.00		WE	22.18	d013/3	0.42	98.81	0.77	100.00
	OE	d012/1	0.32	98.26	1.42	100.00		OE	9.25	d012/3	0.92	99.82	0.18	100.00
3 (A2)	SW	d011/2	1.09	97.83	1.28	100.00	3 (B2)	SW	62.90	d011/4	1.05	98.83	2.12	100.00
	WE	d013/2	0.25	99.02	0.73	100.00		WE	21.76	d008/5		98.31	1.69	100.00
	OE	d012/2		99.54	0.46	100.00		OE	8.98	d012/4		98.90	1.10	100.00
7 (A1)	SW	d026/1	0.56	98.95	0.49	100.00	7 (B1)	SW	62.96	d026/3	0.66	98.92	0.42	100.00
	WE	d018/1	0.21	99.17	0.62	100.00		WE	19.79	d018/3	0.21	98.89	0.90	100.00
	OE	d017/1		98.36	1.64	100.00		OE	8.93	d017/3	0.46	98.20	1.34	100.00
7 (A2)	SW	d026/2	0.41	97.65	1.95	100.00	7 (B2)	SW	60.91	d026/4	0.41	99.27	0.32	100.00
	WE	d018/2		99.35	0.65	100.00		WE	19.60	d018/4	0.41	99.52	0.07	100.00
	OE	d017/2	0.25	98.90	0.85	100.00		OE	8.96	d017/4	2.43	97.15	0.42	100.00
14 (A1)	SW	d019/1	0.63	98.79	0.58	100.00	14 (B1)	SW	59.04	d019/3	0.62	99.38	0.00	100.00
	WE	d021/1	0.49	98.36	1.15	100.00		WE	16.71	d021/3	0.56	98.36	1.08	100.00
	OE	d020/1	0.49	98.52	0.99	100.00		OE	9.09	d020/3	0.46	95.33	4.21	100.00
14 (A2)	SW	d019/2	0.60	98.84	0.56	100.00	14 (B2)	SW	57.05	d019/4	0.51	98.59	0.90	100.00
	WE	d021/2	0.37	98.07	1.56	100.00		WE	16.79	d021/4	0.35	99.24	0.41	100.00
	OE	d020/2	0.63	97.46	1.91	100.00		OE	9.44	d020/4	1.07	93.53	5.40	100.00
28 (A)	SW	d022/1	0.71	99.07	0.22	100.00	28 (B1)	SW	50.92	d022/3	0.56	99.40	0.04	100.00
	WE	d025/1	1.42	96.66	1.92	100.00		WE	16.02	d025/3	1.13	97.55	1.32	100.00
	OE	d023/1	1.49	97.43	1.08	100.00		OE	8.36	d023/3	2.77	95.49	1.74	100.00
28 (B)	SW	d022/2	0.60	98.85	0.55	100.00	28 (B2)	SW	48.66	d022/4	0.55	98.81	0.84	100.00
	WE	d025/2	1.17	96.37	2.46	100.00		WE	16.08	d025/4	0.92	97.54	1.54	100.00
	OE	d023/2	1.23	97.73	1.04	100.00		OE	8.20	d023/4	2.69	96.19	1.12	100.00
56 (A)	SW	d027/1	0.88	98.47	0.67	100.00	56 (A)	SW	37.74	d027/3	0.54	98.69	0.77	100.00
	WE	d028/1	2.31	93.20	4.49	100.00		WE	11.99	d028/3	1.63	93.18	5.19	100.00
	OE	d029/1	4.44	89.91	5.65	100.00		OE	7.09	d029/3	6.60	90.23	3.17	100.00
56 (B)	SW	d027/2	0.77	99.07	0.16	100.00	56 (B)	SW	35.51	d027/4	0.65	98.95	0.40	100.00
	WE	d028/2	1.87	93.87	4.26	100.00		WE	12.27	d028/4	1.54	94.46	4.00	100.00
	OE	d029/2	4.54	91.57	3.89	100.00		OE	7.12	d029/4	6.59	87.35	6.06	100.00
100 (A)	SW	d030/1	1.76	96.88	1.36	100.00	100 (A)	SW	14.97	d030/3	1.16	97.50	1.34	100.00
	WE	d031/1	2.21	96.35	1.44	100.00		WE	7.78	d031/3	0.89	96.76	2.35	100.00
	OE	d032/1	6.80	72.41	20.79	100.00		OE	4.94	d032/3	9.27	70.43	20.30	100.00
100 (B)	SW	d030/2	1.99	95.97	2.04	100.00	100 (B)	SW	17.23	d030/4	1.29	95.53	3.18	100.00
	WE	d031/2	1.83	95.81	2.36	100.00		WE	6.14	d031/4	1.39	96.32	2.29	100.00
	OE	d032/2	7.35	74.61	18.04	100.00		OE	4.63	d032/4	10.99	65.70	23.31	100.00

Figure B.8.1.2.1.2_CA-46: Raw results of the TLC analysis of radioactivity in extracts
(copied from the study report).

The results obtained in Laacherhof AXXa (Sandy loam) soil are presented below in numerical form in the table B.8.1.2.1.2._CA-102 and in graphical form on figure B.8.1.2.1.2._CA-47.

Table B.8.1.2.1.2._CA-102: The numerical results of the experiment performed on Laacherhof AXXa soil.

Radioactivity			Measured on DAT						
			0	3	7	14	28	56	100
In extract [%AR]	Supernatant	Rep. 1	66.0	64.3	62.1	57.5	46.8	36.1	15.7
		Rep 2.	66.5	62.9	61.8	56.8	49.3	38.5	15.4
		Mean	66.3	63.6	61.9	57.1	48.1	37.3	15.6
	Water extract	Rep. 1	22.1	22.4	21.4	19.1	16.6	12.4	7.7
		Rep 2.	21.8	22.5	21.2	19.1	16.4	12.7	7.8
		Mean	21.9	22.5	21.3	19.1	16.5	12.6	7.8
	Organic extract	Rep. 1	9.9	10.5	10.2	10.9	10.3	8.7	6.0
		Rep 2.	9.5	11.2	10.2	11.1	9.8	8.9	6.2
		Mean	9.7	10.8	10.2	11.0	10.0	8.8	6.1
	Total extracted	Rep. 1	90.2	97.2	93.7	87.5	73.7	57.2	29.4
		Rep 2.	97.8	96.6	93.2	87.0	75.5	60.1	29.4
		Mean	97.9	96.9	93.4	87.2	74.6	58.6	29.4
Identified (TLC) as FOE Sulfonic acid [% AR]	Supernatant	Rep. 1	65.0	62.6	61.4	56.8	46.4	35.6	15.2
		Rep 2.	65.4	61.4	60.3	55.9	48.8	38.1	14.8
		Mean	65.2	62.0	60.9	56.4	47.6	36.9	15.0
	Water extract	Rep. 1	20.8	22.1	21.2	18.8	16.6	11.6	7.4
		Rep 2.	21.1	22.3	21.0	18.7	15.8	11.9	7.5
		Mean	21.0	22.2	21.1	18.8	16.2	11.7	7.5
	Organic extract	Rep. 1	9.0	10.3	10.0	10.7	10.0	7.8	4.3
		Rep 2.	9.1	11.1	10.1	10.8	9.5	8.2	4.6
		Mean	9.1	10.7	10.1	10.8	9.8	8.0	4.5
	Total extracted	Rep. 1	94.8	95.0	92.7	86.3	73.0	54.9	27.0
		Rep 2.	95.7	94.8	91.4	85.4	74.1	58.2	26.9
		Mean	95.2	94.9	92.1	85.9	73.5	56.6	26.9
FOE Sulfonic acid recovered [µg/100 g soil]		Rep. 1	12.2	12.2	11.9	11.1	9.3	7.1	3.5
		Rep 2.	12.3	12.2	11.7	11.0	9.5	7.5	3.5
		Mean	12.23	12.19	11.82	11.04	9.41	7.26	3.46
NER fraction [% AR]		Rep. 1	2.1	3.0	4.8	7.1	14.4	20.8	30.3
		Rep 2.	2.0	3.0	5.2	7.2	12.7	19.6	31.0
		Mean	2.1	3.0	5.0	7.2	13.5	20.2	30.7
Total radioactivity recovered [% AR]		Rep. 1	100.1	100.2	98.5	94.6	88.1	78.0	59.7
		Rep 2.	99.9	99.5	98.3	94.1	88.1	79.6	60.5
		Mean	100.0	99.9	98.4	94.4	88.1	78.8	60.1
Theoretical level of mineralisation [% AR] ¹⁾		Rep. 1	0.0	0.0	1.5	5.4	11.9	22.0	40.3
		Rep 2.	0.1	0.5	1.7	5.9	11.9	20.4	39.5
		Mean	0.0	0.1	1.6	5.6	11.9	21.2	39.9

Footnotes to the table:

- 1) The theoretical level of mineralisation calculated by the RMS by subtracting the appropriate value representing the “Total radioactivity recovered” from the theoretical level of applied radioactivity – 100%. For DAT-0 samples that value was set to 0, as for that time point no mineralisation was expected to occur. In cases when the amount of radioactivity recovered at the given time point was higher than 100% the level of would-be mineralisation was also set to zero.

The results obtained in Laacherhof AIII (Silt loam) soil are presented below in numerical form in the table B.8.1.2.1.2._CA-103 and in graphical form on figure B.8.1.2.1.2._CA-47.

Table B.8.1.2.1.2._CA-103: The numerical results of the experiment performed on Laacherhof AIII soil.

Radioactivity			Measured on DAT						
			0	3	7	14	28	56	100
In extract [%AR]	Supernatant	Rep. 1	69.2	63.8	63.0	59.0	50.9	37.7	15.0
		Rep 2.	67.2	62.9	60.9	57.0	48.7	35.5	17.2
		Mean	68.4	63.4	61.9	58.0	49.8	36.6	16.1
	Water extract	Rep. 1	21.5	22.2	19.8	18.7	16.0	12.0	7.8
		Rep 2.	20.9	21.8	19.6	18.8	16.1	12.3	6.1
		Mean	21.2	22.0	19.7	18.7	16.1	12.1	7.0
	Organic extract	Rep. 1	8.3	9.3	8.9	9.1	8.4	7.1	4.9
		Rep 2.	8.2	9.0	9.0	9.4	8.2	7.1	4.6
		Mean	8.2	9.1	8.9	9.3	8.3	7.1	4.8
	Total extracted	Rep. 1	99.0	95.3	91.7	86.8	75.3	56.5	27.7
		Rep 2.	96.7	93.7	89.5	85.2	73.0	54.9	27.9
		Mean	97.8	94.4	90.6	86.1	74.1	55.9	27.8
Identified (TLC) as FOE Sulfonic acid [% AR]	Supernatant	Rep. 1	67.7	62.3	62.3	58.7	50.6	37.2	14.6
		Rep 2.	65.7	60.9	60.5	56.2	48.0	35.1	16.5
		Mean	66.7	61.6	61.4	57.5	49.3	36.2	15.5
	Water extract	Rep. 1	20.6	21.9	19.6	18.4	15.6	11.2	7.5
		Rep 2.	20.0	21.4	19.5	18.6	15.7	11.6	5.9
		Mean	20.3	21.7	19.5	18.5	15.7	11.4	6.7
	Organic extract	Rep. 1	7.7	9.2	8.7	8.7	8.0	6.4	3.5
		Rep 2.	7.6	8.9	8.7	8.8	7.9	6.2	3.0
		Mean	7.7	9.1	8.7	8.7	7.9	6.3	3.3
	Total extracted	Rep. 1	96.0	93.5	90.6	85.7	74.2	54.8	25.6
		Rep 2.	93.4	91.2	88.7	83.7	71.6	52.9	25.4
		Mean	94.7	92.3	84.7	84.70	72.9	53.9	25.5
FOE Sulfonic acid recovered [µg/100 g soil]		Rep. 1	12.6	12.2	11.9	11.2	9.7	7.2	3.4
		Rep 2.	12.2	11.9	11.6	11.0	9.4	6.9	3.3
		Mean	12.40	12.09	11.74	11.10	9.55	7.06	3.34
NER fraction [% AR]		Rep. 1	2.4	3.4	4.4	6.2	11.3	17.8	28.3
		Rep 2.	2.2	3.4	6.0	6.8	12.6	19.0	28.5
		Mean	2.2	3.4	5.2	6.5	11.9	18.4	28.4
Total radioactivity recovered [% AR]		Rep. 1	101.3	98.6	96.0	93.1	86.6	74.6	56.0
		Rep 2.	98.7	97.1	95.5	92.1	85.5	73.9	56.5
		Mean	100.0	97.9	95.8	92.6	86.1	74.3	56.2
Theoretical level of mineralisation [% AR] ¹⁾		Rep. 1	0.0	1.4	4.0	6.9	13.4	25.4	44.0
		Rep 2.	0.0	2.9	4.5	7.9	14.5	26.1	43.5
		Mean	0.0	2.1	4.2	7.4	13.9	25.7	43.8

Footnotes to the table:

- 1) The theoretical level of mineralisation calculated by the RMS by subtracting the appropriate value representing the “Total radioactivity recovered” from the theoretical level of applied radioactivity – 100%. For DAT-0 samples that value was set to 0, as for that time point no mineralisation was expected to occur. In cases when the amount of radioactivity recovered at the given time point was higher than 100% the level of would-be mineralisation was also set to zero.

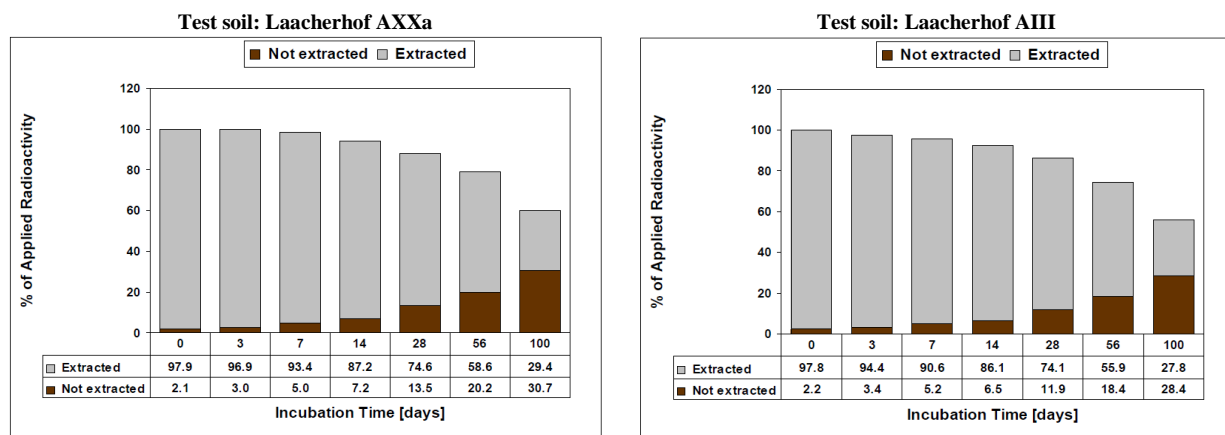


Figure B.8.1.2.1.2._CA-47: The graphical results of the determination of the distribution of radioactivity in the test soils - Laacherhof AXXa (left) and Laacherhof AIII (right); schemes copied from the study report.

The values used to determine Freundlich sorption isotherms are presented below, for both test soils, in the table B.8.1.2.1.2._CA-104. The Log_{10} -transformed concentrations at equilibrium were calculated by the RMS. These values were inserted into the modelling tool – CurveExpert Pro 1.0 in order to determine Freundlich sorption isotherms.

Table B.8.1.2.1.2._CA-104: The results obtained in the study used to determine Freundlich sorption isotherms.

The results obtained in the experiment with the test soil <i>Laacherhof AXXa</i>										
Time point (DAT)	Results obtained for Replicate 1					Results obtained for Replicate 2				
	Total concentration of FOE SA [$\mu\text{g}/100 \text{ g soil}$]	Concentration at equilibrium				Total concentration of FOE SA [$\mu\text{g}/100 \text{ g soil}$]	Concentration at equilibrium			
		In solution		In soil			In solution		In soil	
		C _e [$\mu\text{g}/\text{mL}$]	Log C _e	(x/m) [$\mu\text{g}/\text{g}$]	Log (x/m)		C _e [$\mu\text{g}/\text{mL}$]	Log C _e	(x/m) [$\mu\text{g}/\text{g}$]	Log (x/m)
0	12.2	0.110	-0.9586	0.0120	-1.9208	12.3	0.108	-0.9666	0.0145	-1.8386
3	12.2	0.104	-0.9830	0.0177	-1.7520	12.2	0.105	-0.9788	0.0166	-1.7799
7	11.9	0.103	-0.9872	0.0159	-1.7986	11.7	0.101	-0.9957	0.0160	-1.7959
14	11.1	0.094	-1.0269	0.0166	-1.7799	11.0	0.095	-1.0223	0.0150	-1.8239
28	9.3	0.077	-1.1135	0.0161	-1.7932	9.5	0.080	-1.0969	0.0146	-1.8356
56	7.1	0.059	-1.2291	0.0111	-1.9547	7.5	0.064	-1.1938	0.0110	-1.9586
100	3.5	0.029	-1.5376	0.0061	-2.2147	3.5	0.028	-1.5528	0.0068	-2.1675
The results obtained in the experiment with the test soil <i>Laacherhof AIII</i>										
Time point (DAT)	Results obtained for Replicate 1					Results obtained for Replicate 2				
	Total concentration of FOE SA [$\mu\text{g}/100 \text{ g soil}$]	Concentration at equilibrium				Total concentration of FOE SA [$\mu\text{g}/100 \text{ g soil}$]	Concentration at equilibrium			
		In solution		In soil			In solution		In soil	
		C _e [$\mu\text{g}/\text{mL}$]	Log C _e	(x/m) [$\mu\text{g}/\text{g}$]	Log (x/m)		C _e [$\mu\text{g}/\text{mL}$]	Log C _e	(x/m) [$\mu\text{g}/\text{g}$]	Log (x/m)
0	12.6	0.113	-0.9469	0.0125	-1.9031	12.2	0.109	-0.9626	0.0137	-1.8633
3	12.2	0.107	-0.9706	0.0152	-1.8182	11.9	0.105	-0.9788	0.0149	-1.8268
7	11.9	0.104	-0.9830	0.0145	-1.8386	11.6	0.102	-0.9914	0.0145	-1.8386
14	11.2	0.099	-1.0044	0.0131	-1.8827	11.0	0.095	-1.0223	0.0151	-1.8210
28	9.7	0.084	-1.0757	0.0129	-1.8894	9.4	0.081	-1.0915	0.0125	-1.9031
56	7.2	0.062	-1.2076	0.0096	-2.0177	6.9	0.060	-1.2218	0.0093	-2.0315
100	3.4	0.027	-1.5686	0.0069	-2.1611	3.3	0.030	-1.5229	0.0028	-2.5528

The results of the determination Freundlich sorption isotherms for FOE Sulfonic acid in Laacherhof AXXa and Laacherhof AIII test soils are presented below, in graphical form on figure B.8.1.2.1.2._CA-48 and in numerical form in the table B.8.1.2.1.2._CA-105.

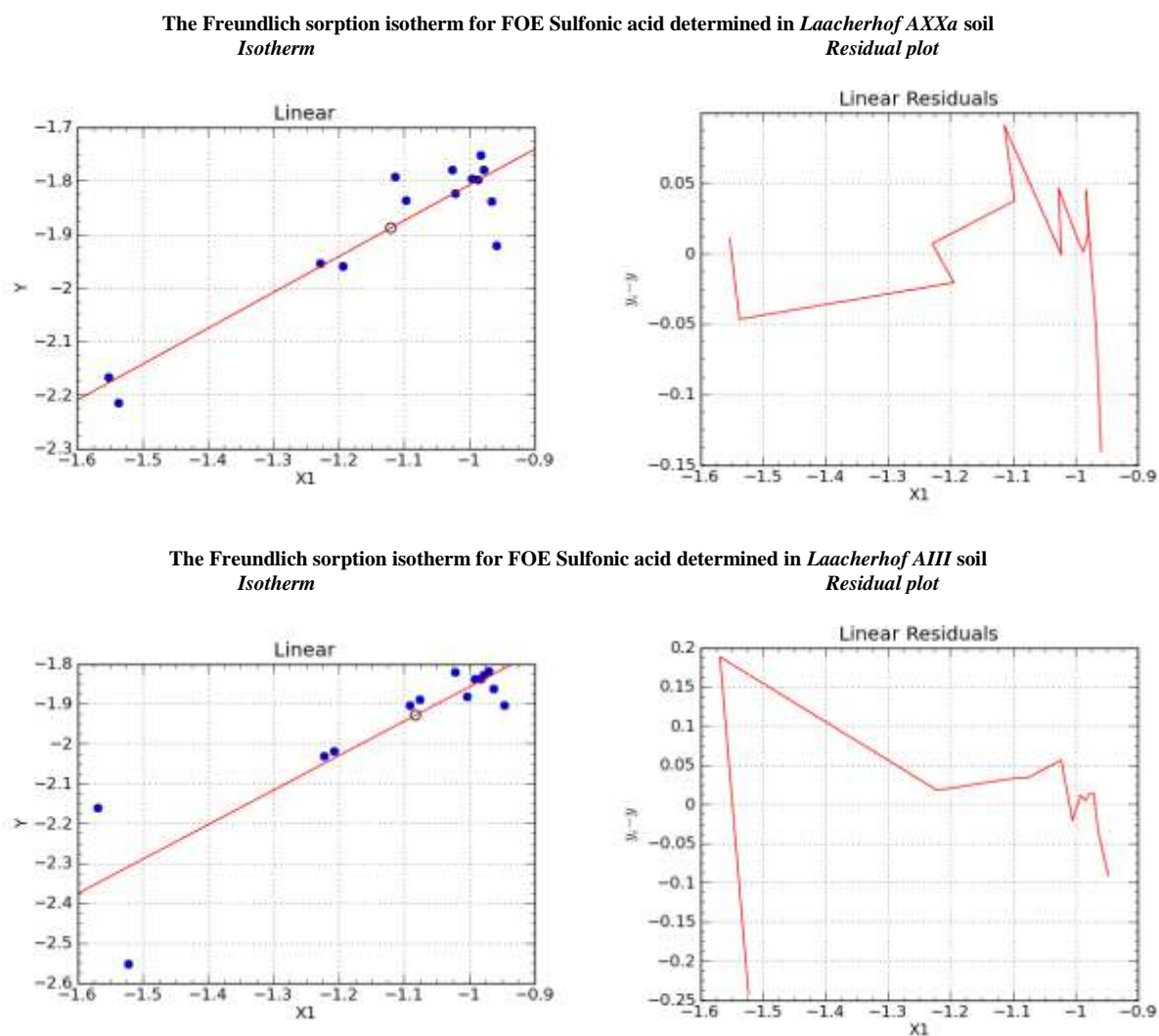


Figure B.8.1.2.1.2._CA-48: The graphical results of the determination of the Freundlich sorption isotherms for FOE Sulfonic acid in Laacherhof AXXa and Laacherhof AIII test soils.

Table B.8.1.2.1.2._CA-104: The numerical results of experiment – the parameters of the Freundlich sorption isotherm for FOE Sulfonic acid in the test soils, determined by the RMS.

Test soil	Parameters of isotherm				Statistical evaluation	
	Log K_F	K_F [mL/g]	$K_{F OC}$ [mL/g]	1/n	SD	Determination coefficient R^2
<i>Laacherhof AXXa</i> <i>Sandy loam</i>	-1.1389	0.073	10.73	0.6693	0.0573	0.8552
<i>Laacherhof AIII</i> <i>Silt loam</i>	-0.9940	0.101	11.48	0.8639	0.0963	0.7830

As indicated at the beginning of the summary the calculated Freundlich sorption isotherm parameters should be considered indicative and not included into the set of EU-agreed endpoints for FOE Sulfonic acid. That is also due to the fact that the quality of the determined isotherms is not fully satisfying.

However, on the basis of these results it may be stated that the adsorption of FOE Sulfonic acid onto soil is not expected to be pH-dependent.

The open-literature search performed by the Applicant and repeated by the RMS did not return any relevant publications in the area of the examination of the Freundlich sorption of the degradation products of Flufenacet onto soil.

As a result of the examination of the fate and behaviour of Flufenacet in the aquatic environment – in aerobic water/sediment systems, an additional degradation product was identified – FOE Methylsulfide. That metabolite was solely aquatic degradation product, not found in any of the experiments examining the transformation of Flufenacet in soil. Probably for that reason in the documentation submitted for evaluation there was no study examining its sorptive behaviour. However, because that degradation product was demonstrated to be a major aquatic metabolite, it is necessary to estimate its adsorption constant for the purpose of the modelling exposure assessment performed for SW compartment.

The Applicant in the study report presenting the substance-specific input parameters used in calculations of PEC_{SW}/PEC_{SED} values for Flufenacet and its major degradation products, proposed the K_{OC} value for FOE Methylsulfide that was determined using PCKOCWIN tool. The reference was provided to the source study report, but the report itself was not submitted for the evaluation. As a result it was not possible to verify the correctness of the determined value.

For that reason RMS decided to perform own estimation of K_{OC} for FOE Methylsulfide using the QSAR methods. The calculations are presented below, in form of a brief summary, as **Study 6**. The full, report of the calculations, provided by the modelling tool used in the estimation – EPISuite, can be found in the Appendix 3 to this Assessment Report

Study 6:

Report: RMS (2016): “Estimation of K_{OC} value for FOE Methylsulfide – a major aquatic metabolite of Flufenacet, using EPISuite tool”; RMS’s internal report;

Guidelines: not applicable.

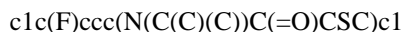
GLP: No, not applicable (modelling exercise);

RMS comments: not applicable

Summary:

The aim of this study was to estimate the K_{OC} value for FOE Methylsulfide – a major aquatic degradation product of Flufenacet, to be subsequently used as a surrogate input value in the SW/SED modelling exposure assessment. The estimation was performed using KOCWIN, a part of EPISuite 4.1 modelling tool.

The estimation was performed for the following SMILES code created for FOE Methylsulfide:



The results of the calculations, as returned by the modelling tool, are presented below

SMILES : c1c(F)ccc(N(C(C)(C))C(=O)CSC)c1

CHEM :

MOL FOR: C12 H16 F1 N1 O1 S1

MOL WT : 241.33

----- EPI SUMMARY (v4.10) -----

Physical Property Inputs:

Water Solubility (mg/L): -----
 Vapor Pressure (mm Hg) : -----
 Henry LC (atm-m3/mole) : -----
 Log Kow (octanol-water): -----
 Boiling Point (deg C) : -----
 Melting Point (deg C) : -----

KOWWIN Program (v1.68) Results:

=====

Log Kow(version 1.68 estimate): 2.77

SMILES : c1c(F)ccc(N(C(C)(C))C(=O)CSC)c1

CHEM :

MOL FOR: C12 H16 F1 N1 O1 S1

MOL WT : 241.33

TYPE	NUM	LOGKOW FRAGMENT DESCRIPTION	COEFF	VALUE
Frag	3	-CH3 [aliphatic carbon]	0.5473	1.6419
Frag	1	-CH2- [aliphatic carbon]	0.4911	0.4911
Frag	1	-CH [aliphatic carbon]	0.3614	0.3614
Frag	6	Aromatic Carbon	0.2940	1.7640
Frag	1	-N [aliphatic N, one aromatic attach]	-0.9170	-0.9170
Frag	1	-F [fluorine, aromatic attach]	0.2004	0.2004
Frag	1	-C(=O)N [aliphatic attach]	-0.5236	-0.5236
Frag	1	-S- [aliphatic attach]	-0.4045	-0.4045
Factor	1	Di-N urea/acetamide aromatic correction	-0.7203	-0.7203
Factor	1	-C-S-C-CO-N- structure correction	0.6500	0.6500
Const		Equation Constant		0.2290

Log Kow = 2.7724

KOCWIN Program (v2.00) Results:

SMILES : c1c(F)ccc(N(C(C)(C))C(=O)CSC)c1

CHEM :

MOL FOR: C12 H16 F1 N1 O1 S1

MOL WT : 241.33

----- KOCWIN v2.00 Results -----

Koc Estimate from MCI:

First Order Molecular Connectivity Index : 7.558
 Non-Corrected Log Koc (0.5213 MCI + 0.60) : 4.5397
 Fragment Correction(s):
 1 Nitrogen to non-fused aromatic ring ... : -0.5225
 1 N-CO-C (aliphatic carbon) : -1.0277
 1 Nitrogen to Carbon (aliphatic) (-N-C).. : -0.2127
 Corrected Log Koc : 2.7767

Estimated Koc: 598 L/kg <=====

Koc Estimate from Log Kow:

Log Kow (Kowwin estimate) : 2.77
 Non-Corrected Log Koc (0.55313 logKow + 0.9251) : 2.4573
 Fragment Correction(s):
 1 Nitrogen to non-fused aromatic ring ... : -0.0216
 1 N-CO-C (aliphatic carbon) : -0.0038
 1 Nitrogen to Carbon (aliphatic) (-N-C).. : -0.0218
 Corrected Log Koc : 2.4101

Estimated Koc: 257.1 L/kg <=====

On the basis of the results presented above the RMS selected the **K_{OC} = 598 L/kg** as a surrogate value to be used as an input parameter for FOE Methylsulfide in SW/SED modelling exposure assessment.

That value is also proposed to be introduced as a surrogate value for FOE Methylsulfide into the List of EndPoints.

Summary: the sorption of the degradation products of Flufenacet onto soil at equilibrium

To cover this data requirement the Applicant submitted four study reports, of which one had already been evaluated for the previous authorisation of Flufenacet in the EU and the remaining three were newly submitted studies. For the purpose of the current assessment these studies were evaluated for their compliance with the provisions of the current Guidelines, in particular the OECD 106 Guideline. All studies were found acceptable, despite the deficiencies they displayed.

The adsorption of FOE Oxalate, FOE Alcohol, FOE Sulfonic acid, FOE Methylsulfoxide and FOE Thiadone onto soil was examined in four US soil. The analysis of their properties showed that in case of one of them – Vero Beach Sand, the OC content was slightly lower than the recommended 0.3% (0.27%). However, it was decided to consider the parameters of the Freundlich sorption isotherms determined in that soil, valid, unless other factors indicated that the isotherm should not be considered reliable. The key results are presented below, individually for each test compound. On their basis it was stated that, according to Briggs' classification, FOE Oxalate and FOE Sulfonic acid should be classified as very mobile/mobile in soil while FOE Thiadone, FOE Alcohol and FOE Methylsulfoxide as intermediately mobile in the same compartment.

The sorption of FOE Methylsulfone onto soil was examined in a separate, newly submitted study, using five test soils – three European and two US soil. The key results of that experiment are presented below in a separate table. On their basis it may be stated that, according to Briggs' classification FOE Methylsulfone displays intermediate mobility in soil.

The soil sorption of Trifluoroacetic acid was examined in another newly submitted study, also using five test soils (three EU and two US soils). The results of that study showed that the compound adsorbed only very weakly, or not at all, onto soil, therefore it is expected to be highly mobile in that compartment. The key results of that experiment are presented in a separate table.

Finally, in the separate, newly submitted, study was examined the sorption of FOE 5043-Trifluoroethane-sulfonic acid. The experiment was performed using five test soils, all originating in the EU. The results of that study showed that also that compound adsorbed only very weakly, or not at all, onto soil, therefore it is expected to be highly mobile in that compartment. The key results of that experiment are presented in a separate table.

Additionally RMS used the results obtained in the study examining time-dependent sorption of FOE Sulfonic acid onto two soils to determine Freundlich sorption isotherms and in that way possibly extend the available data base for that compound. Due to the inadequate quality of the isotherms, the results should only be considered indicative, but the obtained Freundlich sorption constants were in line with those determined for the same compound in the other evaluated study.

Finally, the obtained results demonstrated that for none of the test compounds the soil sorption was pH-dependent.

Table B.8.1.2.1.2._CA-105: The definitive set of Freundlich adsorption and desorption parameters determined for FOE Methylsulfoxide.

Test soil – USDA type (name)	Key soil properties		Freundlich adsorption isotherm parameters			Freundlich desorption isotherm parameters		
	pH ¹⁾	OC [%]	K _F [mL/g]	K _{F OC} [mL/g]	1/n	K _F [mL/g]	K _{F OC} [mL/g]	1/n
<i>Sand (Winder)</i>	5.8	0.27	0.133	49.26	1.059	0.084	31.11	0.630
<i>Sandy loam (Shipshe)</i>	6.3	0.75	0.349	46.53	0.900	0.287	38.27	0.938
<i>Silty clay loam (Drummer)</i>	6.6	2.13	2.042	95.87	0.893	2.576	120.94	0.890
<i>Silty clay (Oska-Martin)</i>	6.0	1.21	5.598	462.64	0.914	6.109	504.88	0.921
Geomean			0.853	100.41	----	0.785	92.34	----
Arithmetic mean			----	----	0.942	----	----	0.845

Footnotes to the table:

1) Measured in water;

Table B.8.1.2.1.2._CA-106: The definitive set of Freundlich adsorption parameters determined for FOE Sulfonic acid.

Test soil – USDA type (name)	Key soil properties		Freundlich adsorption isotherm parameters			Freundlich desorption isotherm parameters		
	pH ¹⁾	OC [%]	K _F [mL/g]	K _{F OC} [mL/g]	1/n	K _F [mL/g]	K _{F OC} [mL/g]	1/n
<i>Sand (Winder)</i>	5.8	0.27	0.051	18.88	0.865	Not determined		
<i>Sandy loam (Shipshe)</i>	6.3	0.75	0.106	14.13	1.002	Not determined		
<i>Silty clay loam (Drummer)</i>	6.6	2.13	0.204	9.58	0.931	Not determined		
<i>Silty clay (Oska-Martin)</i>	6.0	1.21	0.072	5.95	1.183	Not determined		
Geomean			0.094	11.10	----	Not determined		
Arithmetic mean			----	----	0.995	Not determined		

Footnotes to the table:

1) Measured in water;

Table B.8.1.2.1.2._CA-107: The definitive set of Freundlich adsorption and desorption parameters determined for FOE Oxalate.

Test soil – USDA type (name)	Key soil properties		Freundlich adsorption isotherm parameters			Freundlich desorption isotherm parameters		
	pH ¹⁾	OC [%]	K _F [mL/g]	K _{F OC} [mL/g]	1/n	K _F [mL/g]	K _{F OC} [mL/g]	1/n
<i>Sandy loam (Shipshe)</i>	6.3	0.75	09.096	12.80	0.933	Not determined		
<i>Silty clay loam (Drummer)</i>	6.6	2.13	0.153	7.18	0.824	Not determined		
<i>Silty clay (Oska-Martin)</i>	6.0	1.21	0.157	12.97	0.978	Not determined		
Geomean			0.132	10.60	----	Not determined		
Arithmetic mean			----	----	0.912	Not determined		

Footnotes to the table:

1) Measured in water;

Table B.8.1.2.1.2._CA-108: The definitive set of Freundlich adsorption and desorption parameters determined for FOE Alcohol.

Test soil – USDA type (name)	Key soil properties		Freundlich adsorption isotherm parameters			Freundlich desorption isotherm parameters		
	pH ¹⁾	OC [%]	K _F [mL/g]	K _{F OC} [mL/g]	1/n	K _F [mL/g]	K _{F OC} [mL/g]	1/n
<i>Sand (Winder)</i>	5.8	0.27	0.226	83.70	0.947	0.395	52.67	0.946
<i>Sandy loam (Shipshe)</i>	6.3	0.75	0.780	104.00	0.887	1.384	184.53	0.970
<i>Silty clay loam (Drummer)</i>	6.6	2.13	2.018	94.74	0.940	3.191	149.81	1.142
<i>Silty clay (Oska-Martin)</i>	6.0	1.21	3.802	314.21	0.950	3.917	323.72	0.986
Geomean			1.078	126.88	----	1.617	147.35	----
Arithmetic mean			----	----	0.931	----	----	1.011

Footnotes to the table:

1) Measured in water;

Table B.8.1.2.1.2._CA-109: The definitive set of Freundlich adsorption and desorption parameters determined for FOE Thiadone.

Test soil – USDA type (name)	Key soil properties		Freundlich adsorption isotherm parameters			Freundlich desorption isotherm parameters		
	pH ¹⁾	OC [%]	K _F [mL/g]	K _{F OC} [mL/g]	1/n	K _F [mL/g]	K _{F OC} [mL/g]	1/n
<i>Sand (Winder)</i>	5.8	0.27	0.115	42.59	0.781	0.467	172.96	0.909
<i>Sandy loam (Shipshe)</i>	6.3	0.75	0.332	44.27	0.806	1.368	182.40	0.867
<i>Silty clay loam (Drummer)</i>	6.6	2.13	0.611	28.68	0.672	1.559	73.91	0.654
<i>Silty clay (Oska-Martin)</i>	6.0	1.21	0.703	58.10	0.796	2.104	173.88	0.887
Geomean			0.358	42.10	----	1.203	141.90	----
Arithmetic mean			----	----	0.764	----	----	0.829

Footnotes to the table:

1) Measured in water;

Table B.8.1.2.1.2._CA-110: The definitive set of Freundlich adsorption and desorption parameters determined for FOE Methylsulfone.

Test soil – USDA type (name)	Key soil properties		Freundlich adsorption isotherm parameters			Freundlich desorption isotherm parameters		
	pH ¹⁾	OC [%]	K _F [mL/g]	K _{F OC} [mL/g]	1/n	K _F [mL/g]	K _{F OC} [mL/g]	1/n
<i>Loam (Wurmwiese)</i>	5.5	1.8	0.658	37.4	0.891	0.769	43.7	0.898
<i>Silt loam (Höfchen am Hohenseh 4a)</i>	6.8	2.4	1.280	52.9	0.888	1.467	60.6	0.893
<i>Clay loam (Dollendorf II)</i>	7.4	4.6	1.569	33.2	0.900	1.820	38.6	0.912
<i>Sandy loam (Guadalupe, CA)</i>	6.8	0.7	0.525	75.0	0.910	0.567	81.0	0.905
<i>Silt loam (Springfield, NE)</i>	7.2	1.7	2.920	171.8	0.860	3.594	211.4	0.883
Geomean			1.152	61.03	----	1.332	70.57	----
Arithmetic mean			----	----	0.860	----	----	0.898

Footnotes to the table:

1) Measured in water;

Table B.8.1.2.1.2._CA-111: The definitive set of Freundlich adsorption parameters determined for Trifluoroacetic acid.

Test soil – USDA type (name)	Key soil properties		Freundlich adsorption isotherm parameters			Freundlich desorption isotherm parameters		
	pH ¹⁾	OC [%]	K _F [mL/g]	K _{F OC} [mL/g]	1/n	K _F [mL/g]	K _{F OC} [mL/g]	1/n
<i>Loam (Wurmwiese)</i>	5.5	1.8	0.0	0.0001	1.0	Not determined		
<i>Silt loam (Höfchen am Hohenseh 4a)</i>	6.8	2.4	0.0	0.0001	1.0	Not determined		
<i>Clay loam (Dollendorf II)</i>	7.4	4.6	0.0	0.0001	1.0	Not determined		
<i>Sandy loam (Guadalupe, CA)</i>	6.8	0.7	0.0	0.0001	1.0	Not determined		
<i>Silt loam (Springfield, NE)</i>	7.2	1.7	0.0	0.0001	1.0	Not determined		
Geomean			0.0	0.0001	----	Not determined		
Arithmetic mean			----	----	1.0	Not determined		

Footnotes to the table:

1) Measured in water;

Table B.8.1.2.1.2._CA-112: The definitive set of Freundlich adsorption parameters determined for FOE 5043-Trifluoroethanesulfonic acid.

Test soil – USDA type (name)	Key soil properties		Freundlich adsorption isotherm parameters			Freundlich desorption isotherm parameters		
	pH ¹⁾	OC [%]	K _F [mL/g]	K _{F OC} [mL/g]	1/n	K _F [mL/g]	K _{F OC} [mL/g]	1/n
<i>Loamy sand (Laacher Hof AXXa)</i>	6.6	1.8	0.0	0.0001	1.0	Not determined		
<i>Silt loam (Höfchen am Hohenseh 4a)</i>	6.7	1.7	0.0	0.0001	1.0	Not determined		
<i>Silt loam (Hanscheider Hof)</i>	5.3	2.8	0.0	0.0001	1.0	Not determined		
<i>Loam (Dollendorf II)</i>	7.5	5.0	0.0	0.0001	1.0	Not determined		
<i>Sandy loam (Wurmwiese)</i>	5.4	1.9	0.0	0.0001	1.0			
Geomean			0.0	0.0001	----	0.0001		
Arithmetic mean			----	----	1.0	----		

Footnotes to the table:

1) Measured in water;

Additionally the surrogate K_{OC} value was estimated for FOE Methylsulfide – an aquatic major degradation product of Flufenacet. That was done using KOCWIN tool – a part of the EPISuite 4.1 tool. The estimated value (determined by RMS) is **K_{OC} = 598 L/kg**. That value is proposed to be used as an input parameter in the SW/SED model exposure assessment and to be reported in the EU-agreed List of EndPoints as a surrogate value for that compound.

B.8.1.2.2. – Aged sorption

The Applicant submitted one study report addressing the problem of aged sorption in soil. The report examined the phenomenon of the aged sorption of FOE Sulfonic acid – one of the major degradation products of Flufenacet in aerobic soil. The results of that study have already been used twice in this Renewal Assessment Report – as the data enabling the determination of the degradation kinetics of FOE Sulfonic acid in aerobic soils (**Study 10** and **Study 13** summarised under the point B.8.1.1.2.1.1) and to estimate Freundlich adsorption parameters in alkaline soils (**Study 5** under the point B.8.1.2.1.2). For that reason RMS decided not to provide its extended summary. Instead, in the short summary provided below are presented its key results – the determined K_d and K_{dOC} values in function of time.

Study 1:

Report: Hellpointner E., (2003): “Time-Dependent Sorption of FOE5043-Sulfonic Acid in Soil.”; Bayer Crop Science AG, Development – Global Regulatory Affairs, D-40789 Monheim, Germany; unpublished study Report No. MEF-229/03; 2003-10-13; study reference number: M-111445-01-1;

Guidelines: Due to the aims of the study – examination of the time-dependent sorption of FOE Sulfonic acid, it was declared to be performed in such way, to comply with the foillowing Guidelines:

- examination of soil sorption of the test compound: OECD Guideline for Testing of Chemicals No. 106, Adsorption and Desorption;
- in the area of incubation of the test flasks – ageing and processing of test soils:
 - BBA Guidelines for the Official Testing of Plant Protectants, Part IV, 4-1 (1986);
 - SETAC-Europe Procedures for Assessing the Environmental Fate and Ecotoxicology of Pesticides (*ed.* Mark Lynch), March 1995;
 - US. EPA Guideline 162-1 Aerobic Soil Metabolism (supplemental);

GLP: Yes

RMS comments: This is a newly submitted study. Its was to examine the time-dependent sorption of FOE Sulfonic acid in soil. The study had already been evaluated, and found acceptable, with regard to its aspects aimed on the examination of the rate of degradation of the test compound in aerobic soils. At present the study was evaluated for its compliance with the following guideline:

- OECD Guideline for Testing of Chemicals No. 106, Adsorption and Desorption; to determine its suitability for the determination of Freundlich sorption isotherm for FOE Sulfonic acid in each test soil.

It was verified by the RMS and found acceptable in the area of the examination of the equilibrium sorption of FOE Sulfonic acid onto soil. Its extended summary in the area of the examination of soil sorption at equilibrium was presented above, under the point B.8.1.2.1.2. as **Study 5**. Therefore this summary contains only brief characteristic of the soils used in the experiment, test item, and the key results regarding soil sorption – the K_d and K_{dOC} values in function of time. The numeration of the figures and graphs is continuous in relation to this section of the Assessment Report.

Summary:

The aim of the study was to examine the phenomenon of the time-dependent sorption, i.e. increase with time of the K_{OC} value, of FOE Sulfonic acid onto soil. That was done in order to clarify the reasons for the observed discrepancies of the results of different studies, namely:

- high mobility and leaching potential of FOE Sulfonic acid in soil, demonstrated by the results of the batch equilibrium sorption studies – average K_{OC} = 12.5 mL/g, and modelling GW exposure assessment, with PEC_{GW} for cereals in range of 3.1 – 9.2 µg/L;
- moderate concentrations of the compound in lysimeter studies – up to 1.69 µg/L in the average 1st year leachates when the compound was applied twice in the same year;
- the fact stated in the regulatory study by Hellpointner [1999], examining the degradation of FOE Sulfonic acid in soil (summarised under the point B.8.1.1.2.1.1. as **Study 9**), that the compound was not as easily extracted from soil, especially at later time points, as it might be suggested by its K_{OC} value.

The experiment was performed using the [Phenyl-U-¹⁴C] FOE Sulfonic acid in form of ammonium salt. Its structural formula is presented below on figure B.8.1.2.2._CA-1. The specific activity of the test compound was 2.66 MBq/mg (21.0 mCi/mMole) and its radiochemical purity was 98%.

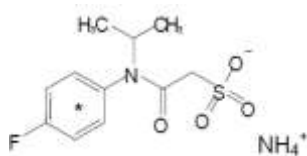


Figure B.8.1.2.2._CA-1: The structural formula of the test compound (copied from the study report).

Two test soils were used in the study. The soil were freshly sampled, shortly before the beginning of the experiment, from the 0-20 cm layer. Their characteristic is presented below in the table B.8.1.2.2._CA-1.

Table B.8.1.2.2._CA-1: The characteristic of soils used in the study.

Parameter		Soil	
		<i>Laacherhof AXXa</i>	<i>Laacherhof AIII</i>
Soil origin		Monheim, Germany	Monheim, Germany
Soil type (USDA)		Sandy loam	Silt loam
Particle size distribution	Sand (50 µm – 2 mm) [%]	72.4	36.9
	Silt (2 – 50 µm) [%]	22.6	51.1
	Clay (< 2 µm) [%]	5.0	12.0
pH value in CaCl ₂		6.3	6.8
pH value in H ₂ O		6.9	7.6
pH value in KCl		6.3	7.2
Organic carbon content (OC) [%]		1.47	0.88
Organic matter content (OM) [%]		2.53	1.51
Cation Exchange Capacity – CEC [mEq/100g]		10.3	9.8
Water holding capacity	Max. [g H ₂ O/100 g soil]	34.42	36.40
	In air-dried and sieved soil [%]	8.62	7.22
Bulk density [g/cm ³]		2.5	2.55
Soil microbial biomass [mg microbial C/kg soil]	At start of incubation period – DAT 0	242	275
	At the end of incubation period – DAT 100	209	195
Soil microbial biomass [% OC] ¹⁾	At start of incubation period – DAT 0	1.65	3.13
	At the end of incubation period – DAT 100	1.42	2.22

Footnotes to the table:

1) Value calculated by the RMS.

In the laboratory the test soils were air-dried and sieved to a particle size ≤ 2 mm. Then the soil moisture content was measured in sieved soil by drying it at 105⁰C and determining the loss of weight.

The whole analytical procedure has been characterised when the study was summarised under the point B.8.1.2.1.2. of this Renewal Assessment Report as **Study 5**. That summary can be found on pages 961 – 973 of the Report.

Results and their discussion:

The detailed results of the study and their discussion were presented when it was summarised under the point B.8.1.2.1.2. of this Renewal Assessment Report as **Study 5**. That summary can be found on pages 961 – 973 of the Report.

The key results of the examination of time-dependent sorption of FOE Sulfonic acid onto the test soils are presented below in two tables – B.8.1.2.2._CA-2 for the test soil Laacherhof AXXa and B.8.1.2.2._CA-3 for the test soil Laacherhof AIII.

Table B.8.1.2.2._CA-2: The key results of the examination of the time-dependent sorption of FOE Sulfonic acid onto **Lacherhof AXXa** test soil.

Time point (DAT)	Obtained results									
	Replicate 1				Replicate 2				Averaged sorption parameters	
	Concentration at equilibrium		Sorption parameters		Concentration at equilibrium		Sorption parameters			
	C _e [µg/mL]	(x/m) [µg/g]	K _d [mL/g]	K _{d oc} [mL/g]	C _e [µg/mL]	(x/m) [µg/g]	K _d [mL/g]	K _{d oc} [mL/g]		
0	0.110	0.0120	0.11	7	0.108	0.0145	0.13	9	0.12	8
3	0.104	0.0177	0.17	12	0.105	0.0166	0.16	11	0.16	11
7	0.103	0.0159	0.15	11	0.101	0.0160	0.16	11	0.16	11
14	0.094	0.0166	0.18	12	0.095	0.0150	0.16	11	0.17	11
28	0.077	0.0161	0.21	14	0.080	0.0146	0.18	12	0.20	13
56	0.059	0.0111	0.19	13	0.064	0.0110	0.17	12	0.18	12
100	0.029	0.0061	0.21	14	0.028	0.0068	0.25	17	0.23	16

Table B.8.1.2.2._CA-3: The key results of the examination of the time-dependent sorption of FOE Sulfonic acid onto **Lacherhof AIII** test soil.

Time point (DAT)	Obtained results									
	Replicate 1				Replicate 2				Averaged sorption parameters	
	Concentration at equilibrium		Sorption parameters		Concentration at equilibrium		Sorption parameters			
	C _e [µg/mL]	(x/m) [µg/g]	K _d [mL/g]	K _{d oc} [mL/g]	C _e [µg/mL]	(x/m) [µg/g]	K _d [mL/g]	K _{d oc} [mL/g]		
0	0.113	0.0125	0.11	13	0.109	0.0137	0.13	14	0.12	13
3	0.107	0.0152	0.14	16	0.105	0.0149	0.14	16	0.14	16
7	0.104	0.0145	0.14	16	0.102	0.0145	0.14	16	0.14	16
14	0.099	0.0131	0.13	15	0.095	0.0151	0.16	18	0.15	17
28	0.084	0.0129	0.15	17	0.081	0.0125	0.15	18	0.15	17
56	0.062	0.0096	0.15	17	0.060	0.0093	0.15	18	0.15	18
100	0.027	0.0069	0.26	30	0.030	0.0028	0.09	11	0.18	20

The Applicant calculated the increase factor for K_{d OC} during ageing period. In case of the experiment carried out with Laacherhof AXXa soil this factor was 2, while for the experiment on the Laacherhof AIII soil it was 1.5. At the same time it was stated that although the increase of the sorption strength was observed, the obtained sorption coefficients indicate that the classification of test compound – FOE Sulfonic acid, with regard to its mobility in soil remains unchanged – the compound should be classified as mobile according to Briggs' and Verdam et al.'s classification criteria.

The corresponding kinetic endpoints determined for FOE Sulfonic acid in each test soil, reported for completeness, are following:

- in Laacherhof AXXa Sandy loam soil: the not normalised (persistence) DT₅₀ = 62.31 days and the normalised (modelling) DT₅₀ = 49.85 days;
- in Laacherhof AIII Silt loam soil: the not normalised (persistence) DT₅₀ = 60.26 days and the normalised (modelling) DT₅₀ = 40.37 days.

B.8.1.2.3. – Summary: adsorption and desorption in soil

The sorption of Flufenacet onto soil at equilibrium was extensively examined in four studies using fourteen test soils. The results of that examination were used to obtain Freundlich sorption isotherms for adsorption and desorption processes and to derive Freundlich sorption isotherm parameters. In case of adsorption reliable parameters of Freundlich isotherm were obtained for ten test soils, while for desorption the reliable Freundlich parameters were derived using nine test soils. They are presented below in two tables: B.8.1.2.3._CA-1 for adsorption and B.8.1.2.3._CA-2 for desorption. The results obtained for adsorption indicate that Flufenacet is moderately to strongly sorbed onto soil and that the process is not preferential. It was also determined that it was not pH-dependent.

Table B.8.1.2.3._CA-1: The results of the determination of the adsorption of Flufenacet onto soil at equilibrium – the reliable parameters of the Freundlich adsorption isotherm.

Soil name	Soil properties			Adsorption distribution coefficients		Freundlich adsorption isotherm parameters			
	Soil type (USDA)	pH	OC [%]	K_d [mL/g]	$K_{d oc}$ [mL/g]	K_f [mL/g]	$K_{f oc}$ [mL/g]	1/n	R^2
<i>Stanley (307)</i>	Silt loam	5.9	1.68	----	----	3.18	189.28	0.848	0.9971
<i>Hagerstown (318)</i>	Clay loam	6.4	1.28	----	----	2.81	219.53	0.878	0.9986
<i>Howe (395)</i>	Loamy sand	6.4	0.23	----	----	1.48	643.48	0.894	0.9932
<i>Monheim (3253)</i>	Sandy loam	6.4	1.4	----	----	4.55	325.00	0.920	0.9991
<i>Laacher Hof AXXa (AA)</i>	Loamy sand	5.8	2.2	----	----	3.55	161.6	0.928	0.9991
<i>Hoefchen am Hohenseh (HH)</i>	Silt loam	6.5	1.6	----	----	3.28	205.0	0.926	0.9965
<i>Hanscheider Hof (HN)</i>	Silt loam	5.3	2.7	----	----	5.10	188.9	0.926	0.9992
<i>Dollendorf II (DD)</i>	Loam	7.3	4.4	----	----	7.49	178.5	0.903	0.9994
<i>Wurmweise (WW)</i>	Sandy loam	5.1	1.7	----	----	3.39	195.2	0.980	0.9966
<i>Kamikawa</i>	Loam	4.9	2.1	----	----	8.96	426.5	0.958	0.9984
Geomean (n = 10)						3.89	245.9	----	----
Arithmetic mean (n = 10)						----	----	0.916	----
pH dependence						No			----

Table B.8.1.2.3._CA-2: The results of the determination of the desorption of Flufenacet onto soil at equilibrium – the reliable parameters of the Freundlich desorption isotherm.

Soil name	Soil properties			Desorption distribution coefficients		Freundlich desorption isotherm parameters			
	Soil type (USDA)	pH	OC [%]	K_d [mL/g]	$K_{d oc}$ [mL/g]	K_f [mL/g]	$K_{f oc}$ [mL/g]	1/n	R^2
<i>Stanley (307)</i>	Silt loam	5.9	1.68	----	----	3.81	226.79	0.864	0.9998
<i>Hagerstown (318)</i>	Clay loam	6.4	1.28	----	----	2.75	214.84	0.893	0.9996
<i>Howe (395)</i>	Loamy sand	6.4	0.23	----	----	2.10	913.04	0.911	0.9992
<i>Monheim (3253)</i>	Sandy loam	6.4	1.4	----	----	5.25	375.00	0.928	0.9993
<i>Laacher Hof AXXa (AA)</i>	Loamy sand	5.8	2.2	----	----	5.58	253.6	0.944	0.9988
<i>Hoefchen am Hohenseh (HH)</i>	Silt loam	6.5	1.6	----	----	5.64	352.3	0.943	0.9980
<i>Hanscheider Hof (HN)</i>	Silt loam	5.3	2.7	----	----	8.49	314.4	0.937	0.9996
<i>Dollendorf II (DD)</i>	Loam	7.3	4.4	----	----	11.71	278.7	0.908	0.9996
<i>Wurmweise (WW)</i>	Sandy loam	5.1	1.7	----	----	5.49	349.4	0.989	0.9967
Geomean (n = 9)						5.01	329.38	----	----
Arithmetic mean (n = 9)						----	----	0.924	----
pH dependence						No			----

The additional information on the soil sorption of Flufenacet at equilibrium were provided by three open-literature scientific papers. The key results obtained in them are presented below in the table B.8.1.2.3._CA-3. The values reported below may be considered as indicative and should not be used to derive the regulatory endpoints characterising soil sorption of Flufenacet.

Table B.8.1.2.3._CA-3: The results of the determination of the adsorption of Flufenacet onto soil at equilibrium obtained in the open-source literature scientific papers.

Study	Soil name	Soil properties			Freundlich adsorption isotherm parameters			
		Soil type	pH	OC [%]	K_f [mL/g]	K_{foc} [mL/g]	1/n	r
<i>Gupta, Gajbhiye & Agnihotri; 2001</i>	<i>Inceptisol</i>	Sandy loam	7.1	0.34	2.26	664.71	0.988	0.99
<i>Gajbhiye & Gupta; 2001</i>	<i>Delhi</i>	Loamy sand	7.69	0.501	2.10	419.16	0.996	0.99
	<i>Ranchi</i>	Sandy clay loam	5.54	0.042	3.62	8619.05	0.981	0.98
	<i>Nagpur</i>	Clay	8.35	0.399	3.20	802.00	1.221	0.99
	<i>Kerala</i>	Sandy clay loam	4.45	0.456	4.39	962.72	1.015	0.99
<i>Rouchaud, Neus, Eelen, Bulcke; 2001</i>	<i>Melle</i>	Sandy loam	7.0	1.51 ¹⁾	16	1802	0.89	----
	<i>Zingem</i>	Loamy sand	6.4	1.60 ¹⁾	43	4602	0.91	----
	<i>Zevekote</i>	Clay loam	6.6	2.1 ¹⁾	15	1231	0.93	----
	<i>Cortil-Noirmont</i>	Silt loam	6.7	1.2 ¹⁾	9	1257	0.94	----

Footnotes to the table:

1) OM content reported, no values for OC content

In the studies by [Gupta, Gajbhiye and Agnihotri; 2001] and [Gajbhiye and Gupta; 2001] for adsorption of Flufenacet onto test soil the value of the free Gibbs energy of adsorption – ΔG , was determined. It was in range $\Delta G = (-3.27) - (-5.08)$ [Kcal/mol], indicating that adsorption of Flufenacet onto soil was a spontaneous process and mechanistically it was predominantly physisorption. It was also demonstrated, in the study by [Gupta, Gajbhiye and Agnihotri; 2001], that the soil sorption of Flufenacet was strongly positively correlated with soil OC/OM content. As the results obtained in these two studies are in line with those from reliable regulatory studies, that conclusion may be considered to be a general conclusion with regard to the adsorption of Flufenacet onto soil.

Also examined was sorption onto soil at equilibrium of major soil degradation products of Flufenacet: FOE Oxalate, FOE Sulfonic acid, FOE Methylsulfone, FOE Thiadone, FOE 5043-Trifluoroethanesulfonic acid (FOE TFESA) and Trifluoroacetic acid (TFA). The key results – Freundlich sorption parameters, are presented below, individually for each test compound.

For FOE Oxalate the reliable Freundlich isotherm parameters for adsorption were determined in three test soils. The desorption was not examined because of the low level of adsorption onto soil. The results are presented below in the table B.8.1.2.3._CA-4.

Table B.8.1.2.3._CA-4: The Freundlich adsorption and desorption parameters determined for FOE Oxalate.

Test soil – USDA type (name)	Key soil properties		Freundlich adsorption isotherm parameters			Freundlich desorption isotherm parameters		
	pH ¹⁾	OC [%]	K_F [mL/g]	K_{FOC} [mL/g]	1/n	K_F [mL/g]	K_{FOC} [mL/g]	1/n
<i>Sandy loam (Shipshe)</i>	6.3	0.75	0.096	12.80	0.933	Not determined		
<i>Silty clay loam (Drummer)</i>	6.6	2.13	0.153	7.18	0.824	Not determined		
<i>Silty clay (Oska-Martin)</i>	6.0	1.21	0.157	12.97	0.978	Not determined		
Geomean (n = 3)			0.132	10.60	----			
Arithmetic mean (n = 3)			----	----	0.912			
pH dependence			No					

Footnotes to the table:

1) Measured in water;

For FOE Sulfonic acid the reliable Freundlich isotherm parameters for adsorption were determined in four test soils. The desorption was not examined because of the low level of adsorption onto soil. The results are presented below in the table B.8.1.2.3._CA-5.

Table B.8.1.2.3._CA-5: The Freundlich adsorption and desorption parameters determined for FOE Sulfonic acid.

Test soil – USDA type (name)	Key soil properties		Freundlich adsorption isotherm parameters			Freundlich desorption isotherm parameters		
	pH ¹⁾	OC [%]	K _F [mL/g]	K _F OC [mL/g]	1/n	K _F [mL/g]	K _F OC [mL/g]	1/n
<i>Sand (Winder)</i>	5.8	0.27	0.051	18.88	0.865	Not determined		
<i>Sandy loam (Shipshe)</i>	6.3	0.75	0.106	14.13	1.002	Not determined		
<i>Silty clay loam (Drummer)</i>	6.6	2.13	0.204	9.58	0.931	Not determined		
<i>Silty clay (Oska-Martin)</i>	6.0	1.21	0.072	5.95	1.183	Not determined		
Geomean (n = 4)			0.094	11.10	----			
Arithmetic mean (n = 4)			----	----	0.995			
pH dependence			No					

Footnotes to the table:

1) Measured in water;

For FOE Methylsulfone reliable Freundlich isotherm parameters for adsorption and desorption were determined in five test soils. The results are presented below in the table B.8.1.2.3._CA-6.

Table B.8.1.2.3._CA-6: The of Freundlich adsorption and desorption parameters determined for FOE Methylsulfone.

Test soil – USDA type (name)	Key soil properties		Freundlich adsorption isotherm parameters			Freundlich desorption isotherm parameters		
	pH ¹⁾	OC [%]	K _F [mL/g]	K _F OC [mL/g]	1/n	K _F [mL/g]	K _F OC [mL/g]	1/n
<i>Loam (Wurmwiese)</i>	5.5	1.8	0.658	37.4	0.892	0.769	43.7	0.898
<i>Silt loam (Hoefchen am Hohenseh)</i>	6.8	2.4	1.280	52.9	0.888	1.467	60.6	0.893
<i>Clay loam (Dollendorf II)</i>	7.4	4.6	1.569	33.2	0.900	1.820	38.6	0.912
<i>Sandy loam (Guadalupe)</i>	6.8	0.7	0.525	75.0	0.910	0.567	81.0	0.905
<i>Silt loam (Springfield)</i>	7.2	1.7	2.920	171.8	0.860	3.594	211.4	0.883
Geomean (n = 5)			1.152	61.03	----	1.332	70.57	----
Arithmetic mean (n = 5)			----	----	0.860	----	----	0.898
pH dependence			No			No		

Footnotes to the table:

1) Measured in water;

For FOE Thiadone the reliable Freundlich isotherm parameters for adsorption and desorption were determined in four test soils. The results are presented below in the table B.8.1.2.3._CA-7.

Table B.8.1.2.3._CA-7: The of Freundlich adsorption and desorption parameters determined for FOE Thiadone.

Test soil – USDA type (name)	Key soil properties		Freundlich adsorption isotherm parameters			Freundlich desorption isotherm parameters		
	pH ¹⁾	OC [%]	K _F [mL/g]	K _{F OC} [mL/g]	1/n	K _F [mL/g]	K _{F OC} [mL/g]	1/n
<i>Sand (Winder)</i>	5.8	0.27	0.115	42.59	0.781	0.467	172.96	0.909
<i>Sandy loam (Shipshe)</i>	6.3	0.75	0.332	44.27	0.806	1.368	182.40	0.867
<i>Silty clay loam (Drummer)</i>	6.6	2.13	0.611	28.68	0.672	1.559	73.91	0.654
<i>Silty clay (Oska-Martin)</i>	6.0	1.21	0.703	58.10	0.796	2.104	173.88	0.887
Geomean (n = 4)			0.358	42.10	----	1.203	141.90	----
Arithmetic mean (n = 4)			----	----	0.764	----	----	0.829
pH dependence			No			No		

Footnotes to the table:

1) Measured in water;

For Trifluoroacetic acid Freundlich isotherm parameters for adsorption were determined in five test soils. The desorption was not examined because of the very low level of adsorption onto soil. The results are presented below in the table B.8.1.2.3._CA-8.

Table B.8.1.2.3._CA-8: The of Freundlich adsorption and desorption parameters determined for Trifluoroacetic acid.

Test soil – USDA type (name)	Key soil properties		Freundlich adsorption isotherm parameters			Freundlich desorption isotherm parameters		
	pH ¹⁾	OC [%]	K _F [mL/g]	K _{F OC} [mL/g]	1/n	K _F [mL/g]	K _{F OC} [mL/g]	1/n
<i>Loam (Wurmwiese)</i>	5.5	1.76	0.0	0.0001	1.00	Not determined		
<i>Silt loam (Hoefchen am Hohenseh)</i>	6.8	2.42	0.0	0.0001	1.00	Not determined		
<i>Clay loam (Dollendorf II)</i>	7.4	4.72	0.0	0.0001	1.00	Not determined		
<i>Sandy loam (Guadalupe)</i>	6.8	0.7	0.0	0.0001	1.00	Not determined		
<i>Silt loam (Springfield)</i>	7.2	1.7	0.0	0.0001	1.00	Not determined		
Geomean (n = 5)			0.0	0.0001	----			
Arithmetic mean (n = 5)			----	----	1.00			
pH dependence			No					

Footnotes to the table:

1) Measured in water;

For FOE 5043-Trifluoroethanesulfonic acid reliable Freundlich isotherm parameters for adsorption were determined in five test soils. The desorption was not examined because of the very low level of adsorption onto soil. The results are presented below in the table B.8.1.2.3._CA-9.

Table B.8.1.2.3._CA-9: The of Freundlich adsorption and desorption parameters determined for FOE 5043-Trifluoroethanesulfonic acid.

Test soil – USDA type (name)	Key soil properties		Freundlich adsorption isotherm parameters			Freundlich desorption isotherm parameters		
	pH ¹⁾	OC [%]	K _F [mL/g]	K _{F OC} [mL/g]	1/n	K _F [mL/g]	K _{F OC} [mL/g]	1/n
<i>Loamy sand (Laacher Hof AXXa)</i>	6.6	1.8	0.0	0.0001	1.00	Not determined		
<i>Silt loam (Hoefchen am Hohenseh)</i>	6.7	1.7	0.0	0.0001	1.00	Not determined		
<i>Slit loam (Hnascheider Hof)</i>	5.3	2.8	0.0	0.0001	1.00	Not determined		
<i>Loam (Dollendorf II)</i>	7.5	5.0	0.0	0.0001	1.00	Not determined		
<i>Sandy loam (Wurmweise)</i>	5.4	1.9	0.0	0.0001	1.00	Not determined		
Geomean (n = 5)			0.0	0.0001	----			
Arithmetic mean (n = 5)			----	----	1.00			
pH dependence			No					

Footnotes to the table:

1) Measured in water;

The results showed that FOE Methylsulfone and FOE Thiadone were moderately sorbed onto soil. FOE Oxalate and FOE Sulfonic acid were only weakly sorbed onto soil, while FOE 5043-Trifluoroethanesulfonic acid and Trifluoroacetic acid were practically not sorbed onto soil. No pH-dependence of the adsorption was stated for any of the degradation products, but in case of FOE Thiadone, FOE Sulfonic acid and FOE Oxalate that may be due to the limited number of soils used in the experiment as well as their narrow pH range.

Additionally for FOE Methylsulfide – major aquatic degradation product of Flufenacet, the K_{OC} value was estimated using KOCWIN – a part of EPISuite 4.1 modelling tool. The estimated value is **K_{OC} = 598 L/kg** and is recommended to be used as an input value in SW/SED model exposure assessment.

For FOE Sulfonic acid the additional examination of the soil sorption in function of time – time-dependent sorption, was performed. The key results of that examination – adsorption parameters in function of time, are provided below in the table B.8.1.2.3._CA-10.

Table B.8.1.2.3._CA-10: The key results of the examination of the time-dependent sorption of FOE Sulfonic acid onto soil.

Results obtained for <i>Laacherhof AXXa</i> test soil					Results obtained for <i>Laacherhof AIII</i> test soil				
Soil key properties		Results			Soil key properties		Results		
Parameter	Value	Time point [DAT]	K _d [mL/g]	K _{d OC} [mL/g]	Parameter	Value	Time point [DAT]	K _d [mL/g]	K _{d OC} [mL/g]
<i>Soil type (USDA)</i>	Sandy loam	0	0.12	8	<i>Soil type (USDA)</i>	Silt loam	0	0.12	13
		3	0.16	11			3	0.14	16
		7	0.16	11			7	0.14	16
<i>OC [%]</i>	1.47	14	0.17	11	<i>OC [%]</i>	0.88	14	0.15	17
		28	0.20	13			28	0.15	17
<i>Soil pH (in H₂O)</i>	6.9	56	0.18	12	<i>Soil pH (in H₂O)</i>	7.6	56	0.15	18
		100	0.23	16			100	0.18	20
<i>DT₅₀ [days]</i>	49.8				<i>DT₅₀ [days]</i>	40.4			

The calculated adsorption coefficient increase factor was **2** for Laacherhof AXXa test soil and **1.5** for Laacherhof AIII test soil, indicating that the compound became more strongly sorbed onto soil with elapsing time. However that increase did not strongly influenced the mobility of FOE Sulfonic acid in soil, which remained very mobile, as indicated K_d and K_{d OC} values.

B.8.1.3. – Mobility in soil

The evaluation for Flufenacet in this area covers the following issues:

- column leaching, based on open literature studies,
- aged residue column leaching,
- lysimeter studies,
- determination of the Plant Uptake Factor – PUF, as “Other studies”

These issues are covered below, under the relevant data points.

B.8.1.3.1. – Column leaching studies

No study reports were submitted to address this issue for the first authorisation of Flufenacet in the EU. Instead the following rationale for the non-submission was provided (the text copied from the DAR prepared by the RMS – France): “No column leaching studies were performed. However this requirement is covered by adsorption studies with the active ingredient and relevant metabolites (section 7.2.1) as well as by aged residue column leaching, which is described below (section 7.2.3.)”. Also for the current evaluation the Applicant has not submitted studies addressing the column leaching of Flufenacet. Although in the MII document for Flufenacet, summarising the findings of the examination of fate and behaviour of Flufenacet in soil it is stated that there is a study addressing the issue of the column leaching of the active substance (point CA 7.1.4.1.1) it shall be indicated that the study, evaluated for the previous approval of Flufenacet in the EU, was in fact aimed on the examination of the leaching of aged residues of Flufenacet through the soil columns. Therefore it shall be stated that there is no study to address the issue of column leaching of Flufenacet through soil columns. RMS performing the repeated literature search for Flufenacet identified two publications addressing the problem of the mobility of Flufenacet through soil columns. They are summarised in this section of the Renewal Assessment Report as **Study 2** and **Study 3**.

The Applicant submitted one study report that covers the issue of the column leaching. The study was aimed on the examination of the leaching of one of the degradation products of Flufenacet – Trifluoroacetic acid (TFA), through the soil column. It is summarised below as **Study 1**.

Study 1:

Report: Hein E. –M., (2014): “[1-¹⁴C]trifluoroacetate: Soil column Leaching”; Bayer CropScience AG, BCS-D-EnSa Testing, 40789 Monheim, Germany; study No. M1212045-5; Report No. EnSa-14-0050; 2014-02-20; study reference number: M-477737-01-1;

Guidelines: The study was performed to comply with the following Guidelines:

- OECD Test Guideline No 312, Leaching in Soil Columns, April 2004;
- US. EPA OCSPP Test Guideline No 835.1240, Leaching Studies, October 2008;

GLP: Yes;

RMS comments: This is a new study, submitted specifically for the purpose of the current evaluation in order to refine the findings concerning the adsorption potential of TFA onto soil. It was evaluated for its compliance with the OECD 312 Guideline and found acceptable. It is summarised below.

Summary:

The aim of the study was to examine the mobility and leaching potential of Trifluoroacetic acid in soil. The study’s design was such to enable the determination of K_d and K_{dOC} values for the test item, because in the batch equilibrium sorption study TFA was demonstrated to display a virtually no adsorption potential. The experiment was performed on four test soils. Their characteristic is provided below in the table B.8.1.3.1._CA-1.

Table B.8.1.3.1._CA-1: The characteristic of soils used in the study.

Parameter		Soil			
		<i>Laacherhof AXxa (LH)</i>	<i>Dollendorf II (DD)</i>	<i>Höfchen am Hohenseh (HH)</i>	<i>Laacherhof Wurmweise (WW)</i>
Soil origin		Monheim, North Rhine-Westphalia, Germany	Blankenheim, North Rhein-Westphalia, Germany	Burscheid, North Rhein-Westphalia, Germany	Monheim, North Rhine-Westphalia, Germany
Soil type (USDA)		Loamy sand	Loam	Silt loam	Sandy loam
Particle size distribution	Sand [%]	78	397	19	57
	Silt [%]	16	36	64	28
	Clay [%]	6	25	17	15
Soil pH	in 0.01M CaCl ₂ (1:2)	6.2	7.4	6.5	5.3
	in water (1:1)	6.5	7.5	6.7	5.5
	in 1M KCl (1:1)	6.0	7.1	6.1	4.9
Water holding capacity	maximum. [g H ₂ O/100 g soil]	43.8	79.3	51.8	60.2
	at 0.1 bar (pF 2.0) [%]	13.3	38.2	26.5	20.1
Organic matter content (OM) [%]		3.1	9.0	2.8	3.3
Organic carbon content (OC) [%]		1.8	5.2	1.6	1.9
CEC [meq/100 g]		9.4	22.3	12.2	9.9
Bulk density [g/cm ³]		1.22	1.01	1.12	1.13

The test soils used in the experiment were sampled in June 2011 from the sites covered with grass on which no pesticides were used for 5 consecutive years before sampling. The soil samples were taken with shovel from the top 20-cm layer, placed in either plastic bag or bucket and shipped to the laboratory where it was air-dried, sieved through a 2-mm sieve and stored at $T = 20 \pm 2^{\circ}\text{C}$ until being used.

The test compound used in the study was [¹⁴C] Trifluoroacetic acid, in form of sodium salt, radiolabelled in carboxyl group. It had a specific activity of 3.48 MBq/mg and radiochemical purity, determined by HPLC, >98%. Its structural formula is presented below on figure B.8.1.3.1._CA-1. It was delivered to the test facility in form of a vacuum-dried solid.

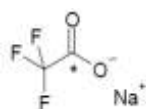


Figure B.8.1.3.1._CA-1: The structural formula of the test item – [¹⁴C]-TFA. Radiolabelling position is indicated by an asterisk (*); (copied from the study report).

The whole delivered sample of the test compound was dissolved in water to obtain a stock solution labelled **KOE7801 ST**, having a nominal concentration of 3480 kBq/mL, corresponding to 1.0 mg/mL. Its concentration was verified by the LSC and determined to be 3477.336 kBq/mL (1.0 mg/mL). The identity of the test item in the solution was confirmed by IC-MS/MS. That solution was subsequently used to prepare the application solutions of the test item, labelled **Ja64AS1** and **Ja64AS1a**. Prior to that the stock solution was stored in refrigerator in the dark.

In the study two other radiolabelled compounds were used. One of them was [¹⁴C]-atrazine, uniformly radiolabelled in triazole ring, having a specific activity of 160 mCi/mmol, corresponding to ~27.4 MBq/mg, and radiochemical and chemical purity, determined by HPLC, of 99%, used as a reference item. It was delivered to the test facility as either solid sample or MeOH-solution. Depending on the form in which it was delivered, it was used to prepare two stock solutions in water – stock solution **Ja66 SS Atr** prepared from the solid sample and stock solution **I12999-SS** prepared from MeOH-solution.

The stock solution **Ja66 SS Atr** was prepared by gradual dissolving of the whole delivered solid sample of [¹⁴C]-atrazine in water to the final volume of 10 mL. So prepared solution had a concentration, determined by LSC, of 84238 Bq/mL, corresponding to 3.10 µg/mL. The identity of the compound in the solution was confirmed by HPLC-MS/MS. That solution was used to prepare the application solution **Ja64 AS2** and until then was stored refrigerated in the darkness.

The stock solution **I12999-SS** was prepared by gradual diluting the whole amount of the delivered MeOH-solution of [^{14}C]-atrazine – 0.75 mL (having a nominal concentration of 0.1 mCi/mL, corresponding to 3.7 MBq/mL), with 6.75 mL of water. The so prepared solution had a concentration, determined by LSC, of 412 kBq/mL, corresponding to 15.0 $\mu\text{g/mL}$. The identity of the compound in the solution was confirmed by HPLC-MS/MS. That solution was used to prepare the application solution **Ja64 AS2a** and until then was stored refrigerated in the darkness.

The structural formula of the reference item is presented below on figure B.8.1.3.1._CA-2.

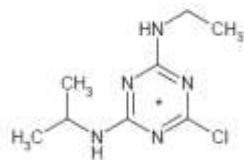


Figure B.8.1.3.1._CA-2: The structural formula of [^{14}C]-atrazine used as reference compound. Radiolabelling position is indicated by the asterisk (*); (copied from the study report).

Second additional compound used in the study was tritiated water, radiolabelled with [^3H], having a specific activity of 1 mCi/mL, corresponding to ~37 MBq/mL. That compound was used as a tracer (control item). It was used to prepare a stock solution labelled **Ja64 SS TW**. For that purpose 0.25-mL aliquot of the delivered sample was diluted with 24.75 mL of deionised water to obtain a solution having a nominal specific activity (concentration of $^3\text{H}_2\text{O}$) of 370 kBq/mL. The measured specific activity, determined by LSC, was 623.702 kBq/mL. That solution was used to prepare application solutions containing the tracer. Until being used it was stored refrigerated in the darkness. The structural formula of the control item (tracer) is presented below on figure B.8.1.3.1._CA-3.

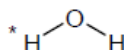


Figure B.8.1.3.1._CA-3: The structural formula of [^3H]-water used as the control item (tracer). The radiolabelling position is indicated by the asterisk (*); (copied from the study report).

The characterised above stock solutions of the test compound, reference compound and the tracer were used to prepare four following application solutions:

- **Ja 64 AS1**, containing the test compound and the tracer;
- **Ja64 AS1a**, containing the test compound and the tracer;
- **Ja64 AS2**, containing the reference compound and the tracer;
- **Ja64 AS2a**, containing the test compound and the tracer.

The application solution **Ja64 AS1** was prepared by mixing 0.22 mL of the stock solution **KOE7801 ST** with 1.6 mL of the stock solution **Ja64 SS TW**. The solution was then brought to the volume of 10 mL with deionised water. The final concentration of the constituents of that solution, determined by LSC was 75907.2 Bq/mL (21.8 $\mu\text{g/mL}$) for the test compound (TFA) and 104747.6 Bq/mL for the tracer. The radiochemical purity of the test item – TFA, in that solution was demonstrated to be 100%.

The application solution **Ja64 AS1a** was prepared by mixing 0.33 mL of the stock solution **KOE7801 ST** with 2.4 mL of the stock solution **Ja64 SS TW**. The solution was then brought to the volume of 15 mL with deionised water. The final concentration of the constituents of that solution, determined by LSC, was 77966.8 Bq/mL (22.4 $\mu\text{g/mL}$) for the test compound (TFA) and 101473.4 Bq/mL for the tracer. The radiochemical purity of the test item – TFA, in that solution was demonstrated to be 100%.

The application solution **Ja64 AS2** was prepared by mixing 8.4 mL of the stock solution **Ja66 SS Atr** with 1.6 mL of the stock solution **Ja64 SS TW**. The final concentration of the constituents of that solution, determined by LSC, was 75756.0 Bq/mL (2.8 $\mu\text{g/mL}$) for the reference compound (atrazine) and 110100.8 Bq/mL for the tracer. The radiochemical purity of the reference item – atrazine, in that solution was demonstrated to be 97.8%.

The application solution **Ja64 AS2a** was prepared by mixing 2.79 mL of the stock solution **I12999-SS** with 2.4 mL of the stock solution **Ja64 SS TW**. The solution was then brought to the volume of 15 mL with deionised water. The final concentration of the constituents of that solution, determined by LSC, was 75181.6 Bq/mL (2.7 µg/mL) for the reference compound (atrazine) and 106626.6 Bq/mL for the tracer. The radiochemical purity of the reference item – atrazine, in that solution was demonstrated to be 98.2%.

The solution used for equilibration of the columns containing test soils and for leaching was artificial rain – 0.01M CaCl_2 _{aq} solution, prepared by dissolving 2.94 g $\text{CaCl}_2 \cdot 2 \text{H}_2\text{O}$ with deionised water in 2-L volumetric flask.

The experiment was performed using the glass columns, 45-cm long and having 5 cm of the inner diameter, filled with the test soils to ~30-cm height. They were prepared in the following way: firstly the lower, conical section of the column, was filled with a layer of a quartz wool followed by a layer of washed sea sand to retain the test soil within it. Next, the column was dry-packed with the given air-dried test soil up to its height of ~30 cm, while gently vibrating it. The amount of the test soil used per column was 675 – 856 g. So prepared columns were equilibrated to the study conditions in the darkness and at constant temperature $T = 20 \pm 2^\circ\text{C}$. That was done by saturation the soil in the columns with 400 mL 0.01M CaCl_2 _{aq} solution (artificial rain) administered from the bottom of the column to minimise air entrapment in soil pores. That resulted in 10-20 mm layer of the solution above the soil surface. The saturated columns were left for 16 hours, then drained, bringing the solution to the soil surface level. The volume of the removed supernatant was measured and the saturation volume of each soil column calculated. As in some columns soil swelled during saturation, the height of the soil column was measured again.

Next, the columns were allowed to drip off for ~5 hours and the liquid, defined as dripping volume or excess volume, was collected and measured. It was used to determine the void volume of the soil column, defined as a difference between the saturation volume and the excess volume.

Finally the columns were once again saturated with 0.01M CaCl_2 _{aq} administered from the bottom until the soil surface was covered. So prepared test columns were used in the leaching experiment. The soil columns were prepared in duplicate for each variant of the experiment

The leaching experiment was performed in two different variants – as **Study design A** and **Study design B**. The **Study design A** provided the information on the distribution of the test item in the leachate and soil column, while **Study design B** only on that of the test item in leachate.

The detailed characteristic of the **Study design A**, as provided by the Applicant in the study report, is presented on figure B.8.1.3.1._CA-4. The next two figures – B.8.1.3.1._CA-5 and B.8.1.3.1._CA-6 present soil column parameters. In a similar way are presented the detailed characteristic of the **Study design B** – on figure B.8.1.3.1._CA-7 and the parameters of the soil column – on figure B.8.1.3.1._CA-8. The values presented in tables reproduced on figures B.8.1.3.1._CA-5, B.8.1.3.1._CA-6 and B.8.1.3.1._CA-8 were used to calculate the sorption parameters – K_d and K_{dOC} values for TFA in each test soil.

Parameters	Description		
Test apparatus	Glass tubes (45 x 5 cm [length x diameter]), connected to a reservoir of artificial rain via a peristaltic pump. Flow was regulated via a post-column peristaltic pump. Leachates were collected by a programmable fraction collector.		
Test item application to soil columns			
• Identity of application solvent	Ja64 AS1, Ja64 AS1a and Ja64 AS2: water Ja64 AS2a: water with approx. 2% methanol (v/v)		
• Application volume per treatment	500 µL for all application solutions		
• Identity of application solution applied to the respective soil columns	Ja64 AS1 Ja64 DD1 / DD2 / WW1 / WW2 Ja64 AS1a Ja64LH1a / LH2a / HH1a / HH2a Ja64 AS2 Ja64 DD3 / DD4 / WW3 / WW4 Ja64 AS2a Ja64 LH3a / LH4a / HH3a / HH 4a		
• Applied radioactivity per soil column	Soil Column ID	TFA	³ H ₂ O
	Ja64 DD1 / DD2 / WW1 / WW2	36925 Bq	51996 Bq
	Ja64 LH1a / LH2a / HH1a / HH2a	39203 Bq	51625 Bq
	Soil Column ID	atrazine	³ H ₂ O
	Ja64 DD3 / DD4 / WW3 / WW4	37175 Bq	54730 Bq
	Ja64 LH3a / LH4a / HH3a / HH4a	37755 Bq	53943 Bq
• Application method	Small droplets on top of the soil column using a pipette.		
• Evaporation of application solvent	No		
Indication of test item adsorption to walls of test apparatus	No		
Number of soil columns / replicates	test item + tracer: two soil columns per soil (total 8) reference item + tracer: two soil columns per soil (total 8)		
Soil column dimensions	height: 30 to 32.5 cm diameter: 5 cm		
Weight of soil per column	699 to 856 g (dry weight)		
Soil condition	Sieved to 2 mm, air-dried		
Column packing and wetting technique	Columns were dry-packed uniformly under gentle vibration. Afterwards, soils were saturated with 0.01 M CaCl ₂ solution from bottom to top, and equilibrated for approx. 16 hours.		
Leaching solution	0.01 M CaCl ₂ solution		
Experimental conditions			
• Delivery of leaching solution to column	Delivery to open column top by peristaltic pump, maintaining a supernatant of approx. 10-20 mm above soil level.		
• Flow rate, conditions and control	Constant saturated flow of 8.2 mL/h; pressureless, with effluent control by peristaltic pump.		
• Total irrigation volume	392 mL (equal to constant rainfall of 200 mm)		
• Temperature	20.1 °C (19.8 to 20.4 °C)		
• Continuous darkness	Yes		
• Sampling time / volume per fraction	6 h / approx. 50 mL		
• Total sampling time	48 hours		
• Number / height of soil column segments	5 segments of approx. 6 cm		

Figure B.8.1.3.1._CA-4: The detailed characteristic of the **Study design A**, as provided by the Applicant (copied from the study report).

Test Item + Tracer	Lacherhof AXXa		Dollendorf II		Lacherhof Wurmweise		Höfchen am Hohenseh	
	Ja64 LH1a	Ja64 LH2a	Ja64 DD1	Ja64 DD2	Ja64 WW1	Ja64 WW2	Ja64 HH1a	Ja64 HH2a
Weight of empty column [g]	385	383	407	410	390	378	407	389
Weight of column filled with soil [g]	1219	1219	1121	1132	1154	1130	1198	1179
Weight of soil column (air dried) [g]	834	836	714	722	764	752	791	810
Moisture air dried soil [% DM]	1.35	1.35	4.97	4.97	2.40	2.40	2.46	2.46
Weight of soil column (dry weight) [g]	822.7	824.7	678.5	686.1	745.7	734.0	771.5	790.1
Volume of residual water in air dried soil column [g] $\hat{=}$ [mL]	11.3	11.3	35.5	35.9	18.3	18.0	19.5	19.9
Height of soil column [cm]	30.0	30.0	32.5	32.5	30.5	30.5	30.0	30.0
Volume of soil column [cm ³] $\hat{=}$ [mL]	589.0	589.0	638.1	638.1	598.9	598.9	589.0	589.0
Organic carbon [%]	1.8	1.8	5.2	5.2	1.9	1.9	1.8	1.8
Saturation volume [mL]	286	290	358	352	305	296	273	290
Excess/drainage/dripping volume [mL]	9	10	20	23	34	34	8	13
Particle density of soil (long-term average, measured) [g/ cm ³]	2.58	2.58	2.52	2.52	2.59	2.59	2.51	2.51
Bulk density of soil (P_{bulk}) ¹ [g/ cm ³]	1.40	1.40	1.06	1.08	1.25	1.23	1.31	1.34
Porosity factor of soil column (ϕ) ¹ [-]	0.459	0.457	0.578	0.573	0.519	0.527	0.478	0.466
Void volume (V_v) ¹ [mL]	270.2	269.4	368.9	365.9	311.0	315.5	281.7	274.3

¹ according to Ketelle and Swoboda (see Section 3.7.2.1)

Figure B.8.1.3.1._CA-5: The soil column parameters for the soil columns treated with the test compound – TFA, and the tracer in the **Study design A**, as provided by the Applicant (copied from the study report).

Reference Item + Tracer	Ja64 LH3a	Ja64 LH4a	Ja64 DD3	Ja64 DD4	Ja64 WW3	Ja64 WW4	Ja64 HH3a	Ja64 HH4a
Weight of empty column [g]	390	382	383	400	373	392	393	391
Weight of column filled with soil [g]	1246	1220	1082	1105	1157	1148	1200	1187
Weight of soil column (air dried) [g]	856	838	699	705	784	756	807	796
Moisture air dried soil [% DM]	1.35	1.35	4.97	4.97	2.40	2.40	2.46	2.46
Weight of soil column (dry weight) [g]	844.4	826.7	664.3	670.0	765.2	737.9	787.1	776.4
Volume of residual water in air dried soil column [g] $\hat{=}$ [mL]	11.6	11.3	34.7	35.0	18.8	18.1	19.9	19.6
Height of soil column [cm]	30.0	30.0	32.5	32.5	30.5	30.5	30.0	30.0
Volume of soil column [cm ³] $\hat{=}$ [mL]	589.0	589.0	638.1	638.1	598.9	598.9	589.0	589.0
Organic carbon [%]	1.8	1.8	5.2	5.2	1.9	1.9	1.6	1.6
Saturation volume [mL]	293	290	350	340	306	296	327	295
Excess/drainage/dripping volume [mL]	10	14	22	24	33	32	13	12
Particle density of soil (long-term average, measured)	2.58	2.58	2.52	2.52	2.59	2.59	2.51	2.51
Particle density of soil (calculated) [g / cm ³]	2.97	2.87	2.62	2.55	2.79	2.59	3.25	2.83
Bulk density of soil (P_{bulk}) ¹ [g / cm ³]	1.43	1.40	1.04	1.05	1.28	1.23	1.34	1.32
Porosity factor of soil column (ϕ) ¹ [-]	0.444	0.456	0.587	0.583	0.507	0.524	0.468	0.475
Porosity of soil column (θ) ² [-]	0.517	0.512	0.603	0.588	0.542	0.525	0.589	0.534
Void volume (V_v) ¹ [mL]	261.7	268.6	374.5	374.5	303.4	314.0	275.4	279.7
Column factor α ³ [mL/cm] = [cm ²]	8.72	8.95	11.52	11.52	9.95	10.29	9.18	9.32
Column factor β ³ [g/cm]	28.15	27.56	20.44	20.44	25.09	24.19	26.24	25.88
Ratio of distance moved by test item and height of added water column ² [-]	0.15	0.15	0.16	0.16	0.15	0.15	0.15	0.15

¹ according to Ketelle and Swoboda (see Section 3.7.2.1)

² according to Hamaker / McCall (see Section 3.7.2.2.2)

³ according to Lambert (see Section 3.7.2.2.1)

Figure B.8.1.3.1._CA-6: The soil column parameters for the soil columns treated with the reference compound (atrazine) and the tracer in the **Study design A**, as provided by the Applicant (copied from the study report).

Parameters	Description		
Test apparatus	Glass tubes (45 x 5 cm [length x diameter], connected to a reservoir of artificial rain via a peristaltic pump. Flow was regulated via a post-column peristaltic pump. Leachates were collected by a programmable fraction collector.		
Test item application to soil columns			
• Identity of application solvent	water		
• Application volume per treatment	500 µL		
• Identity of application solution applied to the respective soil columns	Ja64 AS1a Ja64 LH5 / LH6 / HH5 / HH6 Ja64 DD5 / DD6 / WW5 / WW6		
• Applied radioactivity per soil column	Soil Column ID	TFA	³ H ₂ O
	Ja64 LH5 / LH6 / HH5 / HH6 Ja64 DD5 / DD6 / WW5 / WW6	39507 Bq	52485 Bq
• Application method	Small droplets on top of the soil column using a pipette.		
• Evaporation of application solvent	No		
Indication of test item adsorption to walls of test apparatus	No		
Number of soil columns / replicates	test item + tracer: two soil columns per soil (total 8)		
Soil column dimensions	height: 30 cm diameter: 5 cm		
Weight of soil per column	678 to 847 g (dry weight)		
Soil condition	Sieved to 2 mm, air-dried		
Column packing and wetting technique	Columns were dry-packed uniformly under gentle vibration. Afterwards, soils were saturated with 0.01 M CaCl ₂ solution from bottom to top, and equilibrated for approx. 16 hours.		
Leaching solution	0.01 M CaCl ₂ solution		
Experimental conditions			
• Delivery of leaching solution to column	Delivery to open column top by peristaltic pump, maintaining a supernatant of approx. 10-20 mm above soil level.		
• Flow rate, conditions and control	Constant saturated flow of 8.2 mL/h; pressureless, with effluent control by peristaltic pump.		
• Total irrigation volume	984 mL (equal to constant rainfall of 502 mm)		
• Temperature	20.1 °C (19.8 to 20.4 °C)		
• Continuous darkness	Yes		
• Sampling time / volume per fraction	6 h, approx. 50 mL 12 h, approx. 100 mL		
• Total sampling time	120 hours		
• Number / height of soil column segments	The soil columns were not analyzed		

Figure B.8.1.3.1._CA-7: The detailed characteristic of the **Study design B**, as provided by the Applicant (copied from the study report).

Test Item + Tracer	Lacherhof AXXa		Dollendorf II		Lacherhof Wurmweise		Höfchen am Hohenseh	
	Ja64 LH5	Ja64 LH6	Ja64 DD5	Ja64 DD6	Ja64 WW5	Ja64 WW6	Ja64 HH5	Ja64 HH6
Weight of empty column [g]	385	404	377	390	398	403	386	391
Weight of column filled with soil [g]	1221	1251	1059	1068	1144	1151	1182	1153
Weight of soil column (air dried) [g]	836	847	682	678	746	748	796	762
Moisture air dried soil [% DM]	1.35	1.35	4.97	4.97	2.40	2.40	2.46	2.46
Weight of soil column (dry weight) [g]	824.7	835.6	648.1	644.3	728.1	730.0	776.4	743.3
Volume of residual water in air dried soil column [g] \triangleq [mL]	11.3	11.4	33.9	33.7	17.9	18.0	19.6	18.7
Height of soil column [cm]	30.0	30.0	30.0	30.0	30.0	30.0	30.0	30.0
Volume of soil column [cm ³] \triangleq [mL]	589.0	589.0	589.0	589.0	589.0	589.0	589.0	589.0
Organic carbon [%]	1.8	1.8	5.2	5.2	1.9	1.9	1.6	1.6
Saturation volume [mL]	294	303	333	330	311	307	294	297
Excess/drainage/dripping volume [mL]	9	8	29	22	29	30	14	23
Particle density of soil (long-term average, measured) [g / cm ³]	2.58	2.58	2.52	2.52	2.59	2.59	2.51	2.51
Bulk density of soil [g / cm ³]	1.4	1.4	1.10	1.09	1.24	1.24	1.32	1.26
Porosity factor of soil column (ϕ) ¹								
Void volume [-]	0.457	0.450	0.563	0.566	0.523	0.521	0.475	0.497
Weight of empty column [mL]	269.4	265.2	331.9	333.4	307.9	307.2	279.7	292.9

¹ according to Ketelle and Swoboda (see Section 3.7.2.1)

Figure B.8.1.3.1._CA-8: The soil column parameters for the soil columns treated with the test compound – TFA, and the tracer in the **Study design B**, as provided by the Applicant (copied from the study report).

At the beginning of the leaching experiment 0.5 mL of the appropriate application solution was introduced onto the headspace of each test column. In case of the test compound the application dose was 11 µg/g soil column, what corresponded to the field application rate of Flufenacet equal to 250 g/ha, assuming the conversion factor Flufenacet → TFA of 0.75 and a ratio $M_{TFA}/M_{Flufenacet} = 0.3$.

After application a glass funnel with a glass frit attached to it was placed upside down in the top section of each column, above the soil surface. The columns were then attached to the artificial rain container, two peristaltic pumps set to obtain the pre-defined flow rate and the fractions collector. The whole experimental set-up is presented below on figure B.8.1.3.1._CA-9.

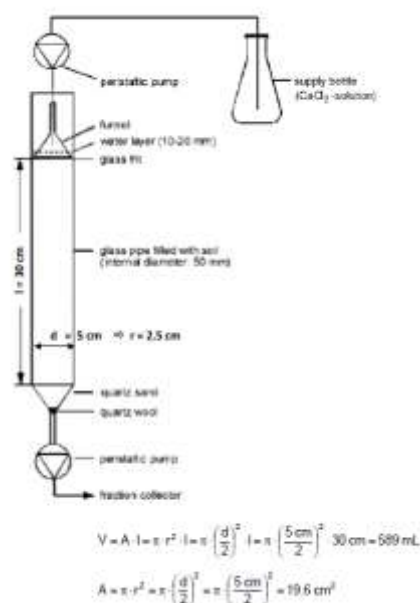


Figure B.8.1.3.1_CA-9: The schematic presentation of the test column set-up (copied from the study report).

The columns were kept throughout the whole experiment in the darkness and under the constant temperature $T = 20 \pm 2^\circ\text{C}$.

In case of the **Study design A** the leaching lasted 48 hours – the time required for the passing through the column 392 mL of the artificial rain administered at a rate 8.2 mL/h, the amount corresponding to 200 mm of the continuous rainfall. The fractions of the leachate were collected in 6-hours intervals, rendering the volume collected in each fraction of approx. 50 mL. The volume of each collected fraction was measured. Each fraction was characterised for its pH immediately after collection, and for the content of radioactivity, by LSC, within three days after collection. Afterwards the collected fractions were stored refrigerated in the darkness until being further analysed. The soil columns after draining were deep-frozen and divided into 6-cm segments for further analysis. The whole applied sample-processing procedure is presented below on figure B.8.1.3.1_CA-10.

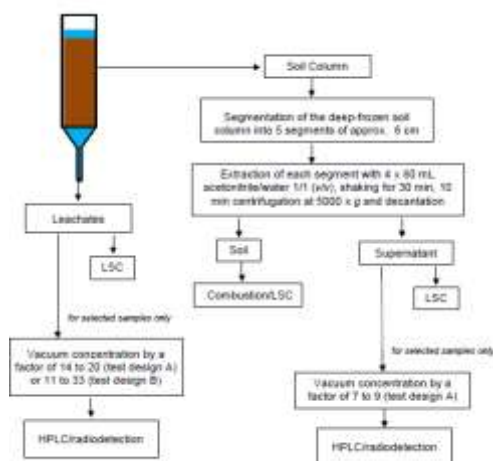


Figure B.8.1.3.1_CA-10: The schematic presentation of the sample processing procedure used in the study (copied from the study report).

In case of the **Study design B** the leaching lasted 120 hours – the time required for the passing through the column 984 mL of the artificial rain administered at a rate 8.2 mL/h, the amount corresponding to 502 mm of the

continuous rainfall. The fractions of the leachate were collected in either 6-hours intervals (approx. 50-mL fractions), or 12-hours intervals (approx. 100-mL fractions). The volume of each collected fraction was measured. Each fraction was characterised for its pH immediately after collection, and for the content of radioactivity, by LSC, within three days after collection. Afterwards the collected fractions were stored refrigerated in the darkness until being further analysed. The soil columns after draining were deep-frozen. They were however not analysed as all radioactivity introduced in form of the test item was recovered in leachates. Therefore, the whole applied sample-processing procedure was identical to that presented on figure B.8.1.3.1._CA-10, except that the recovered soil columns were not analysed.

The LSC analysis was performed using LS 6500 or LKB-Wallac 1219 Spectral counters. The radioactivity (^3H and $^3\text{H} + ^{14}\text{C}$ in parallel) in liquid samples – leachates, soil extracts, application solutions, was determined in maxi vials using the aliquots up to 2 mL and 10 mL of Quicksafe A + 5% water LS cocktail. The average sample counting time was 10 minutes, background for ^3H : 2.0 – 2.8 cpm and background for ^{14}C : 15.5 – 17.2 cpm.

Radioactivity in stock solutions was determined in mini-vials using the aliquots up to 1 mL and 2 mL of Quicksafe A + 5% water LS cocktail. The average sample counting time was 10 minutes and the background 13 cpm.

The $^{14}\text{CO}_2$ generated during combustion of the extracted soil samples was absorbed in 15 mL of Oxsolve C400 LS cocktail and analysed by LSC. The average sample counting time was 10 minutes and the background 19.1 – 19.6 cpm.

The instrumental LOD and LOQ values for the LSC analysis were determined individually for ^{14}C and ^3H measurements. They are presented below in the table B.8.1.3.1._CA-2. These values were used to calculate the LOD and LOQ values for each type of sample analysed by LSC. The obtained values – worst case LOD and LOQ for each type of analysed sample, are presented in the table B.8.1.3.1._CA-3

Table B.8.1.3.1._CA-2: The instrumental LOD and LOQ values for LSC analysis of various types of samples.

Measurement	Sample type	Scintillation cocktail	Scintillator No.	LOD _{instrumental}	LOQ _{instrumental}
^{14}C -measurement	Stock solutions	5 mL Quicksafe A + 5% water	1	0.4 Bq	0.7 Bq
	Leachate fractions and soil extracts	10 mL Quicksafe A + 5% water	2	0.6 Bq	0.9 Bq
	^{14}C from soil combustion	15 mL Oxsolve C400	3	0.7 Bq	1.0 Bq
^3H -measurement	Leachate fractions and soil extracts	10 mL Quicksafe A + 5% water	1	0.1 Bq	0.1 Bq

Table B.8.1.3.1._CA-2: The LOD and LOQ values for LSC analysis of various types of samples.

Measurements	Scintillator No.	Sample type	Volume/mass of the sample		LOD (worst case)	LOQ (worst case)
			Total (max.)	Aliquot (min.)		
^{14}C	1	Leachate fractions	104 mL/ 54 mL	2 mL/ 1 mL	298.Bq (<0.1% AR)	44.7 Bq (0.1% AR)
	1	Soil extracts	365 mL	1 mL	209.3 Bq (0.6% AR)	313.9 Bq (0.8% AR)
	2	Soil column segments (^{14}C formed during combustion)	194.2 g	0.9 g	141.0 Bq (0.4% AR)	211.5 Bq (0.6% AR)
^3H	1	Leachate fractions	104 mL/ 51 mL	2 mL/ 1 mL	4.9 Bq (<0.1% AR)	4.9 Bq (<0.1% AR)
	2	Soil extracts	365 mL	1 mL	51.1 Bq (<0.1% AR)	51.1 Bq (<0.1% AR)

The selected leachates and soil extracts were analysed using RP-HPLC method with radioactivity detection. The RP-HPLC analysis was performed in a gradient mode. The system consisted of HP 1200 chromatograph equipped with a quaternary pump, autosampler, on-line degasser, column oven and a Variable Wavelength UV detector set at $\lambda = 254$ nm, coupled with Ramona Star radioactivity detector equipped with a 370 μL glass solid phase scintillator flowcell. The chromatographic separation was performed on Purosphere Star RP 18e 250 mm * 4.6 mm, 5 μm , chromatographic column preceded by Purosphere Star RP 18e 4 mm * 4 mm, 5 μm , guard column.

It worked in the following gradient regime:

- **Mobile phase A:** 985 mL Water + 10 mL HCOOH + 5 mL $\text{NH}_4\text{COOH}_{(\text{aq})}$ (5 mM NH_4COOH /265 mM HCOOH);

- **Mobile phase B:** 985 mL CH₃CN + 10 mL HCOOH + 5 mL NH₄COOH_(aq) (5 mM NH₄COOH/265 mM HCOOH);
- **Gradient mode:** is shown below in the table B.8.1.3.1._CA-4;
- Total run time was 70 minutes.

The flow rate was set to 1.0 mL/min. The chromatographic column was kept under the constant temperature T = 40°C.

Table B.8.1.3.1._CA-4: The gradient mode used in the radio-HPLC analysis

Elution time [min]		0	5	55	60	62	70
Composition of the mobile phase	Solvent A [%]	100	100	5	5	100	100
	Solvent B [%]	0	0	95	95	0	0

The retention times (R_t) for the chromatographed compounds were following:

- for TFA R_t ≈ 7.4 min.;
- for atrazine R_t ≈ 37.5 min.;

The total LOD values calculated for the HPLC analysis were following:

- for leachate fractions max total LOD = 0.2% AR;
- for soil extracts max. total LOD = 1.4 % AR.

Values representing the LOQ were not provided.

Selected samples were also analysed using LC-MS/(MS) techniques – either HPLC-MS/(MS) or IC-MS/(MS) method. The analysis was carried out in order to confirm the identity of the test compound – TFA.

The HPLC-MS/(MS) analysis was performed using HP 1100 instrument equipped with Nucleodur C18 Gravity 250 • 2 mm, 5 µm, chromatographic column and UV detector, coupled to Ramona Star radioactivity detector and Q-Exactive XL MS detector. The chromatographic analysis was performed in a gradient mode using a gradient programme presented below in the table B.8.1.3.1._CA-5. The flow rate was 0.2 mL/min and elution lasted for 35 minutes. The chromatographic column was kept in a chromatographic oven set to T = 40°C. The changes in the gradient of mobile phase were linear.

Table B.8.1.3.1._CA-5: The gradient mode used in the HPLC-MS/(MS) analysis.

Time [min]	Solvent ratio	
	Solvent A – Water + 0.1% HCOOH	Solvent B – CH ₃ CN + 0.1% HCOOH
0	95	5
5	95	5
25	5	95
35	5	95

The IC-MS/(MS) analysis was performed using Dionex-ICS-5000 instrument equipped with AS20 250 • 2 mm column and conductivity detector coupled to radioactivity detector and MS detector (specification of none of them provided in the study report). The column was kept under the constant temperature T = 30°C. Elution was performed in isocratic mode using 20 mM KOH aqueous solution and it lasted 15 minutes. The flow rate was set to 0.25 mL/min.

The results obtained in both leaching experiments were used to derive the K_d and K_{dOC} values for TFA. The calculations were performed for TFA as a test item, tritiated water as a tracer and atrazine as a reference compound.

For TFA and tritiated water calculations were performed using the following equations (copied from the study report; where calculations were characterised as performed according to Ketelle and Swoboda):

(1) The soil adsorption coefficient K_d is derived from the soil column data using the following formulae:

$$K_d = \left(\frac{V_e}{V_v} - 1 \right) \cdot \frac{V_v}{m_{\text{soil}} (\text{g})}$$

with

K _d	Adsorption constant [mL/g]
V _e	Volume of artificial rain required to leach 50% AR of the test item or reference item through the soil column [mL]
V _v	Void volume of the soil column [mL]
m _{soil} (g)	Dry weight of the soil column [g]

The void volume (V_v) of each soil column was calculated as follows, taken into account the porosity fraction (ϕ) and the volume of soil column ($V_{\text{soil column}}$).

$$\begin{aligned} V_v &= \phi \cdot V_{\text{soil column}} \\ &= \left(1 - \frac{\rho_{\text{bulk}}}{\rho_{\text{particle}}} \right) \cdot V_{\text{soil column}} \\ &= \left(1 - \frac{\frac{m_{\text{soil}}(\text{DM})}{V_{\text{soil column}}}}{\rho_{\text{particle}}} \right) \cdot V_{\text{soil column}} \end{aligned}$$

with:

V_v	Void volume of soil column [mL]
ϕ	Porosity factor of soil column [-]
$V_{\text{soil column}}$	Volume of soil column [cm ³ = mL], calculated by: $V_{\text{soil column}} = \pi \cdot r^2 \cdot h$
ρ_{bulk}	Bulk density of soil [g/cm ³], calculated by: $\rho_{\text{bulk}} = \frac{m_{\text{soil}}(\text{DM})}{V_{\text{soil column}}}$
ρ_{particle}	Particle density of soil [g/cm ³], determined in separate GLP study
$m_{\text{soil}}(\text{DM})$	Dry weight of soil column [g]

The calculations for atrazine were performed using two methods: by Lambert and by Hamker/McCall. The results were subsequently averaged.

The equations used in calculations according to Lambert, as they were presented in the study reports, are shown below:

(1) The soil adsorption coefficient K_d according to Lambert is derived from the soil column data using the following formula:

$$K_d = \frac{V_{\text{total irrigation}} \cdot \alpha + X_0}{\beta \cdot X_0}$$

with:

K_d	Adsorption constant [mL/g]
$V_{\text{total irrigation}}$	Total irrigation volume [mL]
X_0	Distance, measured from top of soil column to segment of max. compound concentration [cm]
α	Column factor [mL/cm + cm ²]
β	Column factor [g/cm]

The input data are described in Table 7 (parameters of soil columns). Based on the experimental results, the distance (X_0) the compound has moved during irrigation is determined using the following formula:

$$X_0 = \frac{h_{\text{soil column}}}{N_{\text{total}}} \cdot N_{\text{max}} - \left(\frac{h_{\text{soil column}}}{2 \cdot N_{\text{total}}} \right)$$

with:

X_0	Distance, measured from top of soil column to segment of max. compound concentration [cm]
$h_{\text{soil column}}$	Height of soil column [cm]
N_{total}	Total number of soil column segments [-]
N_{max}	Number of soil column segment with max. compound concentration (1 = top (start), 5 = bottom (finish) of soil column) [-]

The column factors α and β are calculated as follows:

$$\alpha = \frac{V_v}{h_{\text{soil column}}} \quad \beta = \frac{m_{\text{soil}}(\text{DM})}{h_{\text{soil column}}}$$

with:

V_v	Void volume of soil column [mL = cm ³]
$h_{\text{soil column}}$	Height of soil column [cm]
$m_{\text{soil}}(\text{DM})$	Dry weight of soil column [g]

The equations used in calculations according to Hamaker/McCall, as they were presented in the study reports, are shown below:

(1) The soil adsorption coefficient K_d according to Hamaker / McCall is derived from the soil column data using the following formula:

$$K_d = \left(\frac{\theta^{2/3} - \frac{1}{R}}{\theta^{2/3} - 1} \right) \cdot \frac{1}{\rho_{\text{solid soil constituents}}}$$

with:

K_d	Adsorption constant [mL/g]
θ	Porosity [-]
R	Ratio of distance moved by compound and height of added water column [-]
$\rho_{\text{solid soil constituents}}$	Particle density [g/cm ³ = g/mL]

The input data are described in Table 7 (parameters of soil columns). Based on the experimental results, the porosity (θ) of the soil column, the density of the solid soil constituents (particle density, $\rho_{\text{solid soil constituents}}$), the distance (X_0) the compound has moved during irrigation and the ratio of the distance (R) moved by the compound and the height of added water column are determined using the following formulae:

$$\theta = \frac{V_s + V_r}{V_{\text{soil column}}}$$

with:

θ	Porosity
V_s	Saturation volume of soil column [mL]
V_r	Volume of residual water in air dried soil column [mL]
$V_{\text{soil column}}$	Volume of soil column [mL]

$$\rho_{\text{solid soil constituents}} = \frac{m_{\text{solid}} (\text{gwt})}{\frac{V_{\text{soil column}}}{(1 - \theta)}}$$

with

$\rho_{\text{solid soil constituents}}$ Density of the solid soil constituents (particle density)

$V_{\text{soil column}}$ Volume of soil column

$m_{\text{solid}} (\text{gwt})$ Mass of soil column (dry weight)

θ Porosity

$$K_s = \frac{h_{\text{test column}}}{h_{\text{total}}} \cdot N_{\text{max}} - \left(\frac{h_{\text{test column}}}{2 \cdot h_{\text{total}}} \right)$$

with

h_s Distance, measured from top of soil column to segment of max. compound concentration [cm]

$h_{\text{test column}}$ Height of soil column [cm]

N_{max} Total number of soil column segments [-]

N_{max} Number of soil column segment with max. compound concentration (1 = top (start); 5 = bottom (finish) of soil column) [-]

$$R = \frac{h_s}{V_{\text{total irrigation}}} \cdot A_{\text{column}}$$

with

R Ratio of distance moved by test item and height of added water column [-]

h_s Distance, measured from top of column to segment of max. test item concentration [cm]

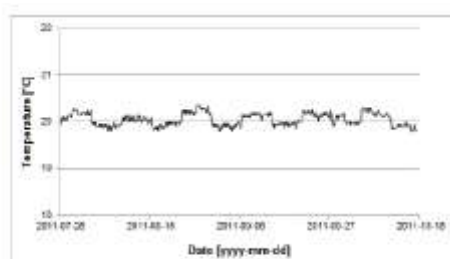
$V_{\text{total irrigation}}$ Total irrigation volume [ml = cm³]

A_{column} Surface of soil column [cm²]

Results and their discussion:

The characteristic of the test soils used in the study has been presented at the beginning of this summary in table B.8.1.3.1._CA-1. It may be stated that the test soils generally meet the acceptability criteria with regard to their textural characteristic, pH range and OC content range.

The leaching experiment was carried out in the dark, in a walk-in climatic chamber at constant temperature. The results of its monitoring during the experiment are presented below on figure B.8.1.3.1._CA-11. On their basis it was stated that the mean $T = 20.1^{\circ}\text{C}$ and its range was $19.8 - 20.4^{\circ}\text{C}$. It was therefore within the pre-defined limits of $T = 20 \pm 2^{\circ}\text{C}$. It may be also stated that the temperature was constant within the study period, therefore that factor had no influence on the obtained results, in particular calculated K_d/K_{dOC} values.



Temperatures were recorded by a data logger (Squirrel 1256, Grant Instr. Ltd.).

Record start date (equilibration of first soil columns)	2011-07-26
Record end date (end of last soil columns)	2011-10-17
Total Readings	3660
Reading interval [min]	30
Minimum [°C]	19.8
Maximum [°C]	20.4
Mean [°C]	20.1
SD [°C]	0.1
RSD [%]	0.7

Figure B.8.1.3.1._CA-11: The graphical results of the monitoring of the temperature during the study (copied from the study report).

The verification of the application rate showed that the amount of the given compound applied per column was on average:

- 38.5 kBq, corresponding to ~11 µg, for the test item – TFA

- 37.5 kBq, corresponding to ~1.4 µg, for the reference item – atrazine;
- 53.0 kBq for the tracer – $^3\text{H}_2\text{O}$.

The verification of the analytical procedure demonstrated its good suitability, reflected by high recoveries of the applied radioactivity – in the experiment labelled **Study design A** the extractable residues were in range 98.6 – 101.8% AR for the test item (TFA) and 90.2 – 94.0% AR for the reference item (atrazine).

The total recovered radioactivity in the experiment labelled **Study design A** was in range 93.5 – 103.2% AR for the test item (TFA) and tracer ($^3\text{H}_2\text{O}$) and 93.2 – 102.6% AR for the reference item (atrazine) and tracer ($^3\text{H}_2\text{O}$). In case of the experiment labelled **Study design B** the total recovered radioactivity for the test item (TFA) and tracer ($^3\text{H}_2\text{O}$) was in range 92.9 – 102.6%.

It was stated that in case of the test compound in the **Study design A**, > 90% of the applied amount was found in leachates from Laacherhof AXXa and Höfchen am Hoheneseh. In Dollendorf II and Laacherhof Wurmweise soil it was more strongly retained by soil, with 62 – 82% of applied recovered in leachates from columns with Dollendorf II soil and 62 – 70% of applied recovered in leachates from columns with Laacherhof Wurmweise soil. Similar observations were made in case of the tracer compound applied alongside. In this experiment atrazine – the reference compound, was demonstrated to be strongly retained by soil – only up to 1% of the applied dose was recovered in leachates. The graphical results of the determination of the mass balance in this experiment are presented below on figure B.8.1.3.1_CA-12. The following abbreviations were used to denominate the test soils used in the experiment:

- LH for soil Laacherhof AXXa,
- DD for soil Dollendorf II,
- HH for soil Höfchen am Hoheneseh,
- WW for soil Laacherhof Wurmweise.

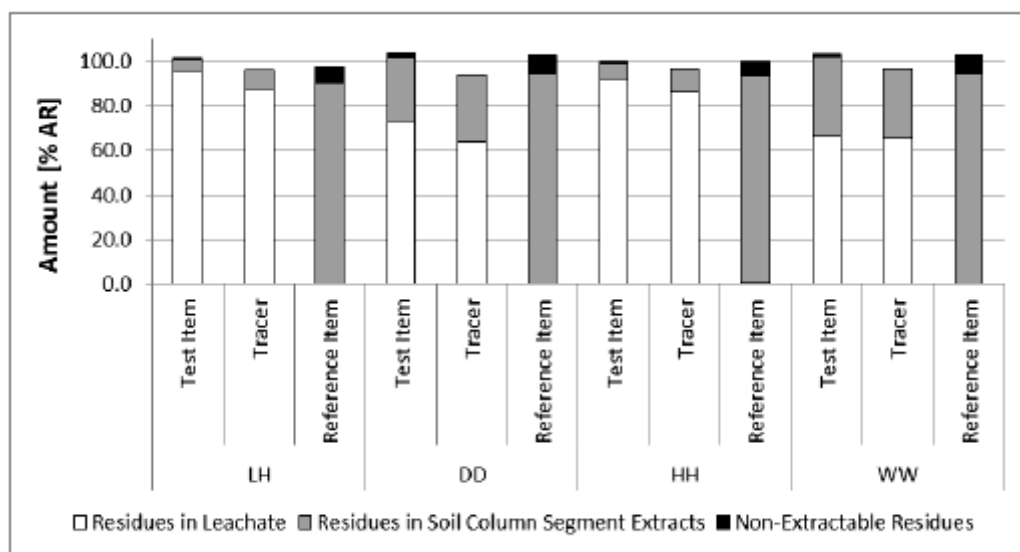


Figure B.8.1.3.1_CA-11: The graphical results of the determination of the mass balance in the experiment labelled **Study design A** (copied from the study report).

The detailed numerical results of the study obtained for the experiment labelled **Study design A** are presented below. To maintain their clarity RMS decided to reproduce them as they were provided by the Applicant in the study report. They are followed by their graphical presentation.

Results obtained for columns filled with the test soil Laacherhof AXXa:**Replicate column 1**

Column ID: Ja64 LH 1a

						TFA [Test Item]	H ₂ O [Tracer]
Leachate							
Fraction (L)	Sampling Time [h]	V _{fraction} [mL]	Σ V _{fraction} [mL]	Total [% AR]			Total [% AR]
L1	0-6	52	52	< 0.1			< 0.1
L2	6-12	62	114	2.5			0.5
L3	12-18	62	176	18.5			10.7
L4	18-24	62	238	20.5			19.3
L5	24-30	60	298	18.9			20.1
L6	30-36	58	356	19.3			18.0
L7	36-42	58	414	13.6			15.8
L8	42-48	29	443	4.0			5.9
L9	48-x *	0	443	n.d.			n.d.
Subtotal Leachate		443		97.8			96.3
Soil Column							
Segment (S)		h _{segment} [cm]	Σ h _{segment} [cm]	Total [% AR]	Org. extract [% AR]	Combustion [% AR]	Org. extract [% AR]
S1		0-6	6	0.9	0.5	0.4	0.2
S2		6-12	12	0.5	0.2	0.3	n.d.
S3		12-18	18	0.1	< 0.1	0.1	< 0.1
S4		18-24	24	0.4	0.2	0.3	0.4
S5		24-30	30	3.1	2.7	0.4	5.4
Subtotal Soil Column		30		5.0	3.5	1.4	6.1
Total Extractable Residues ¹				109.5			96.3
Material Balance				109.3			96.3

* Dripping time approx. 16-20 h

¹ Sum of residues in leachate and organic extract**Replicate column 2**

Column ID: Ja64 LH 2a

						TFA [Test Item]	H ₂ O [Tracer]
Leachate							
Fraction (L)	Sampling Time [h]	V _{fraction} [mL]	Σ V _{fraction} [mL]	Total [% AR]			Total [% AR]
L1	0-6	46	46	< 0.1			< 0.1
L2	6-12	58	104	4.3			3.1
L3	12-18	58	162	16.8			11.1
L4	18-24	57	219	17.3			14.5
L5	24-30	56	275	14.8			15.4
L6	30-36	54	329	12.5			13.9
L7	36-42	54	383	12.8			13.3
L8	42-48	52	435	12.6			12.6
L9	48-x *	13	448	2.8			3.1
Subtotal Leachate		448		93.5			84.8
Soil Column							
Segment (S)		h _{segment} [cm]	Σ h _{segment} [cm]	Total [% AR]	Org. extract [% AR]	Combustion [% AR]	Org. extract [% AR]
S1		0-6	6	0.1	0.1	< 0.1	< 0.1
S2		6-12	12	0.1	< 0.1	0.1	n.d.
S3		12-18	18	0.1	< 0.1	0.1	< 0.1
S4		18-24	24	0.3	0.2	0.1	1.4
S5		24-30	30	6.7	6.0	0.0	9.3
Subtotal Soil Column		30		7.3	6.3	0.8	10.7
Total Extractable Residues ¹				99.8			86.5
Material Balance				100.7			86.5

* Dripping time approx. 16-20 h

¹ Sum of residues in leachate and organic extract

Mean Material Balance	TFA [Test Item]	H ₂ O [Tracer]
Ja64 LH 1a / Ja64 LH 2a	101.3	95.9

Figure B.8.1.3.1_CA-12: Tables presenting the numerical results of the examination of column leaching obtained for the test item (TFA) and tracer (copied from the study report).**Replicate column 1**

Column ID: Ja64 LH 3a

						Atrazine [Reference Item]	H ₂ O [Tracer]
Leachate							
Fraction (L)	Sampling Time [h]	V _{fraction} [mL]	Σ V _{fraction} [mL]	Total [% AR]			Total [% AR]
L1	0-6	49	49	< 0.1			< 0.1
L2	6-12	59	108	< 0.1			< 0.1
L3	12-18	56	166	< 0.1			2.2
L4	18-24	58	224	0.1			16.9
L5	24-30	56	282	n.d.			26.8
L6	30-36	56	338	n.d.			22.6
L7	36-42	58	396	0.1			17.9
L8	42-48	52	448	n.d.			8.2
L9	48-x *	0	448	n.d.			0.0
Subtotal Leachate		448		0.1			53.9
Soil Column							
Segment (S)		h _{segment} [cm]	Σ h _{segment} [cm]	Total [% AR]	Org. extract [% AR]	Combustion [% AR]	Org. extract [% AR]
S1		0-6	6	61.6	56.8	5.0	0.8
S2		6-12	12	31.5	29.7	1.8	0.4
S3		12-18	18	2.9	2.7	0.2	0.2
S4		18-24	24	0.3	0.3	0.1	0.3
S5		24-30	30	0.2	0.2	< 0.1	1.3
Subtotal Soil Column		30		96.6	89.6	7.0	2.9
Total Extractable Residues ¹				99.7			96.8
Material Balance				96.8			96.8

* Dripping time approx. 16-20 h

¹ Sum of residues in leachate and organic extract**Replicate column 2**

Column ID: Ja64 LH 4a

						Atrazine [Reference Item]	H ₂ O [Tracer]
Leachate							
Fraction (L)	Sampling Time [h]	V _{fraction} [mL]	Σ V _{fraction} [mL]	Total [% AR]			Total [% AR]
L1	0-6	50	50	< 0.1			< 0.1
L2	6-12	51	101	< 0.1			< 0.1
L3	12-18	51	152	< 0.1			1.5
L4	18-24	51	203	< 0.1			5.9
L5	24-30	50	253	n.d.			8.2
L6	30-36	51	304	n.d.			12.5
L7	36-42	50	354	n.d.			18.0
L8	42-48	51	405	n.d.			23.1
L9	48-x *	37	442	0.1			14.4
Subtotal Leachate		442		0.1			84.2
Soil Column							
Segment (S)		h _{segment} [cm]	Σ h _{segment} [cm]	Total [% AR]	Org. extract [% AR]	Combustion [% AR]	Org. extract [% AR]
S1		0-6	6	81.3	75.5	5.8	0.9
S2		6-12	12	13.7	12.9	0.8	0.4
S3		12-18	18	2.1	1.8	0.3	0.2
S4		18-24	24	1.1	0.4	0.6	0.5
S5		24-30	30	0.2	0.1	0.1	0.9
Subtotal Soil Column		30		98.4	89.6	7.7	8.9
Total Extractable Residues ¹				90.7			93.1
Material Balance				98.6			93.1

* Dripping time approx. 16-20 h

¹ Sum of residues in leachate and organic extract

Mean Material Balance	Atrazine [Reference Item]	H ₂ O [Tracer]
Ja64 LH 3a / Ja64 LH 4a	97.8	94.9

Figure B.8.1.3.1_CA-13: Tables presenting the numerical results of the examination of column leaching obtained for the reference item (atrazine) and tracer (copied from the study report).

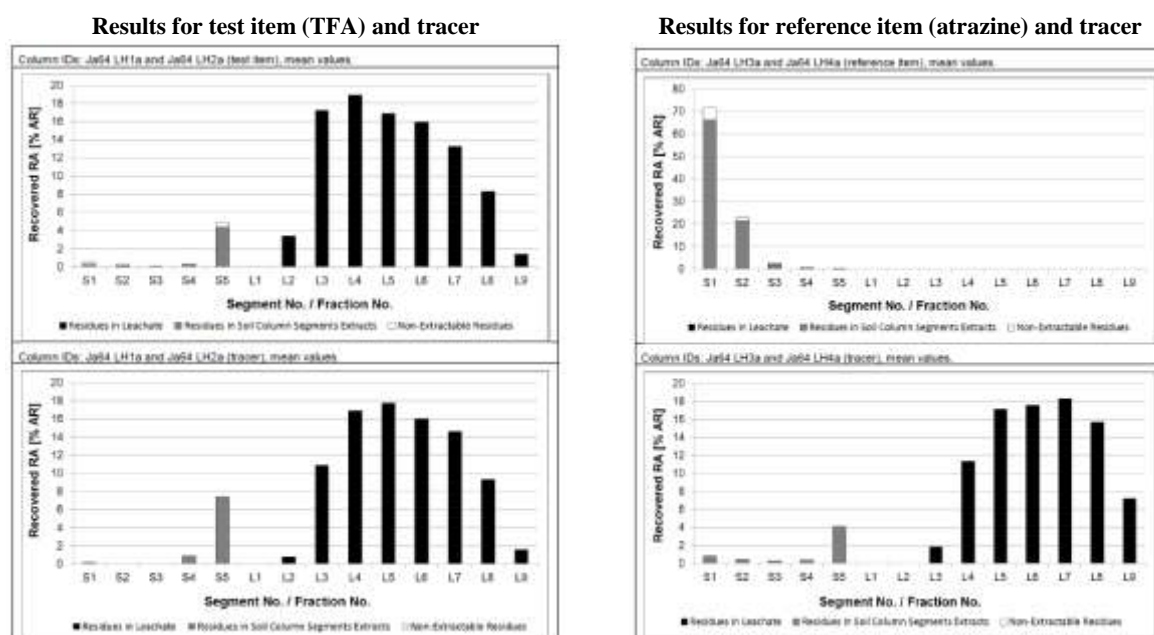


Figure B.8.1.3.1._CA-14: The graphical presentation of the results obtained for columns filled with the test soil Laacherhof AXXa (copied from the study report).

The results of the calculations of the K_d and K_{dOC} values for each compound are presented below in the table B.8.1.3.1._CA-6.

Table B.8.1.3.1._CA-6: The calculated K_d and K_{dOC} values for each of the compounds used in the experiment.

Results obtained for test item and tracer					Results obtained for reference item and tracer				
Column ID	Results obtained for:				Column ID	Results obtained for:			
	TFA		tracer			Atrazine		tracer	
	K _d [mL/g]	K _{dOC} [mL/g]	K _d [mL/g]	K _{dOC} [mL/g]		K _d [mL/g]	K _{dOC} [mL/g]	K _d [mL/g]	K _{dOC} [mL/g]
Ja64 LH 1a	0.0	0.0	0.0	0.0	Ja64 LH 3a	5.0	278.4	0.0	0.0
Ja64 LH 2a	0.0	0.0	0.0	0.0	Ja64 LH 4a	5.1	284.1	0.1	5.7
Mean	0.0	0.0	0.0	0.0	Mean	5.1	281.3	0.1	2.9

Results obtained for columns filled with the test soil Dollendorf II:**Replicate column 1**

Column ID: Ja64 DD1

					TFA (Test Item)	³ H ₂ O (Tracer)	
Leachate							
Fraction	Sampling Time [h]	V _{Fraction} [mL]	Σ V _{Fraction} [mL]	Total [% AR]	Total [% AR]		
L1	0-6	49	49	0.0	0.0		
L2	6-12	49	98	1.8	0.1		
L3	12-18	49	147	14.8	7.6		
L4	18-24	50	197	15.2	14.8		
L5	24-30	50	247	11.2	12.5		
L6	30-36	50	297	9.3	9.3		
L7	36-42	50	347	6.5	7.3		
L8	42-48	50	397	5.2	5.7		
L9	48-x *	12	409	1.1	1.2		
Subtotal Leachate		409		64.6	58.2		
Soil Column							
Segment (S)		h Segment [cm]	Σ h Segment [cm]	Total [% AR]	Org. extract [% AR]	Combustion [% AR]	Org. extract [% AR]
S1		0-6	6	10.9	10.8	0.3	7.0
S2		6-12	12	22.9	8.6	0.3	8.7
S3		12-18	18	34.9	7.9	0.4	8.2
S4		18-24	24	46.9	6.1	0.3	8.2
S5		24-30	30	58.9	4.0	0.2	4.8
Subtotal Soil Column		30		38.6	37.1	1.6	35.9
Total Extractable Residues ¹				101.1			93.2
Material Balance				102.6			93.2

* Dripping time approx. 16-20 h

¹ Sum of residues in leachate and organic extract**Replicate column 2**

Column ID: Ja64 DD2

				TFA [Test Item]	%O [Tracer]		
Leachate							
Fraction (L)	Sampling Time [h]	V fraction [mL]	Σ V fraction [mL]	Total [% AR]	Total [% AR]		
L1	0-6	47	47	< 0.1	0.0		
L2	6-12	48	95	2.6	0.2		
L3	12-18	48	143	16.2	7.6		
L4	18-24	48	191	25.3	16.8		
L5	24-30	48	240	15.2	17.8		
L6	30-36	49	289	9.2	11.5		
L7	36-42	48	338	8.0	8.1		
L8	42-48	48	387	4.5	5.9		
L9	48-x *	20	407	1.5	2.0		
Subtotal Leachate		407		82.4	68.6		
Soil Column							
Segment (S)		R segment [cm]	Σ R segment [cm]	Total [% AR]	Org.- extract [% AR]	Combustion [% AR]	Org.- extract [% AR]
S1		0-6	6	2.6	2.6	0.1	2.6
S2		6-12	12	5.9	5.5	0.4	5.9
S3		12-18	18	4.2	3.7	0.5	4.7
S4		18-24	24	4.0	3.5	0.5	5.2
S5		24-30	30	4.5	4.0	0.5	5.9
Subtotal Soil Column		30		21.4	19.3	2.8	24.3
Total Extractable Residues ¹				101.7			93.8
Material Balance				103.8			93.8

* Dripping time approx. 16-20 h

¹ Sum of residues in leachate and organic extract

Mean Material Balance	TFA [Test Item]	³ H ₂ O [Tracer]
Ja64 DD 1 / Ja64 DD 2	103.2	93.5

Figure B.8.1.3.1._CA-15: Tables presenting the numerical results of the examination of column leaching obtained for the test item (TFA) and tracer (copied from the study report).

Replicate column 1

Column ID: Ja64 DD3

					Atrazine [Reference Item]	³ H ₂ O [Tracer]	
Leachate							
Fraction (L)	Sampling Time [h]	V _{fraction} [mL]	Σ V _{fraction} [mL]	Total [% AR]	Total [% AR]		
L1	0-6	51	51	< 0.1	0.0		
L2	6-12	49	100	< 0.1	1.2		
L3	12-18	51	151	0.1	20.1		
L4	18-24	51	202	< 0.1	18.8		
L5	24-30	51	253	< 0.1	14.3		
L6	30-36	51	304	0.1	9.1		
L7	36-42	51	355	0.1	8.3		
L8	42-48	51	406	0.2	5.8		
L9	48-x *	5	411	< 0.1	0.6		
Subtotal Leachate		411		0.5	75.9		
Soil Column							
Segment (S)		h segment [cm]	Σ h segment [cm]	Total [% AR]	Org. extract [% AR]	Combustion [% AR]	Org. extract [% AR]
S1	0-6	6	49.4	44.6	4.6		8.5
S2	6-12	12	33.2	30.8	2.6		2.4
S3	12-18	18	15.5	15.3	0.2		4.8
S4	18-24	24	2.8	1.5	1.4		4.2
S5	24-30	30	0.6	0.4	0.1		5.9
Subtotal Soil Column		30		101.5	82.5	9.0	19.9
Total Extractable Residue ¹				92.3			95.9
Material Balance				102.0			95.9

* Dripping time approx. 16-20 h

¹ Sum of residues in leachate and organic extract**Replicate column 2**

Column ID: Ja64 DD4

					Atrazine [Reference Item]	³ H ₂ O [Tracer]	
Leachate							
Fraction (L)	Sampling Time [h]	V _{fraction} [mL]	Σ V _{fraction} [mL]	Total [% AR]	Total [% AR]		
L1	0-6	48	48	< 0.1	0.0		
L2	6-12	48	96	< 0.1	0.1		
L3	12-18	48	144	< 0.1	4.8		
L4	18-24	48	192	< 0.1	13.1		
L5	24-30	48	240	< 0.1	12.3		
L6	30-36	48	288	< 0.1	9.7		
L7	36-42	48	336	< 0.1	7.7		
L8	42-48	48	384	< 0.1	6.3		
L9	48-x *	40	424	< 0.1	4.5		
Subtotal Leachate		424		0.1	58.4		
Soil Column							
Segment (S)		h segment [cm]	Σ h segment [cm]	Total [% AR]	Org. extract [% AR]	Combustion [% AR]	Org. extract [% AR]
S1	0-6	6	95.5	79.2	6.4	4.3	
S2	6-12	12	12.1	11.1	1.0	11.9	
S3	12-18	18	3.7	3.4	0.3	8.1	
S4	18-24	24	1.3	1.2	0.1	6.3	
S5	24-30	30	0.2	0.2	< 0.1	5.6	
Subtotal Soil Column		30		102.8	95.0	7.8	37.2
Total Extractable Residues ¹				95.0			95.6
Material Balance				103.9			95.6

* Dripping time approx. 16-20 h

¹ Sum of residues in leachate and organic extract

Mean Material Balance	Atrazine [Reference Item]	³ H ₂ O [Tracer]
Ja64 DD 3 / Ja64 DD 4	102.5	95.3

Figure B.8.1.3.1._CA-16: Tables presenting the numerical results of the examination of column leaching obtained for the reference item (atrazine) and tracer (copied from the study report).

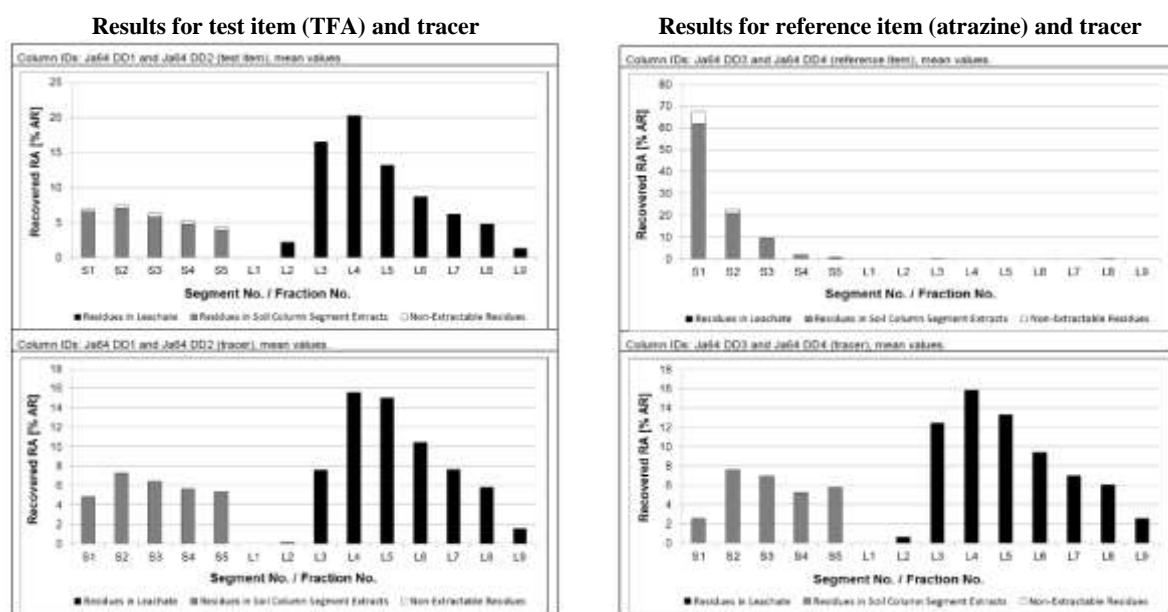


Figure B.8.1.3.1._CA-17: The graphical presentation of the results obtained for columns filled with the test soil Dollendorf II (copied from the study report).

The results of the calculations of the K_d and K_{dOC} values for each compound are presented below in the table B.8.1.3.1._CA-7.

Table B.8.1.3.1._CA-7: The calculated K_d and K_{dOC} values for each of the compounds used in the experiment.

Results obtained for test item and tracer					Results obtained for reference item and tracer				
Column ID	Results obtained for:				Column ID	Results obtained for:			
	TFA		tracer			Atrazine		tracer	
	K _d [mL/g]	K _{dOC} [mL/g]	K _d [mL/g]	K _{dOC} [mL/g]		K _d [mL/g]	K _{dOC} [mL/g]	K _d [mL/g]	K _{dOC} [mL/g]
Ja64 DD 1	0.0	0.0	0.0	0.0	Ja64 DD 3	6.3	120.9	0.0	0.0
Ja64 DD 2a	0.0	0.0	0.0	0.0	Ja64 DD 4	6.2	119.8	0.0	0.0
Mean	0.0	0.0	0.0	0.0	Mean	6.3	120.4	0.0	0.0

Results obtained for columns filled with the test soil Höfchen am Hoheneseh:**Replicate column 1**

Column ID: J064 HH 1a

						TFA [Test Item]	³ H ₂ O [Tracer]
Leachate							
Fraction (L)	Sampling Time [h]	V _{fraction} [mL]	Σ V _{fraction} [mL]	Total [% AR]			Total [% AR]
L1	0-6	51	51	<0.1			0.0
L2	6-12	51	102	1.3			0.0
L3	12-18	51	153	23.7			12.1
L4	18-24	51	204	34.9			33.7
L5	24-30	51	255	17.4			19.2
L6	30-36	51	306	10.5			13.2
L7	36-42	51	357	6.5			6.4
L8	42-48	51	408	5.4			6.4
L9	48-x *	25	433	2.4			2.7
Subtotal Leachate		433		92.1			65.8
Soil Column							
Segment (S)		h segment [cm]	Σ h segment [cm]	Total [% AR]	Org. extract [% AR]	Combustion [% AR]	Org. extract [% AR]
S1		0-6	6	0.2	0.1	0.2	<0.1
S2		6-12	12	0.3	<0.1	0.2	<0.1
S3		12-18	18	0.1	0.1	0.1	0.3
S4		18-24	24	2.0	1.8	0.1	4.5
S5		24-30	30	4.8	4.6	0.2	5.6
Subtotal Soil Column		30		7.3	6.5	0.8	10.4
Total Extractable Residues ¹						65.8	66.1
Material Balance						99.4	96.2

* Dripping Time approx. 16-20 h

¹ Sum of residues in leachate and organic extract**Replicate column 2**

Column ID: J064 HH 2a – This column was not considered in the final evaluation, as the material balance was not in an acceptable range between 90 to 110% AR.

						TFA [Test Item]	³ H ₂ O [Tracer]
Leachate							
Fraction (L)	Sampling Time [h]	V _{fraction} [mL]	Σ V _{fraction} [mL]	Total [% AR]			Total [% AR]
L1	0-6	52	52	0.0			0.0
L2	6-12	52	104	0.0			0.0
L3	12-18	52	156	1.8			0.3
L4	18-24	52	208	8.8			2.8
L5	24-30	52	260	8.8			8.8
L6	30-36	52	312	0.4			0.3
L7	36-42	52	364	12.3			12.3
L8	42-48	52	416	10.8			12.3
L9	48-x *	0	416	0.4			0.4
Subtotal Leachate		416		46.4			42.6
Soil Column							
Segment (S)		h segment [cm]	Σ h segment [cm]	Total [% AR]	Org. extract [% AR]	Combustion [% AR]	Org. extract [% AR]
S1		0-6	6	0.1	<0.1	<0.1	<0.1
S2		6-12	12	0.1	<0.1	<0.1	<0.1
S3		12-18	18	0.1	0.1	<0.1	0.1
S4		18-24	24	0.1	0.1	<0.1	0.4
S5		24-30	30	2.0	2.0	0.1	2.3
Subtotal Soil Column		30		2.4	2.4	0.4	2.8
Total Extractable Residues ¹						48.2	45.4
Material Balance						68.8	45.4

* Dripping time approx. 16-20 h

¹ Sum of residues in leachate and organic extract

Mean Material Balance ²	TFA [Test Item]	³ H ₂ O [Tracer]
J064 HH 1a / J064 HH 2a	99.4	96.2
only soil column J064 HH 1a was considered		

Figure B.8.1.3.1._CA-18: Tables presenting the numerical results of the examination of column leaching obtained for the test item (TFA) and tracer (copied from the study report).**Replicate column 1**

Column ID: J064 HH 3a

						Atrazine [Reference Item]	³ H ₂ O [Tracer]
Leachate							
Fraction (L)	Sampling Time [h]	V _{fraction} [mL]	Σ V _{fraction} [mL]	Total [% AR]			Total [% AR]
L1	0-6	50	50	<0.1			0.0
L2	6-12	51	101	<0.1			0.0
L3	12-18	51	152	<0.1			0.2
L4	18-24	50	202	0.1			2.8
L5	24-30	50	252	0.1			5.8
L6	30-36	51	303	0.1			7.6
L7	36-42	51	354	0.1			11.3
L8	42-48	51	405	0.1			15.0
L9	48-x *	13	418	<0.1			3.5
Subtotal Leachate		418		0.5			46.2
Soil Column							
Segment (S)		h segment [cm]	Σ h segment [cm]	Total [% AR]	Org. extract [% AR]	Combustion [% AR]	Org. extract [% AR]
S1		0-6	6	89.2	85.4	5.8	1.4
S2		6-12	12	8.3	7.7	0.6	1.4
S3		12-18	18	1.4	1.2	0.2	4.6
S4		18-24	24	0.2	0.1	0.1	15.3
S5		24-30	30	0.2	<0.1	0.1	22.8
Subtotal Soil Column		30		99.3	93.3	6.8	45.5
Total Extractable Residues ¹						92.8	91.7
Material Balance						99.6	91.7

* Dripping time approx. 16-20 h

¹ Sum of residues in leachate and organic extract**Replicate column 2**

Column ID: J064 HH 4a – This column was not considered in the final evaluation, as the material balance was not in an acceptable range between 90 to 110% AR.

						Atrazine [Reference Item]	³ H ₂ O [Tracer]
Leachate							
Fraction (L)	Sampling Time [h]	V _{fraction} [mL]	Σ V _{fraction} [mL]	Total [% AR]			Total [% AR]
L1	0-6	52	52	<0.1			0.0
L2	6-12	52	104	2.1			6.4
L3	12-18	52	156	0.6			46.2
L4	18-24	52	208	8.8			18.8
L5	24-30	52	260	8.8			22.8
L6	30-36	52	312	6.4			47.2
L7	36-42	52	364	4.0			42.3
L8	42-48	52	416	1.1			10.1
L9	48-x *	0	416	0.6			1.6
Subtotal Leachate		416		42.6			101.8
Soil Column							
Segment (S)		h segment [cm]	Σ h segment [cm]	Total [% AR]	Org. extract [% AR]	Combustion [% AR]	Org. extract [% AR]
S1		0-6	6	88.1	84.1	4.0	1.6
S2		6-12	12	22.2	21.6	0.6	2.6
S3		12-18	18	4.6	4.1	0.5	9.4
S4		18-24	24	10.4	10.2	0.2	46.6
S5		24-30	30	4.3	4.0	0.3	40.0
Subtotal Soil Column		30		129.6	126.0	5.6	110.6
Total Extractable Residues ¹						144.2	152.4
Material Balance						144.2	152.4

* Dripping time approx. 16-20 h

¹ Sum of residues in leachate and organic extract

Mean Material Balance ²	Atrazine [Reference Item]	³ H ₂ O [Tracer]
J064 HH 3a / J064 HH 4a	99.6	91.7
only soil column J064 HH 3a was considered		

Figure B.8.1.3.1._CA-19: Tables presenting the numerical results of the examination of column leaching obtained for the reference item (atrazine) and tracer (copied from the study report).

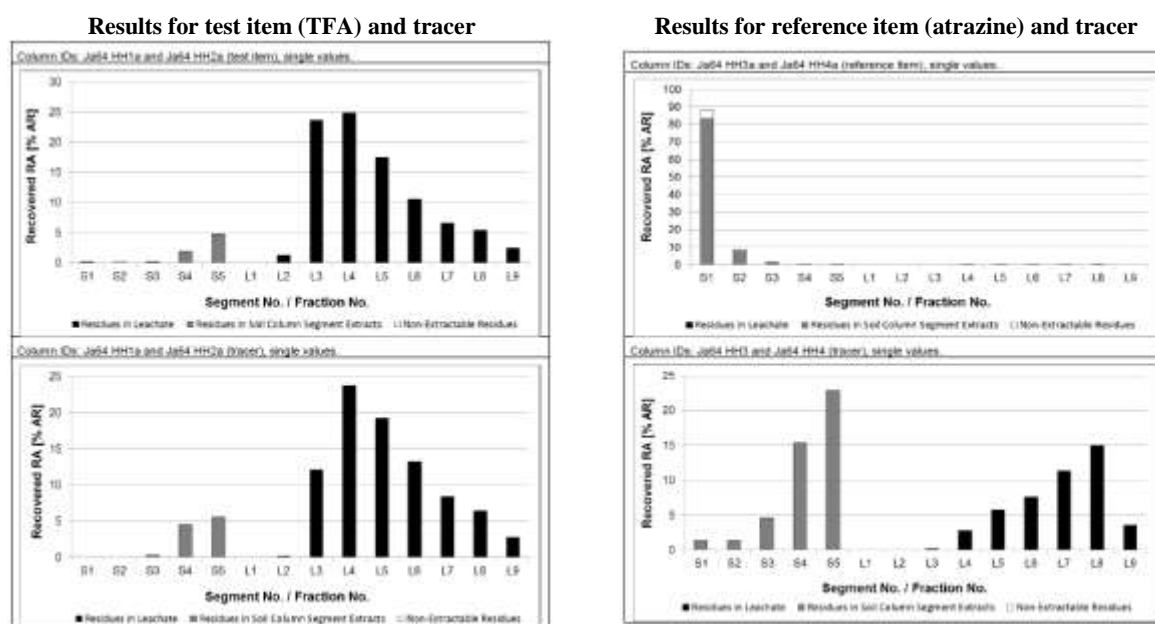


Figure B.8.1.3.1._CA-20: The graphical presentation of the results obtained for columns filled with the test soil Höfchen am Hoheneseh (copied from the study report).

The results of the calculations of the K_d and K_{dOC} values for each compound are presented below in the table B.8.1.3.1._CA-8.

Table B.8.1.3.1._CA-8: The calculated K_d and K_{dOC} values for each of the compounds used in the experiment.

Results obtained for test item and tracer					Results obtained for reference item and tracer				
Column ID	Results obtained for:				Column ID	Results obtained for:			
	TFA		tracer			Atrazine		tracer	
	K _d [mL/g]	K _{dOC} [mL/g]	K _d [mL/g]	K _{dOC} [mL/g]		K _d [mL/g]	K _{dOC} [mL/g]	K _d [mL/g]	K _{dOC} [mL/g]
Ja64 HH 1a	0.0	0.0	0.0	0.0	Ja64 HH 3a	5.4	337.1	0.2	11.1
Ja64 HH 2a	----	----	----	----	Ja64 HH 4a	----	----	----	----
Mean	0.0	0.0	0.0	0.0	Mean	5.4	337.1	0.2	11.1

Results obtained for columns filled with the test soil Laacherhof Wurmwiese:**Replicate column 1**

Column ID: Ja64 WW 1

						TFA [Test Item]	³ H ₂ O [Tracer]
Leachate							
Fraction [L]	Sampling Time [h]	V _{meas} [mL]	Σ V _{meas} [mL]	Total [% AR]			Total [% AR]
L1	0-6	50	50	< 0.1			< 0.1
L2	6-12	49	99	< 0.1			< 0.1
L3	12-18	49	148	12.2			1.7
L4	18-24	49	197	14.3			12.8
L5	24-30	49	246	10.3			16.7
L6	30-36	49	295	6.3			13.6
L7	36-42	49	344	7.2			10.8
L8	42-48	49	393	6.8			9.3
L9	48-x *	17	410	2.4			3.9
Subtotal Leachate		410		62.8			68.5
Soil Column							
Segment [S]		h _{segment} [cm]	Σ h _{segment} [cm]	Total [% AR]	Org.- extract [% AR]	Combustion [% AR]	Org.- extract [% AR]
S1		0-6	6	0.4	0.3	0.1	0.1
S2		6-12	12	3.0	2.9	0.1	2.4
S3		12-18	18	14.6	14.3	0.3	9.5
S4		18-24	24	12.9	12.6	0.3	8.6
S5		24-30	30	10.0	8.6	0.3	7.1
Subtotal Soil Column		30		40.8	39.6	1.1	33.8
Total Extractable Residues [†]				181.6			96.0
Material Balance				182.8			96.1

* Dipping time approx. 16-20 h

† Sum of residues in leachate and organic extract

Replicate column 2

Column ID: Ja64 WW 2

						TFA [Test Item]	³ H ₂ O [Tracer]
Leachate							
Fraction [L]	Sampling Time [h]	V _{meas} [mL]	Σ V _{meas} [mL]	Total [% AR]			Total [% AR]
L1	0-6	50	50	< 0.1			< 0.1
L2	6-12	50	100	< 0.1			< 0.1
L3	12-18	50	150	4.5			1.7
L4	18-24	50	200	15.7			12.8
L5	24-30	50	250	16.1			16.7
L6	30-36	49	299	12.4			13.6
L7	36-42	50	349	9.8			10.8
L8	42-48	50	399	8.4			9.3
L9	48-x *	22	421	3.5			3.9
Subtotal Leachate		421		70.4			68.5
Soil Column							
Segment [S]		h _{segment} [cm]	Σ h _{segment} [cm]	Total [% AR]	Org.- extract [% AR]	Combustion [% AR]	Org.- extract [% AR]
S1		0-6	6	0.2	0.2	0.1	0.1
S2		6-12	12	2.3	2.2	0.1	2.4
S3		12-18	18	11.8	11.4	0.3	9.5
S4		18-24	24	10.6	10.4	0.2	8.6
S5		24-30	30	7.8	7.3	0.3	7.1
Subtotal Soil Column		30		32.5	31.5	1.8	27.7
Total Extractable Residues [†]				181.9			96.2
Material Balance				182.9			96.2

* Dipping time approx. 16-20 h

† Sum of residues in leachate and organic extract

Mean Material Balance	TFA [Test Item]	³ H ₂ O [Tracer]
Ja64 WW 1 / Ja64 WW 2	182.9	96.2

Figure B.8.1.3.1._CA-21: Tables presenting the numerical results of the examination of column leaching obtained for the test item (TFA) and tracer (copied from the study report).**Replicate column 1**

Column ID: Ja64 WW 3

						Atrazine [Reference Item]	³ H ₂ O [Tracer]
Leachate							
Fraction [L]	Sampling Time [h]	V _{meas} [mL]	Σ V _{meas} [mL]	Total [% AR]			Total [% AR]
L1	0-6	49	49	< 0.1			< 0.1
L2	6-12	48	97	< 0.1			< 0.1
L3	12-18	49	146	0.1			1.4
L4	18-24	49	195	0.2			13.2
L5	24-30	49	244	< 0.1			11.6
L6	30-36	49	293	< 0.1			8.9
L7	36-42	49	342	< 0.1			7.6
L8	42-48	49	391	< 0.1			7.2
L9	48-x *	31	422	< 0.1			4.3
Subtotal Leachate		422		0.4			56.8
Soil Column							
Segment [S]		h _{segment} [cm]	Σ h _{segment} [cm]	Total [% AR]	Org.- extract [% AR]	Combustion [% AR]	Org.- extract [% AR]
S1		0-6	6	60.7	74.4	0.3	4.7
S2		6-12	12	9.9	9.2	0.7	10.6
S3		12-18	18	6.4	6.0	0.4	12.3
S4		18-24	24	2.3	2.2	0.1	10.2
S5		24-30	30	1.2	1.0	0.2	8.8
Subtotal Soil Column		36		180.6	92.8	7.7	46.7
Total Extractable Residues [†]				93.1			91.7
Material Balance				186.9			91.7

* Dipping time approx. 16-20 h

† Sum of residues in leachate and organic extract

Replicate column 2

Column ID: Ja64 WW 4

						Atrazine [Reference Item]	³ H ₂ O [Tracer]
Leachate							
Fraction [L]	Sampling Time [h]	V _{meas} [mL]	Σ V _{meas} [mL]	Total [% AR]			Total [% AR]
L1	0-6	49	49	< 0.1			< 0.1
L2	6-12	49	98	< 0.1			< 0.1
L3	12-18	49	147	< 0.1			4.0
L4	18-24	48	195	n.d.			13.2
L5	24-30	49	244	< 0.1			11.6
L6	30-36	49	293	< 0.1			8.9
L7	36-42	49	342	0.1			7.6
L8	42-48	49	391	0.1			7.2
L9	48-x *	29	420	0.1			4.3
Subtotal Leachate		420		0.4			56.8
Soil Column							
Segment [S]		h _{segment} [cm]	Σ h _{segment} [cm]	Total [% AR]	Org.- extract [% AR]	Combustion [% AR]	Org.- extract [% AR]
S1		0-6	6	67.6	60.9	6.7	2.8
S2		6-12	12	21.0	19.4	1.6	1.7
S3		12-18	18	9.4	8.5	0.9	6.1
S4		18-24	24	4.4	4.0	0.4	13.5
S5		24-30	30	1.4	1.3	0.2	12.2
Subtotal Soil Column		30		103.8	94.1	9.8	37.3
Total Extractable Residues [†]				94.4			94.6
Material Balance				184.2			94.7

* Dipping time approx. 16-20 h

† Sum of residues in leachate and organic extract

Mean Material Balance	Atrazine [Reference Item]	³ H ₂ O [Tracer]
Ja64 WW 3 / Ja64 WW 4	182.8	93.2

Figure B.8.1.3.1._CA-22: Tables presenting the numerical results of the examination of column leaching obtained for the reference item (atrazine) and tracer (copied from the study report).

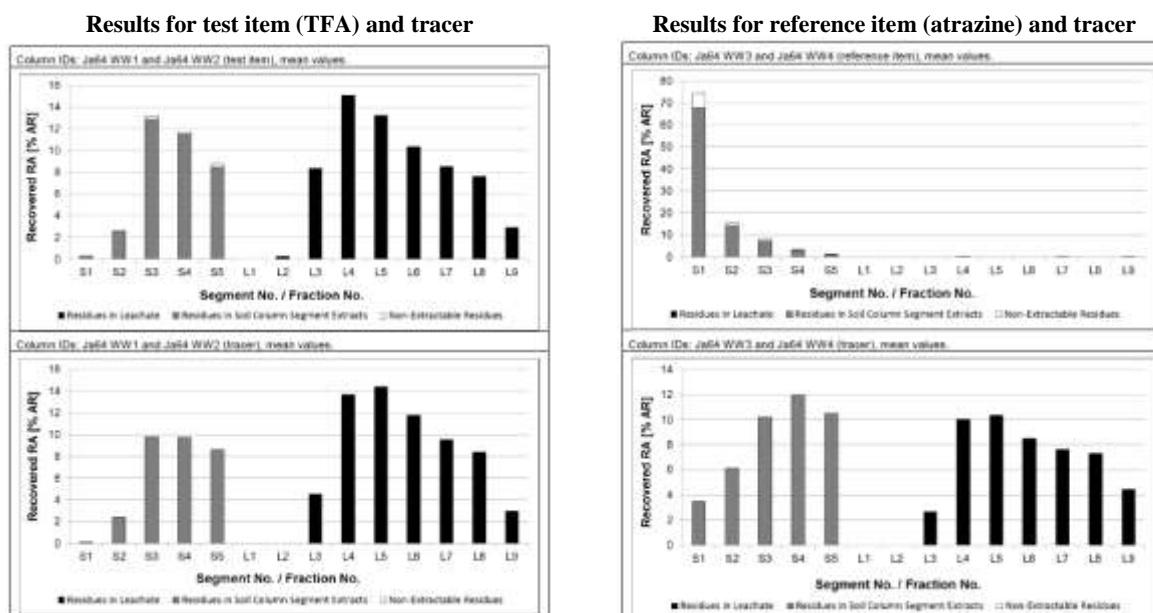


Figure B.8.1.3.1._CA-23: The graphical presentation of the results obtained for columns filled with the test soil Laacherhof Wurmwise (copied from the study report).

The results of the calculations of the K_d and K_{dOC} values for each compound are presented below in the table B.8.1.3.1._CA-9.

Table B.8.1.3.1._CA-9: The calculated K_d and K_{dOC} values for each of the compounds used in the experiment.

Results obtained for test item and tracer					Results obtained for reference item and tracer				
Column ID	Results obtained for:				Column ID	Results obtained for:			
	TFA		tracer			Atrazine		tracer	
	K _d [mL/g]	K _{dOC} [mL/g]	K _d [mL/g]	K _{dOC} [mL/g]		K _d [mL/g]	K _{dOC} [mL/g]	K _d [mL/g]	K _{dOC} [mL/g]
Ja64 WW 1	0.0	0.0	0.0	0.0	Ja64 WW 3	5.5	289.9	0.2	8.5
Ja64 WW 2	0.0	0.0	0.0	0.0	Ja64 WW 4	5.7	299.9	0.2	3.0
Mean	0.0	0.0	0.0	0.0	Mean	5.6	294.9	0.2	5.8

The results of the determination of the pH of collected leachate fractions is presented below, on figure B.8.1.3.1._CA-24 in form of the tables provided by the Applicant in the study report.

Results obtained for test item and tracer									
Sampling Time [h]	Fraction ID	pH values							
		Ja64 LH1a	Ja64 LH2a	Ja64 HH1a	Ja64 HH2a	Ja64 DD1	Ja64 DD2	Ja64 WW1	Ja64 WW2
0-6	L1	7.3	7.4	7.5	7.5	8.1	8.1	7.1	7.1
6-12	L2	7.4	7.5	7.6	7.6	7.9	7.8	7.9	7.9
12-18	L3	7.7	7.7	7.9	7.9	7.7	7.7	7.9	7.9
18-24	L4	7.8	7.8	8.0	8.0	7.6	7.7	7.3	7.3
24-30	L5	7.7	7.8	7.9	8.0	7.6	7.6	7.3	7.3
30-36	L6	7.9	7.9	8.0	8.1	7.7	7.7	7.4	7.4
36-42	L7	8.0	8.0	8.1	8.0	7.8	7.8	7.6	7.6
42-48	L8	8.0	8.0	8.1	8.2	7.8	7.8	7.7	7.6
48-54	L9	-	8.0	8.0	-	8.0	8.0	7.6	7.6

Results obtained for reference item and tracer									
Sampling Time [h]	Fraction ID	pH values							
		Ja64 LH1a	Ja64 LH4a	Ja64 HH1a	Ja64 HH4a	Ja64 DD3	Ja64 DD4	Ja64 WW3	Ja64 WW4
0-6	L1	7.4	7.5	7.5	7.5	8.2	8.2	7.1	7.1
6-12	L2	7.7	7.7	7.7	7.7	7.9	7.9	7.9	7.9
12-18	L3	7.7	7.8	7.8	7.8	7.7	7.7	7.9	7.9
18-24	L4	7.8	7.8	7.8	7.8	7.8	7.8	7.2	7.2
24-30	L5	7.9	8.0	8.1	8.0	7.7	7.7	7.3	7.3
30-36	L6	7.9	8.0	7.9	8.0	7.7	7.7	7.4	7.4
36-42	L7	8.0	8.0	7.9	8.0	7.8	7.8	7.6	7.6
42-48	L8	8.0	8.0	7.9	8.0	7.7	7.8	7.6	7.6
48-54	L9	-	7.9	8.1	7.9	8.0	7.9	7.2	7.2

* x = dripping time

Figure B.8.1.3.1._CA-24: The results of the determination of pH of the leachates (copied from the study report)

The detailed results of the study obtained for the experiment labelled **Study design B** are presented below. First are presented the results of the determination of the pH of collected leachate fraction for each soil column. Next are presented, individually, the numerical results obtained for each type of the soil column, followed by their graphical presentation. To maintain clarity of their reporting RMS decided to reproduce all numerical results as they were provided by the Applicant in the study report.

The results of the determination of the pH of collected leachate fractions are presented below, on figure B.8.1.3.1._CA-25 in form of the table provided by the Applicant in the study report.

Sampling Time [h]	Fraction ID	pH values							
		Ja64 LHS	Ja64 LHS	Ja64 HHS	Ja64 HHS	Ja64 DD5	Ja64 DD5	Ja64 WWS	Ja64 WWS
0-6	L1	7.6	7.5	7.7	7.7	7.7	8.0	7.3	7.3
6-12	L2	7.7	7.7	7.7	7.9	7.7	7.7	7.1	7.1
12-18	L3	7.9	7.9	7.9	7.9	7.6	7.7	7.1	7.1
18-24	L4	8.0	7.9	7.9	7.9	7.7	7.7	7.1	7.2
24-30	L5	8.1	8.1	8.0	8.0	7.6	7.8	7.3	7.3
30-36	L6	8.1	8.1	8.0	8.0	7.7	7.7	7.3	7.3
36-42	L7	8.2	8.1	8.0	8.0	7.8	7.8	7.4	7.4
42-48	L8	8.2	8.2	8.0	8.0	7.8	7.8	7.5	7.5
48-60	L9	8.0	8.1	7.8	7.8	7.7	7.7	7.3	7.2
60-72	L10	7.9	7.9	8.0	8.0	7.7	7.8	7.3	7.4
72-84	L11	8.0	8.0	8.0	8.1	7.8	7.8	7.5	7.5
84-96	L12	8.0	8.0	8.1	8.1	7.8	7.8	7.5	7.6
96-108	L13	8.0	8.0	8.1	8.1	7.9	7.9	7.6	7.6
108-120	L14	7.9	8.0	8.1	8.1	7.9	8.0	7.5	-
120-x*	L15	-	-	-	-	8.1	8.0	-	-

* x = dipping time

Figure B.8.1.3.1._CA-25: The results of the determination of pH of the leachates (copied from the study report)

Results obtained for columns filled with the test soil Laacherhof AXXa:**Replicate column 1**

Column ID: Ja64 LH 5

					TFA [Test Item]	³ H ₂ O [Tracer]
Leachate						
	Fraction	Sampling Time [h]	V _{Fraction} [mL]	Σ V _{Fraction} [mL]	Total [% AR]	Total [% AR]
	L1	0-6	51	51	0.0	0.0
	L2	6-12	52	103	0.0	0.0
	L3	12-18	52	155	2.2	1.1
	L4	18-24	52	207	6.6	6.7
	L5	24-30	52	259	8.9	10.8
	L6	30-36	52	311	13.0	14.6
	L7	36-42	52	363	25.4	19.5
	L8	42-48	49	412	28.6	22.3
	L9	48-60	103	515	13.7	23.7
	L10	60-72	103	618	0.2	0.8
	L11	72-84	103	721	0.0	0.0
	L12	84-96	102	823	0.0	0.0
	L13	96-108	102	925	0.0	0.0
	L14	108-120	75	1000	0.0	0.0
	L15	120-x *	0	1000	n.a	n.a
Total Leachate			1500		99.6	99.6
Soil Column					n.a	
Material Balance					99.6	99.6

* Dripping time approx. 16-20 h

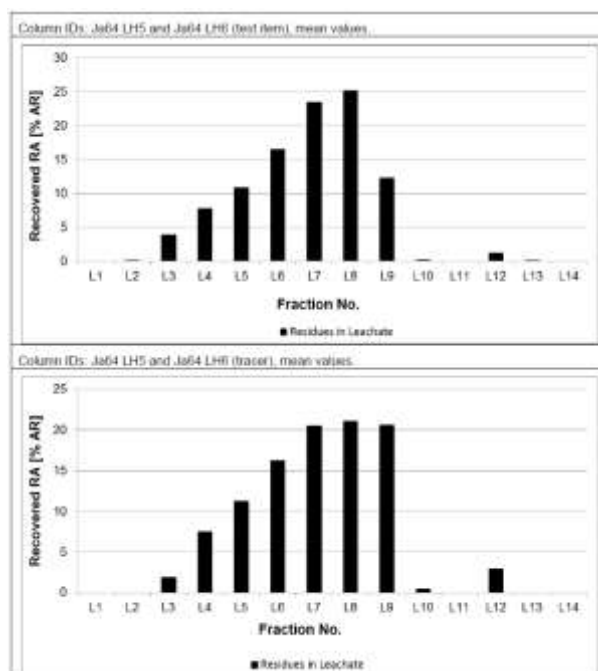
Replicate column 2

Column ID: Ja64 LH 6

					TFA [Test Item]	³ H ₂ O [Tracer]
Leachate						
Fraction (L)	Sampling Time [h]	V _{Fraction} [mL]	Σ V _{Fraction} [mL]	Total [% AR]	Total [% AR]	
L1	0-6	51	51	0.0	0.0	
L2	6-12	52	103	0.1	0.0	
L3	12-18	52	155	5.5	2.7	
L4	18-24	52	207	8.9	8.3	
L5	24-30	52	259	12.7	11.7	
L6	30-36	52	311	19.1	17.9	
L7	36-42	51	362	21.4	21.5	
L8	42-48	49	411	21.6	19.8	
L9	48-60	104	515	10.7	17.7	
L10	60-72	103	618	0.1	0.1	
L11	72-84	103	721	0.0	0.0	
L12	84-96	103	824	2.4	5.8	
L13	96-108	103	927	0.1	0.1	
L14	108-120	77	1004	0.0	0.0	
L15	120-x *	0	1004	n.a	n.a	
Total Leachate		1004		102.6	105.5	
Soil Column					n.a	
Material Balance					102.6	105.5

* Dripping time approx. 16-20 h

Mean Material Balance	TFA [Test Item]	³ H ₂ O [Tracer]
Ja64 LH 5 / Ja64 LH 6	101.1	102.6

Figure B.8.1.3.1._CA-26: Tables presenting the numerical results of the examination of column leaching obtained for the test item (TFA) and tracer (copied from the study report).**Figure B.8.1.3.1._CA-27:** The graphical presentation of the results obtained for columns filled with the test soil Laacherhof AXXa (copied from the study report).

Results obtained for columns filled with the test soil Dollendorf II:**Replicate column 1**

Column ID: Ja64 DD5

					TFA [Test Item]	³ H ₂ O [Tracer]
Leachate						
Fraction	Sampling Time	V _{fraction}	Σ V _{fraction}	Total	Total	
(L)	[h]	[mL]	[mL]	[% AR]	[% AR]	
L1	0-6	49	49	0.0	0.0	
L2	6-12	50	99	5.6	1.6	
L3	12-18	50	149	16.0	11.6	
L4	18-24	50	199	11.7	12.1	
L5	24-30	49	248	8.5	9.4	
L6	30-36	50	298	7.0	7.9	
L7	36-42	49	347	6.6	6.7	
L8	42-48	47	394	6.1	6.0	
L9	48-60	98	492	10.4	11.0	
L10	60-72	98	590	7.4	8.9	
L11	72-84	97	687	6.0	6.7	
L12	84-96	96	783	6.2	5.5	
L13	96-108	96	879	5.4	4.8	
L14	108-120	94	973	2.3	4.0	
L15	120-x *	8	981	0.1	0.4	
Total Leachate		981		99.4	98.6	
Soil Column					n.a.	
Material Balance					99.4	98.6

* Dripping time approx. 16-20 h

Replicate column 2

Column ID: Ja64 DD6

					TFA [Test Item]	³ H ₂ O [Tracer]
Leachate						
Fraction (L)	Sampling Time [h]	V Fraction [mL]	Σ V Fraction [mL]	Total [% AR]	Total [% AR]	
L1	0-6	49	49	0.0	0.0	
L2	6-12	50	99	9.5	3.4	
L3	12-18	50	149	15.7	13.5	
L4	18-24	50	199	10.6	11.6	
L5	24-30	50	249	8.3	9.1	
L6	30-36	50	299	6.8	7.4	
L7	36-42	49	348	5.6	5.9	
L8	42-48	47	395	4.5	5.0	
L9	48-60	98	493	7.6	8.6	
L10	60-72	99	592	5.8	7.6	
L11	72-84	97	689	4.5	5.5	
L12	84-96	97	786	4.1	4.4	
L13	96-108	97	883	4.5	3.7	
L14	108-120	98	981	4.9	3.5	
L15	120-x *	13	994	0.6	0.5	
Total Leachate		994		93.2	89.1	
Soil Column					n.a.	
Material Balance					93.2	89.1

* Dripping time approx. 16-20 h

Mean Material Balance	TFA [Test Item]	³ H ₂ O [Tracer]
Ja64 DD5 / Ja64 DD6	96.3	92.9

Figure B.8.1.3.1._CA-28: Tables presenting the numerical results of the examination of column leaching obtained for the test item (TFA) and tracer (copied from the study report).

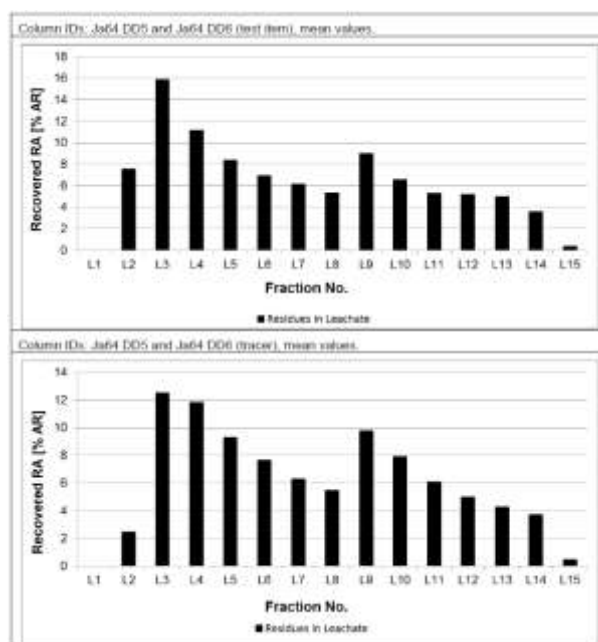


Figure B.8.1.3.1._CA-29: The graphical presentation of the results obtained for columns filled with the test soil Dollendorf II (copied from the study report).

Results obtained for columns filled with the test soil Höfchen am Hoheneseh:**Replicate column 1**

Column ID: Ja64 HH 5

					TFA [Test Item]	³ H ₂ O [Tracer]
Leachate						
Fraction	Sampling Time	V _{Fraction}	Σ V _{Fraction}	Total	Total	
(L)	[h]	[mL]	[mL]	[% AR]	[% AR]	
L1	0-6	50	50	0.0	0.0	
L2	6-12	51	101	0.1	0.0	
L3	12-18	51	152	0.6	0.4	
L4	18-24	50	202	2.1	2.0	
L5	24-30	50	252	3.2	4.0	
L6	30-36	50	302	4.1	5.3	
L7	36-42	50	352	6.6	6.4	
L8	42-48	48	400	14.1	9.6	
L9	48-60	100	500	30.8	29.2	
L10	60-72	100	600	23.5	23.2	
L11	72-84	100	700	10.9	12.8	
L12	84-96	100	800	0.1	0.2	
L13	96-108	100	900	0.5	1.5	
L14	108-120	82	982	0.1	0.4	
L15	120-x *	0	982	n.a	n.a	
Total Leachate		982		97.2	95.0	
Soil Column					n.a	
Material Balance					97.2	95.0

* Dripping time approx. 16-20 h

Replicate column 2

Column ID: Ja64 HH 6

					TFA [Test Item]	³ H ₂ O [Tracer]
Leachate						
Fraction (L)	Sampling Time [h]	V _{Fraction} [mL]	Σ V _{Fraction} [mL]	Total [% AR]	Total [% AR]	
L1	0-6	51	51	0.0	0.0	
L2	6-12	51	102	0.1	0.0	
L3	12-18	51	153	2.1	1.1	
L4	18-24	51	204	3.6	3.6	
L5	24-30	51	255	4.4	4.9	
L6	30-36	51	306	5.8	6.6	
L7	36-42	51	357	11.1	9.5	
L8	42-48	49	406	31.5	17.5	
L9	48-60	102	508	39.0	48.3	
L10	60-72	102	610	1.9	7.3	
L11	72-84	102	712	0.3	0.7	
L12	84-96	101	813	0.0	0.0	
L13	96-108	101	914	0.0	0.1	
L14	108-120	67	981	0.0	0.0	
L15	120-x *	0	981	n.a.	n.a.	
Total Leachate		981		99.9	99.6	
Soil Column					n.a.	
Material Balance					99.9	99.6

* Dripping time approx. 16-20 h

Mean Material Balance	TFA [Test Item]	³ H ₂ O [Tracer]
Ja64 HH 5 / Ja64 HH 6	98.6	97.3

Figure B.8.1.3.1._CA-30: Tables presenting the numerical results of the examination of column leaching obtained for the test item (TFA) and tracer (copied from the study report).

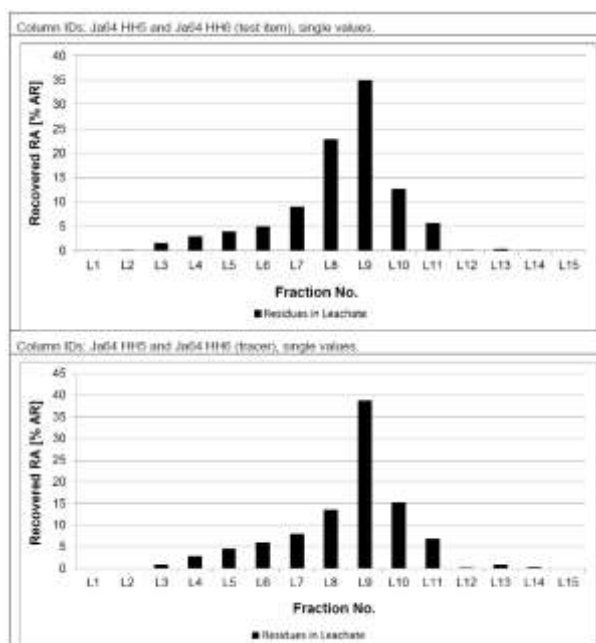


Figure B.8.1.3.1._CA-31: The graphical presentation of the results obtained for columns filled with the test soil Höfchen am Hoheneseh (copied from the study report).

Results obtained for columns filled with the test soil Laacherhof Wurmwiese:**Replicate column 1**

Column ID: Ja64 WW 5

					TFA [Test Item]	³ H ₂ O [Tracer]
Leachate						
Fraction	Sampling Time	V _{Fraction}	Σ V _{Fraction}	Total	Total	
(L)	[h]	[mL]	[mL]	[% AR]	[% AR]	
L.1	0-6	51	51	< 0.1	< 0.1	
L.2	6-12	51	102	< 0.1	< 0.1	
L.3	12-18	51	153	0.9	1.2	
L.4	18-24	51	204	2.5	4.8	
L.5	24-30	51	255	4.6	7.3	
L.6	30-36	51	306	8.8	9.1	
L.7	36-42	51	357	7.9	9.8	
L.8	42-48	48	405	7.6	8.6	
L.9	48-60	101	506	19.9	17.0	
L.10	60-72	101	607	30.8	19.4	
L.11	72-84	100	707	16.2	16.3	
L.12	84-96	100	807	7.7	6.2	
L.13	96-108	100	907	0.3	0.8	
L.14	108-120	100	1007	0.1	0.1	
L.15	120-x *	0	1007	n.a.	n.a.	
Total Leachate		1007		105.2	105.3	
Soil Column					n.a.	
Material Balance					105.2	105.3

* Dipping time approx. 16-20 h

Replicate column 2

Column ID: Ja64 WW 6

				TFA [Test Item]	³ H ₂ O [Tracer]
Leachate					
Fraction (L.)	Sampling Time [h]	V _{Fraction} [mL]	Σ V _{Fraction} [mL]	Total [% AR]	Total [% AR]
L.1	0-6	52	52	< 0.1	< 0.1
L.2	6-12	52	104	4.0	1.8
L.3	12-18	52	156	15.8	15.5
L.4	18-24	52	208	9.7	13.3
L.5	24-30	52	260	8.4	10.4
L.6	30-36	52	312	7.4	8.6
L.7	36-42	52	364	6.6	7.2
L.8	42-48	50	414	5.5	5.8
L.9	48-60	104	518	10.3	9.8
L.10	60-72	104	622	10.1	7.9
L.11	72-84	104	726	10.1	7.3
L.12	84-96	68	794	5.2	4.2
L.13	96-108	90	884	3.8	4.3
L.14	108-120	0	884	n.a.	n.a.
L.15	120-x "	0	884	n.a.	n.a.
Total Leachate		884		95.6	95.0
Soil Column				n.a.	
Material Balance				95.6	95.0

* Dipping time approx. 16-20 h

Mean Material Balance	TFA [Test Item]	³ H ₂ O [Tracer]
Ja64 WW 5 / Ja64 WW 6	100.9	98.2

Figure B.8.1.3.1_CA-32: Tables presenting the numerical results of the examination of column leaching obtained for the test item (TFA) and tracer (copied from the study report).

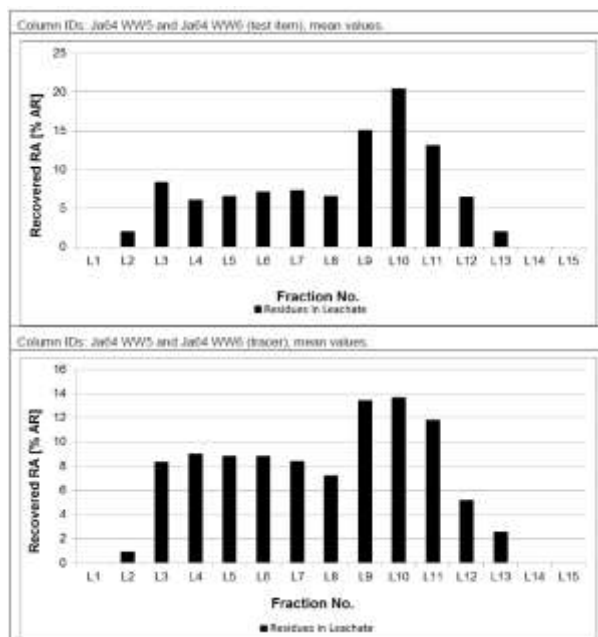


Figure B.8.1.3.1_CA-33: The graphical presentation of the results obtained for columns filled with the test soil Laacherhof Wurmwiese (copied from the study report).

The results of the calculations of the K_d and K_{dOC} values for TFA and the tracer in each test soil are presented below in the table B.8.1.3.1._CA-10. RMS analysing these results noticed that for the same soil and the same K_d the calculated K_{dOC} differed, what may be attributed to the applied calculation and rounding procedures.

Table B.8.1.3.1._CA-10: The calculated K_d and K_{dOC} values for TFA and tracer in each test soil used in the experiment.

Results obtained for test soil Laacherhof AXXa					Results obtained for test soil Dollendorf II				
Column ID	Results obtained for:				Column ID	Results obtained for:			
	TFA		tracer			TFA		tracer	
	K _d [mL/g]	K _{dOC} [mL/g]	K _d [mL/g]	K _{dOC} [mL/g]		K _d [mL/g]	K _{dOC} [mL/g]	K _d [mL/g]	K _{dOC} [mL/g]
Ja64 LH 5	0.1	5.3	0.1	5.8	Ja64 DD 5	0.0	0.0	0.0	0.0
Ja64 LH 6	0.1	3.6	0.1	4.5	Ja64 DD 6	0.0	0.0	0.0	0.0
Mean	0.1	4.5	0.1	5.2	Mean	0.0	0.0	0.0	0.0
Results obtained for test soil Höfchen am Hohenseh					Results obtained for test soil Laacherhof Wurmwielse				
Column ID	Results obtained for:				Column ID	Results obtained for:			
	TFA		tracer			TFA		tracer	
	K _d [mL/g]	K _{dOC} [mL/g]	K _d [mL/g]	K _{dOC} [mL/g]		K _d [mL/g]	K _{dOC} [mL/g]	K _d [mL/g]	K _{dOC} [mL/g]
Ja64 HH 5	0.2	14.2	0.2	15.1	Ja64 WW 5	0.3	14.2	0.2	11.1
Ja64 HH 6	0.1	8.4	0.2	10.7	Ja64 WW 6	0.0	0.0	0.0	0.0
Mean	0.2	11.3	0.2	12.9	Mean	0.2	7.1	0.1	5.6

Conclusions:

The results of the experiment showed that Trifluoroacetic acid may be classified as very mobile in soil.

In the variant with columns eluted for 48 hours with 392 mL of the artificial rain (**Study design A**) the following results were obtained for TFA:

- amount of TFA in the eluates (mean values of the two replicates), expressed as % AR, was:
 - 95.5% AR for columns filled with Laacherhof AXXa test soil;
 - 73.2% AR for columns filled with Dollendorf II test soil;
 - 92.1% AR for columns filled with Höfchen am Hohenseh test soil;
 - 66.2% AR for columns filled with Laacherhof Wurmwielse test soil.
- the extractable radioactivity retained within soil columns attributed to TFA was (mean values of the two replicates):
 - 5.0% AR for columns filled with Laacherhof AXXa test soil;
 - 28.3% AR for columns filled with Dollendorf II test soil;
 - 6.5% of AR for columns filled with Höfchen am Hohenseh test soil;
 - 35.6% AR for columns filled with Laacherhof Wurmwielse test soil.
- the NER fraction attributed to TFA, expressed as % AR, in the soil columns (mean values of the two replicates) was:
 - 1.2% AR for columns filled with Laacherhof AXXa test soil;
 - 1.8% AR for columns filled with Dollendorf II test soil;
 - 0.8% AR for columns filled with Höfchen am Hohenseh test soil;
 - 1.1% AR for columns filled with Laacherhof Wurmwielse test soil.
- the distribution of residues of TFA in soil was following:
 - for columns filled with Laacherhof AXXa test soil they were found predominantly in the lowest segment – S5;
 - for columns filled with Dollendorf II test soil the highest concentration of TFA residues was determined in the top section of the column (segments S1 and S2) with the peak amount in segment S2, and it gradually decreased towards the bottom of the soil column;
 - for columns filled with Höfchen am Hohenseh test soil they were found predominantly in the lowest segment – S5;
 - for columns filled with Laacherhof Wurmwielse test soil the residues of TFA were generally found in the lower part of the column, with the peak amount in the middle section S3.
- The K_d and K_{dOC} values determined for TFA in this experiment were following:
 - for the test soil Laacherhof AXXa $K_d = 0.0$ mL/g and $K_{dOC} = 0.0$ mL/g;

- for the test soil Dollendorf II $K_d = 0.0 \text{ mL/g}$ and $K_{dOC} = 0.0 \text{ mL/g}$;
- for the test soil Höfchen am Hohenseh $K_d = 0.0 \text{ mL/g}$ and $K_{dOC} = 0.0 \text{ mL/g}$;
- for the test soil Laacherhof Wurmweise $K_d = 0.0 \text{ mL/g}$ and $K_{dOC} = 0.0 \text{ mL/g}$;
- mean $K_d = 0.0 \text{ mL/g}$ and $K_{dOC} = 0.0 \text{ mL/g}$.

The results obtained in that experiment for the tracer ($^3\text{H}_2\text{O}$) co-eluted with TFA, also expressed as % AR, were following (mean values of the two replicates):

- amount in the eluates:
 - 87.5% AR for columns filled with Laacherhof AXXa test soil;
 - 63.9% AR for columns filled with Dollendorf II test soil;
 - 85.8% AR for columns filled with Höfchen am Hohenseh test soil;
 - 65.4% AR for columns filled with Laacherhof Wurmweise test soil.
- the extractable radioactivity retained within soil columns attributed to tracer (mean values of the two replicates):
 - 8.4% AR for columns filled with Laacherhof AXXa test soil;
 - 29.7% AR for columns filled with Dollendorf II test soil;
 - 10.4% of AR for columns filled with Höfchen am Hohenseh test soil;
 - 30.8% AR for columns filled with Laacherhof Wurmweise test soil.
- the NER fraction attributed to tracer was not determined in any of the test soils due to the technical reasons:
- the distribution of residues of the tracer in soil was following:
 - for columns filled with Laacherhof AXXa test soil they were found predominantly in the lowest segment – S5;
 - for columns filled with Dollendorf II test soil the highest level was determined in segment S2, and it gradually decreased towards the bottom of the soil column;
 - for columns filled with Höfchen am Hohenseh test soil they were found predominantly in the lowest segment – S5;
 - for columns filled with Laacherhof Wurmweise test soil the residues of TFA were generally found in the lower part of the column, with the peak amount in the middle sections – S3 and S4.

In the variant with columns eluted for 120 hours with 984 mL of the artificial rain (**Study design B**) the following results were obtained for TFA:

- amount of TFA in the eluates (mean values of the two replicates), expressed as % AR, was:
 - 101.1% AR for columns filled with Laacherhof AXXa test soil;
 - 96.3% AR for columns filled with Dollendorf II test soil;
 - 98.6% AR for columns filled with Höfchen am Hohenseh test soil;
 - 100.9% AR for columns filled with Laacherhof Wurmweise test soil.
- the amount of radioactivity retained within soil columns attributed to TFA was not analysed because it was wholly recovered in leachates.
- The K_d and K_{dOC} values determined for TFA in this experiment were following:
 - for the test soil Laacherhof AXXa $K_d = 0.1 \text{ mL/g}$ and $K_{dOC} = 4.5 \text{ mL/g}$;
 - for the test soil Dollendorf II $K_d = 0.0 \text{ mL/g}$ and $K_{dOC} = 0.0 \text{ mL/g}$;
 - for the test soil Höfchen am Hohenseh $K_d = 0.2 \text{ mL/g}$ and $K_{dOC} = 11.3 \text{ mL/g}$;
 - for the test soil Laacherhof Wurmweise $K_d = 0.2 \text{ mL/g}$ and $K_{dOC} = 7.1 \text{ mL/g}$;
 - mean $K_d = 0.2 \text{ mL/g}$ and $K_{dOC} = 9.1 \text{ mL/g}$.

The results obtained in that experiment for the tracer ($^3\text{H}_2\text{O}$) co-eluted with TFA, also expressed as % AR, were following (mean values of the two replicates):

- amount in the eluates:
 - 102.6% AR for columns filled with Laacherhof AXXa test soil;
 - 96.6% AR for columns filled with Dollendorf II test soil;
 - 97.3% AR for columns filled with Höfchen am Hohenseh test soil;
 - 98.2% AR for columns filled with Laacherhof Wurmweise test soil.
- the amount of radioactivity retained within soil columns attributed to the tracer was not analysed because it was wholly recovered in leachates.

The results of this study in format recommended for the List of Endpoints are presented below:

Mobility in soil column leaching transformation products (Regulation (EU) N° 283/2013, Annex Part A, point 7.1.4.1.2 and Regulation (EU) N° 284/2013, Annex Part A, point 9.1.2.1)

Column leaching – TFA

Test compound: <i>TFA applied as parent</i> Elution (mm): <i>200 mm</i> Time period (d): <i>48 hours (2 days)</i>
<p>Test soil: <i>Loamy sand; OC = 1.8; pH = 6.2;</i> Leachate: <i>95.5 %</i> total radioactivity in leachate <i>95.5 %</i> active substance (TFA) <i>6.2 %</i> total radioactivity retained in <i>soil profile</i> Koc (mL/g) = <i>0.0</i>.</p> <p>Test soil: <i>Loam; OC = 5.2; pH = 7.4;</i> Leachate: <i>73.2 %</i> total radioactivity in leachate <i>73.2 %</i> active substance (TFA) <i>30.1 %</i> total radioactivity retained in <i>soil profile</i> Koc (mL/g) = <i>0.0</i>.</p> <p>Test soil: <i>Silt loam; OC = 1.6; pH = 6.5;</i> Leachate: <i>92.1 %</i> total radioactivity in leachate <i>92.1 %</i> active substance (TFA) <i>7.3 %</i> total radioactivity retained in <i>soil profile</i> Koc (mL/g) = <i>0.0</i>.</p> <p>Test soil: <i>Sandy loam; OC = 1.9; pH = 5.3;</i> Leachate: <i>66.2 %</i> total radioactivity in leachate <i>66.2 %</i> active substance (TFA) <i>36.7 %</i> total radioactivity retained in <i>soil profile</i> Koc (mL/g) = <i>0.0</i>.</p>
Test compound: <i>TFA applied as parent</i> Elution (mm): <i>502 mm</i> Time period (d): <i>120 hours (6 days)</i>
<p>Test soil: <i>Loamy sand; OC = 1.8; pH = 6.2;</i> Leachate: <i>101.1 %</i> total radioactivity in leachate <i>101.1 %</i> active substance (TFA) Koc (mL/g) = <i>4.5</i>.</p> <p>Test soil: <i>Loam; OC = 5.2; pH = 7.4;</i> Leachate: <i>96.3 %</i> total radioactivity in leachate <i>96.3 %</i> active substance (TFA) Koc (mL/g) = <i>0.0</i>.</p> <p>Test soil: <i>Silt loam; OC = 1.6; pH = 6.5;</i> Leachate: <i>98.6 %</i> total radioactivity in leachate <i>98.6 %</i> active substance (TFA) Koc (mL/g) = <i>11.3</i>.</p> <p>Test soil: <i>Sandy loam; OC = 1.9; pH = 5.3;</i> Leachate: <i>100.9 %</i> total radioactivity in leachate <i>100.9 %</i> active substance (TFA) Koc (mL/g) = <i>7.1</i>.</p>

Column leaching – TFA

RMS performing the repeated literature search for Flufenacet identified two publications addressing the problem of the mobility of Flufenacet through soil columns. They are summarised below.

Study 2:

Report: Gupta S., Gajbhiye V. T., Agnihotri N. P. (2001): “Adsorption-Desorption, Persistence and Leaching Behavior of Flufenacet in Alluvial Soil of India.”; Division of Agricultural Chemicals, Indian Agricultural Research Institute, New Delhi 110 012, India; published study - published in: “Bulletin of Environmental Contamination and Toxicology”, vol 66, 2001, pp 9-16.

Guidelines: : None declared as this is an open-source study, therefore not submitted for the regulatory purposes.

GLP: no, not applicable – peer-reviewed scientific paper

RMS comments: The paper presents the results of the examination of soil equilibrium sorption (determination of Freundlich sorption isotherms), mobility in soil profile (column leaching experiment) and persistence in aerobic and anaerobic soil, for Flufenacet. The experiments were performed using one test soil. Although in the paper it was not indicated that the experiments were performed in line with any relevant guidelines, it can be stated that the study protocol generally complied with the OECD 307 guideline for soil persistence, OECD 106 Guideline for examining batch sorption and OECD 312 for column leaching. The level of details was sufficient to evaluate the study for its validity. The study may be considered valid, and therefore is summarised below, in this section of the Assessment Report for its part examining the column leaching of Flufenacet. However, RMS is of the opinion that the results it provides may be regarded only as supplementary study and should not be used as a source of regulatory endpoints.

Summary:

The Editor has not provided the abstract for that publication. However the paper contained the introduction, clearly outlining the aims and scope of the research activity described in it, which may be considered a summary of the study. Due to the copyright restrictions, RMS could not present it here and the readers are kindly asked to consult the relevant document. Instead, below is presented the extended summary prepared by the RMS.

Extended summary prepared by RMS:

The aim of the study was to examine the mobility and persistence of Flufenacet in soil. The test soil used in the experiment was an agricultural soil, of the type of inceptisol, having the following physicochemical properties:

- **particle size distribution:** 64.7% sand, 15.6% silt and 19.7% clay;
- **soil texture class:** Sandy loam;
- **pH:** 7.1;
- **OC:** 0.34%;
- **Moisture content at FC (field capacity):** 20%.

The soil used in the experiment was freshly sampled from the top 15-cm layer of the fields of Indian Agricultural Research Institute in New Delhi, India. It was then air-dried and sieved through 2-mm mesh screen before being used.

The test compound was analytical grade Flufenacet, having a purity of > 99.5%, provided by M/s Bayer India Ltd. It was applied to the test soil in form of aqueous solution in 0.01 N CaCl_2 aq, prepared from the stock solution of Flufenacet in acetone, having a concentration of 0.5 mg/mL.

The aliquot of this solution was transferred into the glass tube and left at $T = 25 \pm 2^\circ\text{C}$ to evaporate acetone. The residue was reconstituted in 0.01N CaCl_2 aq. That solution was used to treat soil used in the experiment.

The examination of leaching of Flufenacet through the soil column was performed using PVC columns, 50-cm long and having the internal diameter of 7 cm. It was performed in duplicate plus the control.

The columns were cut longitudinally into half before the experiment began, then the halves rejoined using the adhesive tape. That was done in order to facilitate the removal of intact soil cores after accomplishing the leaching phase of the experiment. The lower end of each column was capped with polyethylene sheet in which small holes were drilled to allow the leachate flow out. Next the columns were filled up to 35 cm with untreated test soils, and the lower end placed overnight in water to allow soil saturate with water. Then to the top was

introduced 10-g portion of the test soil treated with Flufenacet. The amount of the test compound in soil sample was 0.5 g.

The leaching started with introducing water onto the top of the column. The water was in constant supply to keep its level of 2 cm above the soil surface. The amount of water passed through the column was ~2800 mL and the flow rate was 0.5 mL/min. The leaching lasted for ~3 days at room temperature. During that time leachate was collected in 250-mL fractions, which were processed by filtering, diluting with aqueous solution of NaCl and extracting with three 50-mL portions of CH₂Cl₂. The organic phase was collected, combined, dried by passing through anhydrous Na₂SO₄ and the solvent evaporated to dryness. The residues were reconstituted in n-hexane and analysed by GC-ECD.

The soil column after leaching was cut horizontally into seven 5-cm sections. Each so obtained soil sample was homogenised and its two 100-g aliquots extracted with acetone. The extract was further processed by evaporating the organic solvent, diluting the aqueous residue with saturated NaCl_{aq} solution and partitioning it with three 50-mL portions of CH₂Cl₂. The organic phase was collected and processed as described earlier. The resulting processed sample extracts were analysed by GC-ECD.

All samples were analysed using GC-ECD technique on Hewlett Packard 5890 Gas Chromatograph equipped with ⁶³Ni electron capture detector. The separation was performed on megabore HP-1 capillary GC column, 10-metres long, 0.53-mm of internal diameter and having 2.65 µm-thick film. The GC oven was programmed at initial temperature of T = 160°C lasting for 9 minutes, then increasing at rate 30°C/min to T = 260°C, held at that level for 3 minutes. The carrier gas was N₂ administered at a rate 15 mL/min.

For Flufenacet the R_t = 7.4 min. The LOQ = 0.005 µg/g for both soil and aqueous matrices.

The analysis of the leachate showed that no residues of Flufenacet were detected up to collecting 1250 mL of it. The test compound appeared for the first time in fraction 1250 – 1500 mL, in amount 0.005 µg/mL, that gradually increased to reach the level of 0.049 µg/mL in the last fraction – 2750-2810 mL.

The conversion of the volume of leachate into equivalent rainfall showed that to leach Flufenacet through the soil core of the test soil below 35-cm depth, 32.5 cm of continuous rainfall would be required.

The analysis of the soil profile showed gradual downward movement of Flufenacet through it with the peak concentration of 0.336 µg/g recorded in 20-25 cm layer.

On the basis of the obtained results the authors drew the conclusion that even after the continuous rainfall of 65 cm, what is the equivalent of 2500 mL of leachate, Flufenacet would predominately remain confined within the top 35 cm of the test soil.

RMS comments:

The study protocol indicates that it was in line with the provisions of the OECD 312 Guideline, although some deviations were noticed. These were:

- only one test soil was used;
- water instead of 0.01M CaCl₂ solution was used to saturate the column and for leaching.

These deviations however had, in RMS opinion, no significant impact on the results of the experiment and its validity. On the other hand, the fact that the test soil was a non-EU soil that was not well characterised led to the conclusion that the study cannot be used to derive the EU regulatory endpoints. The results may be therefore considered solely as indicative.

Study 3:

Report: Campagna G. Paci F., Fabbi A., Rapparini G., (2006): “Studio in colonna della percolazione di alcuni diserbanti residuali del mais.” (*title in English*: “Percolation of acetochlor, dimethenamid, flufenacet and s-metolachlor applied in columns.”); Centro di Fitofarmacia – Dipartimento di Protezione e Valorizzazione Agroalimentare – Università degli Studi – Viale Fanin, 46 – 40127 Bologna – Italy; published study - published in: “Giornate Fitopatologiche”, 2006, I, 591 – 598;

Guidelines: : None declared as this is an open-source study, therefore not submitted for the regulatory purposes.

GLP: no, not applicable – peer-reviewed scientific paper

RMS comments: The paper presents the results of the examination of mobility of five active substances, used as herbicides in maize, in the soil column. One of the tested compounds was Flufenacet. The experiment was performed using two test soils. In the paper it was not stated that the experiments were performed in line with any relevant guidelines. However the study, in

its part strictly related to the column leaching was in line with the recommendations of OECD 312 Guideline. It shall be noted however that leaching was not continuous and that all test items were administered as formulated products. Finally, the analytical method used to determine the concentrations of the test compounds in soil profiles and leachates was not characterised. Instead in the publication the reference was made to the previous papers presenting it. For these reasons the results presented in that paper may be regarded only as supplementary study and should not be used as a source of regulatory endpoints. Finally, it shall be indicated that the evaluation was based on the translation of the paper into English provided by the Applicant, as the language of the original publication was Italian. RMS however cross-examined both language versions and stated that the translation was well prepared, therefore fully reliable.

Summary:

The publication contained a summary in English. However, because of the copyright restrictions, RMS decided not to present it here and the readers are kindly asked to consult the relevant document. Instead, below is presented the extended summary prepared by the RMS.

Extended summary prepared by RMS:

The aim of the study was to examine the mobility of five herbicides commonly used in maize, including Flufenacet, in soil column.

The experiment was performed using two soils, the brief characteristic of which is presented below in the table B.8.1.3.1._CA-11.

Table B.8.1.3.1._CA-11: The characteristic of soils used in the study.

Parameter		Soil	
		<i>Loose</i>	<i>Clayley silt</i>
Soil type (USDA, determined by RMS)		Sandy loam	Clay loam
Particle size distribution	Sand[%]	76	22
	Silt[%]	14	46
	Clay[%]	10	32
Soil pH (measurement medium not specified)		8.3	7.9
Organic matter content (OM) [%]		0.87	2.37
Cation Exchange Capacity – CEC [mEq/100g]		9.4	28.9

The test soils were typical agricultural soils collected on farms in the province of Bologna. They were collected from the top layer of the fields, sieved and air dried before the experiment began.

The test soils were placed in PVC columns, 50-cm high and 10-cm in diameter. In order to obtain uniform packing of the columns the test soils were homogenised using a pestle. After filling columns were saturated with spring water, stabilised and the excess of water removed to obtain the FC soil moisture level.

The test substances – herbicides, were applied to the top of the test columns in treated sand. Flufenacet was applied in form of Cadou 60 % WP formulation, in amount corresponding to 600 g/ha. Under each column dishes were placed to collect the effluent.

The leaching started with simulation of 25 mm of rain to the top of the column over the period of 10 minutes. That was repeated on the same day to obtain the cumulative rainfall of 50 mm and over the next two days to obtain the cumulative rainfall of 100 mm. The effluents were collected while the column were left to achieve the initial FC level of soil moisture.

Then the columns were vertically cut in half and along the soil profiles the sensitive plant species – *Setaria italica* was sown. That plant was declared to be sensitive to the test compounds present in concentrations ≤ 50 ppb. Next, the untreated soil columns were irrigated with collected effluents and processed in the same way as described above, to determine the would-be amounts of the test substances in leachates.

As a final step periodic checking of the test plants for the toxicity symptoms was performed in order to determine the depth of migration of each test compound.

For Flufenacet it was stated that when applied to Sandy loam soil it migrated down to 7.3 cm after 25 mm of rainfall, 9.7 cm when the cumulative rainfall was 50 mm and to 14 cm after application of the 100 mm of the

cumulative rainfall. In Clay loam soil profile it migrated down to 10 cm after 50 mm of the cumulative rainfall and to 11.1 cm after 100 mm of the cumulative rainfall. Although not explicitly stated the compound was most probably not found in leachates.

RMS comments:

The study, because of its methodology, provides results that are indicative, not definitive with regard to the mobility of Flufenacet in soil profile. For that reason it cannot be used to derive the EU regulatory endpoints. The results may be therefore considered solely as indicative. On the other hand its findings demonstrated that Flufenacet may be expected to be confined to the top 25-cm soil layer.

Summary – column leaching studies

The Applicant did not submit any studies covering the issue of the column leaching of Flufenacet. Instead, in the provided justification for the non-submission, stated that it was covered by the results of the examination of sorption in soil at equilibrium (batch sorption studies) and those aimed on the examination of leaching of the aged residues. That justification was found acceptable by the RMS. It shall be indicated however, that the evaluation of the study examining the leaching behaviour of the aged residues of Flufenacet demonstrated that the study was not acceptable. For the details please refer to the next data point – B.8.1.3.2.

Two additional open-literature studies found by the RMS, considered supplementary, indicated that under typical EU conditions Flufenacet should not move in the soil profile below the depth of 25 cm. Such statement seems to be confirmed by the results of the field dissipation studies performed for Flufenacet and summarised in this document under the point B.8.1.1.2.2.

Additionally, a study was submitted examining the column leaching of one of the major soil degradation products of Flufenacet – TFA. That study, performed using four European soils, showed that TFA was very mobile in soil. The key results of that study are presented below.

The leaching behaviour of TFA was examined using soil columns filled with one of the following test soils:

- Loamy sand (*Laacherhof AXXa*) test soil, having OC = 1.8% and pH = 6.2;
- Loam (*Dollendorf II*) test soil, having OC = 5.2% and pH = 7.4;
- Silt loam (*Höfchen am Hohenseh*) test soil, having OC = 1.6 and pH = 6.5;
- Sandy loam (*Laacherhof Wurmwielse*) test soil, having OC = 1.9 and pH = 5.3.

The experiment was performed in two variants, denominated **Study design A** and **Study design B**, that may be characterised as follows:

- in **Study design A** leaching lasted 48 hours and was performed with 393 mL of artificial rain (0.01M CaCl₂ aq), corresponding to 200 mm of rain;
- in **Study design B** leaching lasted 120 hours and was performed with 984 mL of artificial rain (0.01M CaCl₂ aq), corresponding to 502 mm of rain;

In the variant denominated **Study design A** the following results were obtained for TFA:

- amount of TFA in the eluates (mean values of the two replicates), expressed as % AR, was:
 - 95.5% AR for columns filled with Loamy sand (*Laacherhof AXXa*) test soil;
 - 73.2% AR for columns filled with Loam (*Dollendorf II*) test soil;
 - 92.1% AR for columns filled with Silt loam (*Höfchen am Hohenseh*) test soil;
 - 66.2% AR for columns filled with Sandy loam (*Laacherhof Wurmwielse*) test soil.
- the extractable radioactivity retained within soil columns attributed to TFA was (mean values of the two replicates):
 - 5.0% AR for columns filled with Loamy sand (*Laacherhof AXXa*) test soil;
 - 28.3% AR for columns filled with Loam (*Dollendorf II*) test soil;
 - 6.5% of AR for columns filled with Silt loam (*Höfchen am Hohenseh*) test soil;
 - 35.6% AR for columns filled with Sandy loam (*Laacherhof Wurmwielse*) test soil.
- the NER fraction attributed to TFA, expressed as % AR, in the soil columns (mean values of the two replicates) was:
 - 1.2% AR for columns filled with Loamy sand (*Laacherhof AXXa*) test soil;
 - 1.8% AR for columns filled with Loam (*Dollendorf II*) test soil;
 - 0.8% AR for columns filled with Silt loam (*Höfchen am Hohenseh*) test soil;
 - 1.1% AR for columns filled with Sandy loam (*Laacherhof Wurmwielse*) test soil.

- the distribution of residues of TFA in soil was following:
 - for columns filled with Loamy sand (*Laacherhof AXXa*) test soil they were found predominantly in the lowest segment – S5;
 - for columns filled with Loam (*Dollendorf II*) test soil the highest concentration of TFA residues was determined in the top section of the column (segments S1 and S2) with the peak amount in segment S2, and it gradually decreased towards the bottom of the soil column;
 - for columns filled with Silt loam (*Höfchen am Hohenseh*) test soil they were found predominantly in the lowest segment – S5;
 - for columns filled with Sandy loam (*Laacherhof Wurmwielse*) test soil the residues of TFA were generally found in the lower part of the column, with the peak amount in the middle section S3.
- The K_d and K_{dOC} values determined for TFA in this experiment were following:
 - for the test soil Loamy sand (*Laacherhof AXXa*) $K_d = 0.0$ mL/g and $K_{dOC} = 0.0$ mL/g;
 - for the test soil Loam (*Dollendorf II*) $K_d = 0.0$ mL/g and $K_{dOC} = 0.0$ mL/g;
 - for the test soil Silt loam (*Höfchen am Hohenseh*) $K_d = 0.0$ mL/g and $K_{dOC} = 0.0$ mL/g;
 - for the test soil Sandy loam (*Laacherhof Wurmwielse*) $K_d = 0.0$ mL/g and $K_{dOC} = 0.0$ mL/g;
 - mean $K_d = 0.0$ mL/g and $K_{dOC} = 0.0$ mL/g.

In the variant denominated **Study design B** the following results were obtained for TFA:

- amount of TFA in the eluates (mean values of the two replicates), expressed as % AR, was:
 - 101.1% AR for columns filled with Loamy sand (*Laacherhof AXXa*) test soil;
 - 96.3% AR for columns filled with Loam (*Dollendorf II*) test soil;
 - 98.6% AR for columns filled with Silt loam (*Höfchen am Hohenseh*) test soil;
 - 100.9% AR for columns filled with Sandy loam (*Laacherhof Wurmwielse*) test soil.
- the amount of radioactivity retained within soil columns attributed to TFA was not analysed because it was wholly recovered in leachates.
- The K_d and K_{dOC} values determined for TFA in this experiment were following:
 - for the test soil with Loamy sand (*Laacherhof AXXa*) $K_d = 0.1$ mL/g and $K_{dOC} = 4.5$ mL/g;
 - for the test soil Loam (*Dollendorf II*) $K_d = 0.0$ mL/g and $K_{dOC} = 0.0$ mL/g;
 - for the test soil Silt loam (*Höfchen am Hohenseh*) $K_d = 0.2$ mL/g and $K_{dOC} = 11.3$ mL/g;
 - for the test soil Sandy loam (*Laacherhof Wurmwielse*) $K_d = 0.2$ mL/g and $K_{dOC} = 7.1$ mL/g;
 - mean $K_d = 0.2$ mL/g and $K_{dOC} = 9.1$ mL/g.

B.8.1.3.2. – Aged residues column leaching

One study was submitted to address that data requirement. It is evaluated below.

Study 1:

Report: Kelley I., Wood S., (1993): “Leaching of Aged FOE 5043 Through Soil Columns.”; Miles Inc., Agriculture Division, Research and Development Department, P. O. Box 4913, Kansas City, MO 64120, USA; study No. F3082102 (Miles Inc.); Report No. MR105018; 29 November 1993; study reference number: M-002198-01-1

Guidelines: The study was performed to comply with the following Guidelines:

- BBA Guidelines for the Official Testing of Plant Protectants, Part IV, 4-2 (1986): “Leaching Behaviour of Plant Protectants”.

GLP: Yes;

RMS comments: The study had been evaluated for the previous authorisation of Flufenacet in the EU, by its inclusion into the Annex I of the Directive 91/414/EEC. Its summary can be found under the point B.7.2.3., in section B.7 of the Annex B to the Monograph prepared by the RMS – France, for Flufenacet. For the present authorisation in the EU the study was evaluated for its compliance with the following Guidelines:

- OECD Test Guideline No 312, Leaching in Soil Columns, April 2004;
- US. EPA OCSPP Test Guideline No 835.1240, Leaching Studies, October 2008;

The following deviations from the main Guideline – OECD 312 and other procedural problems were stated:

- The leaching part of the experiment was performed using two test soils – sandy loam soil and loamy sand soil. However in the process of ageing only one of them was used – loamy sand soil. In the evoked Guidelines – OECD 312 and US EPA OPPTS 835.1240, it is stated that the soil used to fill the column shall be the same as that used in ageing process. For that reason RMS decided not to take into account the results of the leaching obtained using the sandy loam soil;
- Additionally, in case of sandy loam soil it was stated that its averaged OC content was below the minimal recommended level of 0.5%.
- For leaching deionised water was used instead of the artificial rain (0.01M CaCl₂ aq solution) recommended by both evoked Guidelines;
- OECD 312 Guideline recommends to use in the experiment 28-cm high layer of untreated soil covered with 2-cm thick layer of aged soil. The total height of the soil column should be therefore, preferably, 30 cm. In the study report it was stated that the layer of untreated soil was 28 cm, but the thickness of the aged soil was not specified. Instead the Applicant gave the mass of aged soil used in the experiment per column – 99.0 g or 96.4g;
- The ageing period lasted for either 30 or 90 days. In case of soil subjected to ageing lasting for 30 days, the leaching experiment using the same soil as that aged – loamy sand, was carried out in duplicate. With soil however aged for 90 days only single column filled with untreated loamy sand soil was subjected to leaching. The OECD Guideline recommends to prepare the columns for the given test soil in, at least, duplicate;
- OECD 312 Guideline recommends that the soil treated with the test compound should be analysed at the end of the ageing period for the content and nature of the residues. In the study report are provided the results of, seemingly, such analysis. However the analytical procedure used in that analysis was not characterised. Additionally it was stated that two degradation products – FOE Methylsulfoxide and FOE Methylsulfone were identified “from the leachates of a parallel aged leaching study”. As a result their initial amounts in soil after ageing are uncertain, hence rendering uncertain the determined mass balance in aged soil. Finally, it was stated that the separation of FOE Oxalate from FOE Thioglycolate sulfoxide was incomplete. As a result the initial concentrations of these two compounds in aged soil are uncertain (in the study report it

is even stated that the factual amounts of FOE Oxalate may be lower due to the inadequate separation of the two metabolites listed above).

- The nature of the residues retained within the soil columns was not examined. That deficiency makes difficult the qualitative analysis of the results;
- Analysing the results RMS noticed that the declared application rate was 176 µg Flufenacet/100 g soil using the solution having a test-item related specific activity of 0.69 kBq/µg. That resulted in the would-be amount of radioactivity applied to 400-g portion of the aged soil equal to 485.76 kB. Presenting results of the mass balance in the system after leaching the Applicant declared that the amount of radioactivity applied per column was 142.63 kBq in case of the experiment with soil aged for 30 days. The amount of the aged soil applied per column in that variant was 99.0 g. Therefore the total amount of radioactivity in the aged soil shall be 576.3 kBq. Similar problem was stated in case of soil aged for 90 days, where it was declared that the amount of radioactivity applied per column was 138.2 kBq and the amount of aged soil applied per column was 96.4 g. Therefore the total amount of radioactivity in the aged soil shall be 574.3 kBq. These values are both significantly higher than the amount declared as application dose. It shall be also indicated that the alleged results of the quantitative and qualitative examination of the aged soil showed that the recovery of the radioactivity after ageing period, reported in the study report, was 98.3% in case of treated soil aged for 30 days and 95.6% in case of treated soil aged for 90 days. The reported level of AR recovered after the leaching using columns filled entirely with loamy sand was 98.5 – 103.7% AR in the variant with soil aged for 30 days and 98.9% AR in variant with soil aged for 90 days. All that puts a questionmark over the correctness of the whole application and analysis procedure. In consequence the reliability of the results of the study is questionable.

RMS, on the basis of the weight of evidence, in particular the stated deficiencies and problem with determining the amount of the test substance applied, stated that the study cannot be considered acceptable. For that reason it was decided not to summarise it, nor include its results into the List of EndPoints. The former summary can be found in the Draft Assessment Report prepared by the then-RMS – France, for the previous authorisation of Flufenacet in the EU.

Summary:

The evaluation of the study performed by the RMS showed that it was not acceptable. For that reason, in order not to overburden the Renewal Assessment Report, RMS decided not to summarise it.

B.8.1.3.3. – Lysimeter studies and/or field leaching studies

To address this data point the Applicant submitted six study reports, that may be divided into three sets of data.

First set contains three reports presenting the results obtained for two lysimeters on which maize (corn) was grown over the period of two years. Two reports are the interim reports presenting the results obtained during the 1st and the 2nd year of the experiment. The third report is the final report of the study, presenting the results obtained for the whole experimental period and it contains the same data as the two interim reports. All three were submitted and evaluated for the previous authorisation of Flufenacet in the EU. The summaries of the interim reports were presented in the Draft Assessment Report for Flufenacet under the point B.7.2.4.1, while the final report was summarised in one of the Addenda – “Addendum to the monograph of Flufenacet (FOE 5043) (Environmental fate).” under the same data point – B.7.2.4.1. For the purpose of the present evaluation RMS decided to rely on the final report, summarised below as **Study 1**. The interim reports were verified for their compliance with the final report. As the differences, if stated, were minimal, RMS decided not to provide their summaries in the RAR. Instead they are cited as **Study 1a** and **Study 1b**.

Second set contains two study reports that present the results of the 2-year lasting lysimeter study carried out in parallel to the experiment briefly characterised above, but in which the crop rotation was maize (corn)/winter wheat. One of those reports is an interim report, presenting the results obtained during the 1st year of the experiment, while the second is the final report of the whole experiment. Both were submitted and evaluated for the previous authorisation of Flufenacet in the EU. Their joint summary was presented in the Draft Assessment Report for Flufenacet under the point B.7.2.4.2. For the purpose of the present evaluation RMS decided to rely on the final report, summarised below as **Study 2**. The interim report was verified for its compliance with the final report. As the differences, if stated, were minimal, RMS decided not to provide its summary in the RAR. Instead it is cited as **Study 2a**.

Last component was a single study presenting the results of the comparative analysis of the results of the lysimeter studies with those obtained as PEC_{GW} values using the simulation model PESTLA. Its is evaluated below as **Study 3**.

Study 1:

Report: Hellpointner E., (1997): “Lysimeter study on the translocation of *FOE 5043* into the subsoil after 2-year use as pre-emergence herbicide in corn.”; Bayer AG, Agrochemical Division, Development, Institute for Metabolism Research and Residue analysis; D-51368 Leverkusen, Germany; report No. PF-4188 (MR-074/97); 19 September 1997; study reference number: M-002187-01-1;

Guidelines: The study was performed to comply with the following Guidelines:

- BBA Guidelines for the Testing of Plant Protection Products in Registration Procedure, Part IV, 43- (February 1990) – “Lysimeter tests for the translocation of plant protection products into the subsoil.”.

GLP: Yes;

RMS comments: The study had been evaluated for the previous authorisation of Flufenacet in the EU, by its inclusion into the Annex I of the Directive 91/414/EEC. Its summary can be found in the “Addendum to the monograph of Flufenacet (FOE 5043) (Environmental fate).” under the point B.7.2.4.1., prepared by the RMS – France, for Flufenacet. RMS re-evaluated the study and found it acceptable. It is summarised below.

Summary:

The aim of the study was to examine for three consecutive years the leaching behaviour of Flufenacet and its degradation products through the undisturbed soil profiles under the climatic and agronomic conditions relevant for Germany.

The experiment was carried out using two undisturbed soil monoliths having a surface area of 1.0 m² and depth 135 cm. They were taken from the field plot located at the Bayer’s Experimental Farm Laacherhof by pressing a stainless steel cylinder, 100-cm long, 100-cm wide and 134-cm high, into the ground until ~4 cm of the frame remained above the soil surface. The soil monolith was separated from the ground below by pulling the cutting plate under the steel frame. Next the soil core was placed into 10-cm high steel tray, slightly sloping towards its centre, where the outlet was located, half filled with gravel (having particle size 8 – 12 mm). Then the cutting plate was removed and the soil core, now standing on the gravel bed, straightened. The total height of so prepared lysimeter was 135 cm, of which top 130 cm was soil monolith and bottom 5 cm gravel layer.

The design of the lysimeter is presented below on figure B.8.1.3.3._CA-1.

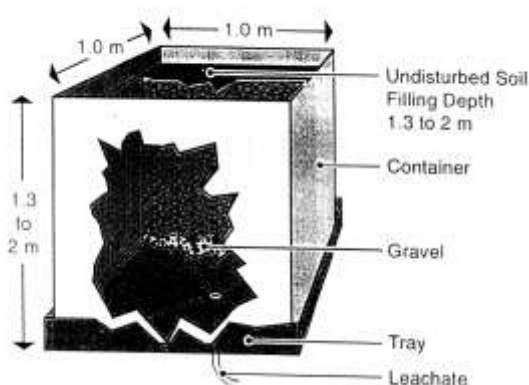


Figure B.8.1.3.3._CA-1: The scheme of the lysimeter used in the study (copied from the study report).

The soil forming soil monolith of the lysimeter was described as brown soil from sand with a low degree of profile differentiation, that originated and then developed from sandy to sandy-loamy sediment overlying the deposits of the lower terrace of the river Rhine. According to German classification it was “Braunerde” from sand and according to FAO Eutric Cambisol. The detailed characteristic of the soil monolith filling the lysimeter is provided in the table B.8.1.3.3._CA-1. The data are presented only for layers down to the depth of 135, as the soil core was sampled down to approximately that depth.

Table B.8.1.3.3._CA-1: The characteristic of soil forming the lysimeter's soil monolith

Parameter		Soil layer (symbol, depth)				
		A_{hs} 0 – 30 cm	B_{vs} 30 – 60 cm	B_{vs} 60 – 100 cm	B_{vs} 100 – 115 cm	IIB_{vs} 115 – 135 cm
Soil texture (USDA)		Sandy loam	Sandy loam	Loamy sand	Loamy sand	Sand
Particle size distribution	Sand (50 – 2000 μm)	71.8	72.2	79.4	82.7	95.5
	Silt (2 – 50 μm)	16.5	16.6	11.0	9.1	2.4
	Clay (<2 μm)	11.8	11.2	9.7	8.2	2.1
Physico-chemical properties	pH in H_2O	7.04	7.24	7.18	7.46	7.41
	pH in CaCl_2	6.05	6.42	6.32	6.61	6.63
	OC [%]	1.41	0.34	0.19	0.17	0.09
	CEC [meq/100g]	9.61	7.43	7.57	8.52	4.73
	Microbial biomass [mg/kg]	235	34	11	13	not determined
	Pore volume [vol. %]	44.94	37.97	42.47	42.90	45.49
Physical parameters	air capacity AC [vol. % H_2O]	12.49	17.36	24.31	21.64	35.74
	field capacity FC [vol. % H_2O]	32.45	20.61	18.16	21.15	9.75
	available water capacity AWC [vol. % H_2O]	23.83	13.10	10.46	11.82	7.34
	permanent wilting point PWC [vol. % H_2O]	8.83	7.51	7.70	9.43	2.41
	saturated hydraulic conductivity K [$\text{cm} \cdot \text{s}^{-1}$]	5.4 E-3	9.8 E-3	7.5 E-3	5.5 E-3	2.9 E-3
	intrinsic permeability k [cm^2]	5.4 E-8	9.8 E-8	7.5 E-8	5.5 E-8	2.9 E-8

The lysimeters were transferred to the open-air lysimeter station located in Bayer AG' Landwirtschaftszentrum, Monheim, Germany (latitude $51^{\circ}4'$ N, longitude $6^{\circ}55'$ E, ~40 m above the sea level), shown on figure B.8.1.3.3._CA-2, and installed in positions #15 and #16. The schematic presentation of the cross-section of the lysimeter station, showing the way the lysimeters were maintained, is presented on figure B.8.1.3.3._CA-3.

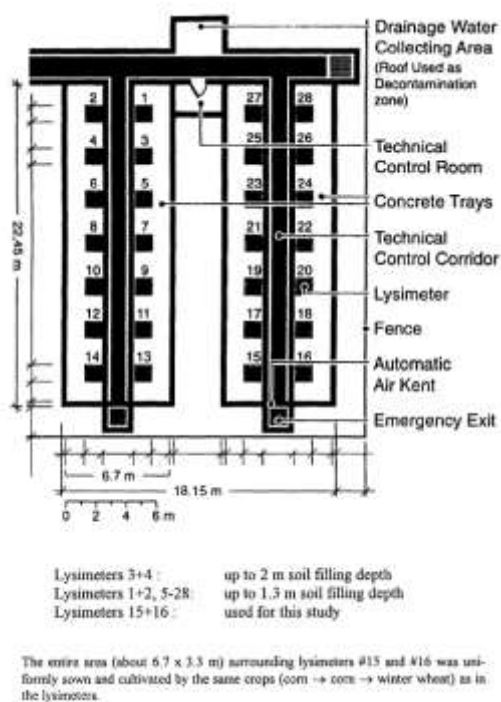


Figure B.8.1.3.3._CA-2: The general view of the lysimeter station of Bayer AG. (copied from the study report).

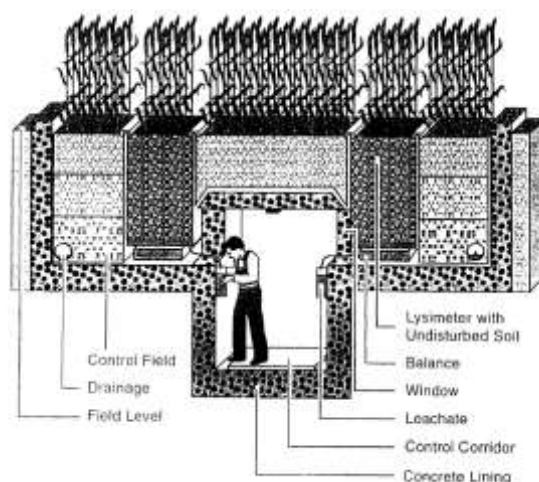


Figure B.8.1.3.3._CA-3: The cross-section general view of the lysimeter station of Bayer AG.
(copied from the study report).

The lysimeters were installed in March 1992, then in April 1992 the grass “Welsches Weidelgras” was sown as a first vegetation after their acquisition. It was broken up and incorporated into top 15 cm. of the soil core in January 1993, then the lysimeters were left until the preparation of the seed bed for the 1st crop – corn (maize), variety Mutin, occurred shortly before its sowing on 10th May 1993.

The experiment started on the 10th of May 1993 by sowing the 1st target crop – maize and ended in May 1996, when the soil was analysed for the residues of Flufenacet.

During that experimental period the following crops were grown on the lysimeters:

- corn (grain maize) var. Mutin as the 1st, target crop; it was sown on the 10th of May 1993 and harvested on the 12th November 1993, 26 weeks after sowing and 1st application of the test compound;
- corn (grain maize) var. Mutin D as the 2nd, target crop, it was sown on the 5th May 1994 and harvested on 10th October 1994, 23 weeks after sowing and 2nd application of the test compound;
- sugar beet var. Sonja as the 3rd, succeeding crop; it was sown on the 13th April 1995 and harvested on 7th November 1995, 30 weeks after sowing;

Corn grown as 1st and 2nd crop was sown in two rows 60-cm apart, at seed density 18 grains/m². Shortly after germination, on 25th May 1993 for the 1st crop and on 2nd June 1994 for the 2nd crop, the number of plants growing was manually reduced to 10 plants/m². The 3rd crop – sugar beet, was sown in three rows, 33-cm apart and 17-cm distant from the walls of lysimeter, at seed density 9 seeds/m² (3 seeds per row).

After harvest of the 1st and 2nd crop – corn, the plant residues – corn stubble and straw, left on the lysimeter were incorporated into the top soil layer (15 cm) as organic fertiliser.

All major crop maintenance measures used during the experiment are presented below in the table B.8.1.3.3._CA-2. In the table, in the columns for crop protection, are also presented the applications of the test compound, marked red. Additionally, when necessary, artificial irrigation was performed as maintenance measure. That was done in order to supply the crops growing on the surface of lysimeters with water in periods of relative drought (in summer, when the level of soil water available to plants is low). The details on that maintenance measure will be provided further down the summary, together with the characteristic of precipitation recorded on site.

Table B.8.1.3.3._CA-2: Major crop maintenance measures used during the experiment.

Fertilisation			Crop Protection			Other measures	
Date	Fertiliser used	Dose rate	Date	Crop protection measure	Dose rate	Date	Measure
April 1992	Thomas phosphate potash	1500 kg/ha	----	----	----	April 1992	Sowing of grass “Welsches Weidelgras”
	Lime ammonium salpêtre	500 kg/ha					
19 March 1993	Thomas phosphate potash	1500 kg/ha	10 May 1993	Corn seeds treated with TMTD	not specified	January 1993	Digging up and incorporation of residues of grass into the top soil layers (~15 cm)
	Lime ammonium salpêtre	500 kg/ha					
03 June 1993	Basfoliar	8 L/ha	12 May 1993	1 st application of the test compound – [¹⁴ C] Flufenacet	48.14 mg/ha (480 g/ha)	10 May 1993	Digging up the top soil layer, tilling, crumbling and seed bed preparation for corn; sowing of the 1 st crop
08 June 1993	Nitrophoska permanent	400 kg/ha					
18 June 1993	Basfoliar	8 L/ha	02 June 1993	E605 forte	0.1%	25 May 1993	Manual reduction of the number of growing corn plants
24 June 1993	Basfoliar	10 L/ha				12 November 1993	Harvest of the 1 st crop
07 December 1993	Organic fertilisation (corn straw)	----				07 December 1993	Incorporation of the corn stubble and straw into the top soil layer
03 May 1994	Thomas phosphate potash	1500 kg/ha				February 1994	Digging up top soil layer (“ploughing”)
	Lime ammonium salpêtre	360 kg/ha	05 May 1994	Corn seeds treated with TMTD	not specified		
13 June 1994	Basfoliar	8 L/ha	05 May 1994	2 nd application of the test compound – [¹⁴ C] Flufenacet	48.05 mg/ha (480 g/ha)	05 May 1994	Tilling, crumbling and seed bed preparation for corn; sowing of the 2 nd crop
20 June 1994	Basfoliar	8 L/ha	24 May 1994	Metasystox R special	0.125%	02 June 1994	Manual reduction of the number of growing corn plants
	Lime ammonium salpêtre	180 kg/ha					
21 November 1994	Organic fertilisation (corn straw)	----	13 June 1994	E605 forte	0.05%	10 October 1994	Harvest of the 2 nd crop
						21 November 1994	Incorporation of the corn stubble and straw into the top soil layer
23 March 1995	Thomas phosphate potash	1500 kg/ha	13 April 1995	Sugar beet seeds treated with TMTD, Hymexazole and Imidachloprid 90 FS 600	----	23 March 1995	Digging up the top soil layer, tilling, crumbling and seed bed preparation for sugar beet
	Lime ammonium salpêtre	660 kg/ha				13 April 1995	Sowing of sugar beet – 3 rd crop
23 June 1995	Lime ammonium salpêtre	280 kg/ha	25 August 1995	Bardos	1.0 L/ha	07 November 1995	Harvest of the 3 rd crop – sugar beet
			22 September 1995	Bardos	1.0 L/ha		

The test substance used in the study was [Phenyl-UL-¹⁴C] Flufenacet, having a specific activity of 2.0 MBq/mg (54 µCi/mg) and radiochemical and chemical purity of >99%. Its structural formula is presented below on figure B.8.1.3.3._CA-4. It was used to prepare the application solution.

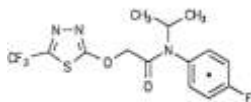


Figure B.8.1.3.3_CA-4: The structural formula of the test compound – the [^{14}C]-Flufenacet. Asterisk (*) denotes the radiolabelling position (copied from the study report).

It was stated that the test compound should be applied as 60 WG (Water Dispersible Granule) formulation. However, because it was not possible at of the experiment to prepare in microscale a representative and homogenous WG formulation containing the radiolabelled active substance, the pure solution of [^{14}C]-Flufenacet was used instead.

The first application of the test substance took place on the 12th of May 1993, 2 days after the 1st crop – corn, was sown. The assumed application rate was 480 g Flufenacet/ha and the actual was 48.14 mg/m² (+0.3% of the intended amount). For that purpose the whole delivered sample of Flufenacet was dissolved in 4 mL of C₂H₅OH. Next for the given lysimeter 0.976 mL of that solution was mixed with 100 g of the lysimeter top soil (mixing lasted 1 hour). Then the volume of soil was increased to obtain a final amount of ~4000g of fortified soil. That amount was uniformly distributed onto the lysimeter's surface. The application was terminated by irrigation with 5 mm/m² of water to minimise losses due to wind erosion. The amount of radioactivity introduced that way onto each lysimeter #15 and #16 was 96273 kBq. The overall loss of radioactivity during application was 27.5 kBq/Lysimeter. That value was taken into account inn further calculations.

The second application of the test compound occurred on the 5th May 1994, just after sowing the 2nd crop – corn. The assumed application rate was 480 g Flufenacet/ha and the actual was 48.05 mg/m² (+0.1% of the intended amount). For that purpose the whole delivered sample of Flufenacet was dissolved in 5 mL of C₂H₅OH. Next for the given lysimeter 2.36 mL of that solution was mixed with 100 g of the lysimeter top soil (mixing lasted 1 hour). Then the volume of soil was increased to obtain a final amount of ~4000g of fortified soil. That amount was uniformly distributed onto the lysimeter's surface. The application was terminated by irrigation with 5 mm/m² of water to minimise losses due to wind erosion. The amount of radioactivity introduced that way was 96090 kBq for Lysimeter No. #15 and 96097 kBq for Lysimeter No. #16. The overall loss of radioactivity during application was 11.6 kBq for Lysimeter #15 and 4.4 kBq for Lysimeter #16.

The experiment lasted for three consecutive years, from May 1993, when the 1st crop was sown and first application of the test compound occurred, until June 1996, when soil monolith filling the lysimeter was analysed for the amount and nature of the residues of Flufenacet (active substance and its degradation products) retained within it.

During that whole period the weather conditions on the experimental site, such as air temperature, soil temterature at various depths, duration of sunshine, wind velocity, rainfall air humidity, were constantly monitored and daily recorded by wheather station of the experimental facility, located within 1 km from the test site. At the test site the soil temperature at the depth of 20 cm was measured continuously in one of the lysimeters. The collected data were processed to obtain monthly and yearly averages, presented in section **Results and their discussion** of this summary. The weights of each lysimeter were continuously recorded. They will be presented, in graphical form, also in section **Results and their discussion** of this summary.

The leachates from each lysimeter were collected in two replacable 20-L steel containers attached in sequence to the lysimeter's outlet. The collected leachates were taken for analysis in 2-week intervals, or shorter if necessary. To do that the containers were emptied, the volume of the collected leachates determined gravimetrically and their pH measured.

The gross radioactivity in the fresh leachate was determined by LSC using 10-mL aliquots. For that purpose three 10-mL aliquots were mixed with 0.1 mL of 1M NaOH. Next to each of them 10 mL of Quickszint 401 LS cocktail was added and the samples were analysed by LSC. The results represented the content of radioactive residues adjusted to alkaline pH.

Another three aliquots were mixed with 0.1 mL of 18% HCl_{aq}, ultrasonicated in open vessels for ~30 minutes in order to release of ¹⁴CO₂ possibly forming in sample and analysed by LSC after addition of 10 mL of Quickszint 401 LS cocktail. The results represented the content of radioactive residues adjusted to acidic pH.

10% of leachates collected at each sampling were stored combined in the container for annual leachate sample. That container was stored in the deep-freeze storage room. Another 10% of each leachate was stored as a separate sample in the deep-freeze storage room.

The deep-frozen leachates were stored for up to 13 months between collection and analysis. The selected leachates obtained from each lysimeter – 1st-year early leachate, 1st-year leachate with the highest radioactivity

content, 1st-year late leachate, annual 1st-year leachate and annual 2nd-year leachate were analysed qualitatively and quantitatively by TLC. The profiling of radioactivity in leachates – identification and quantitation of Flufenacet and its degradation products, was performed in processed leachates. In case of 1st-year leachates the processing started by concentrating 500 mL of leachate under vacuum to the volume of 50 mL. Its 10-mL aliquot was passed through SPE cartridge. The eluate was discarded and the residue eluted from the SPE column using 5 mL of CH₃CN + 0.4% CH₃COOH (9:1) solution. That eluate was collected and analysed by TLC.

The processing of the 2nd-year annual leachate began with concentrating its 100 mL aliquot to 10 mL. Then the procedure was the same as described above for the 1st-year leachates.

Annual leachates were also analysed for pH, TOC, and content of Cl⁻, SO₄²⁻, NO₂⁻, NO₃⁻ and NH₄⁺.

The plant material collected at harvest for 1st and 2nd target crop – corn, were kernels, cobs and hulls, while straw was left at spot, in line with agricultural practice, and then incorporated into lysimeter's topsoil as organic fertilizer. The harvested fresh plant material was homogenised under liquid nitrogen, dried at T = 50°C and its aliquots were analysed, after combustion, for radioactivity content.

The plant material collected at harvest for the 3rd (succeeding) crop – sugar beets, were tubers and leaves. They were processed in the same way as described above for corn.

After harvest of the 3rd crop the surface of the lysimeters was left bare. It was covered with a protective plastic plate and left to dry.

The two top layers – 0-10 cm and 10-20 cm, were completely removed from each lysimeter on 16th of July 1996.

From each layer 5 portions of soil were taken for further processing. Their fresh weight was recorded, then they were combined and thoroughly mixed. The mixed soil was divided into 5 subsamples, and each was weighed to determine its dry weight. Finally five aliquots of each subsample were taken for the determination of the content of radioactivity by LSC after combustion.

For the deeper layers – from 20 to 110 (120) cm depth five soil cores, each having the diameter of 8 cm², were taken using an electric soil corer. The cores were sampled on the 18th July 1996. The distribution of the sampling points is presented below on figure B.8.1.3.3._CA-5.

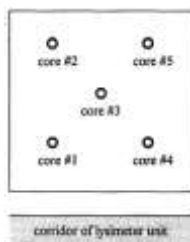


Figure B.8.1.3.3._CA-5: The sampling scheme for the soil cores taken from the lysimeters (copied from the study report).

The obtained 20-cm segments were cut into two 10-cm sections. These 10-cm sections from each core were combined and their total fresh weight recorded. Next, the soil was let to dry for 6 days, homogenised and 5 aliquots of so prepared soil samples analysed for radioactivity content using LSC.

The deepest layers were not reached by the corer. Therefore the individual soil sample representing them was taken after the lysimeter was removed from the frame. It was analysed for the radioactivity content using LSC.

Also the gravel filling the bottom of the lysimeter was sampled to determine the amount of radioactivity it retained. For that purpose two 500-g aliquots of gravel were extracted for two hours with 200 mL CH₃CN/0.1M HCl 1:1 (v/v) solution. The extract was analysed for radioactivity content.

The profiling of radioactivity in soil – identification and quantitation of Flufenacet and its degradation products, was performed down to the depth of 40 cm. For that purpose two 30-g aliquots of each layer (0-10 cm, 10-20 cm, 20-30 cm and 30-40 cm) from each lysimeter were extracted with two 100-mL portions of CH₃CN/0.1M HCl 1:1 (v/v) solution. Each extraction step lasted 1 hour and was followed by 20-minutes centrifugation. The extracts were filtered through paper filter, combined, and their volume recorded. Next, they were analysed for radioactivity content by LSC.

40 mL of crude extract was concentrated to ~5 mL and brought to the volume of 10 mL using 0.005M HCl_{aq}. Then it was analysed by TLC.

The LSC analysis of the liquid samples was carried out using one of the following LS counters: PW 4700, Wallac 1410, Rackbeta 1219, Beckman LS 6000 LL or Beckman LS 6500.

In case of non-processed leachates their 10-mL aliquots were used, mixed with 10 mL of Quickszint 401 LS cocktail. The minimum sensitivity of LSC analysis for those samples was 3.1 E-7 ppm. It corresponded to 58 cpm when expressed as Lowest Acceptable Gross Count Rate (LAGC) and 29 cpm for Lowest Acceptable Net Count Rate (LANC), assuming Average Background (BCGK) of 29 cpm ($LAGC = 2 \cdot BCGK$ and $LANC = LAGC - BCGK$). The greatest probable error GPE = 5.61%.

In case of the organic extracts their 0.1 – 2 mL aliquots were used, mixed with 7 mL of Instant Scint Gel or 2 mL of Quicksafe A LS cocktails. The minimum sensitivity of LSC analysis for those samples was 1.5 E-6 ppm. It corresponded to 58 cpm when expressed as Lowest Acceptable Gross Count Rate (LAGC) and 29 cpm for Lowest Acceptable Net Count Rate (LANC), assuming Average Background (BCGK) of 29 cpm ($LAGC = 2 \cdot BCGK$ and $LANC = LAGC - BCGK$). The greatest probable error GPE = 5.61%.

The radioactivity in the solid samples was determined after their combustion in an oxidiser (Oxidiser 306 Tri-Carb or OX 300). The generated $^{14}\text{CO}_2$ was absorbed in the LS cocktail (the mixture of 8 mL Carbosorb and 10 mL Permafluor, or 15 mL Oxsolv C 400) and analysed by LSC. The analysis was performed for soil samples weighing 1.0 g and plant material samples weighing 0.055 g. The minimum sensitivity of LSC analysis was 2.7 E-6 ppm for soil and 5.0 E-5 ppm for plant samples. It corresponded to 48 cpm when expressed as Lowest Acceptable Gross Count Rate (LAGC) and 24 cpm for Lowest Acceptable Net Count Rate (LANC), assuming Average Background (BCGK) of 24 cpm ($LAGC = 2 \cdot BCGK$ and $LANC = LAGC - BCGK$). The greatest probable error GPE = 4.46%.

The TLC analysis was carried out in one of the three following variants:

- 1) on 20 • 20 cm, 0.25 mm thick, silica gel 60 F₂₅₄ TLC plates developed at room temperature in closed glass chamber using following solvent system $\text{CHCl}_3/\text{CH}_3\text{COOC}_2\text{H}_5$ 3:1 (v/v), it was used for identification and quantitation of Flufenacet and FOE Alcohol;
- 2) on 20 • 20 cm, 0.25 mm thick, silica gel 60 F₂₅₄ TLC plates developed at room temperature in closed glass chamber using following solvent system: $\text{CH}_3\text{CN}/(\text{CH}_3)_2\text{CHOH}/\text{CH}_3\text{COOC}_2\text{H}_5/\text{H}_2\text{O}$ 60:9:6:3 (v/v/v/v); it was used for identification and quantitation of Flufenacet, FOE Oxalate, FOE Sulfonic acid and FOE Thioglycolate sulfoxide (it shall be pointed out that in the study report that variant was indicated to be not suitable for the analysis of Flufenacet);
- 3) on 20 • 20 cm, 0.25 mm thick, RP-18 F₂₅₄ TLC plates developed at room temperature in closed glass chamber using following solvent system: $\text{CH}_3\text{CN}/(\text{CH}_3\text{OH}/0.5\% \text{ NaCl}_{\text{aq}})$ 2:2:1 (v/v/v); that method was not further used because of the stated poor separation of polar compounds;

The detectors used in the analysis were:

- TLC Scanner CS-930 or UV light chamber for “cold” reference standards;
- Radio-TLC-Scanner RITA 6800 used only in the purity check of the applied parent compound
- Bio-Imaging Analyser BAS 2000 for radiolabelled standard solutions and samples;

The identification was performed by means of the comparison of the R_f values of the constituents of the analysed samples with those of the known reference compounds.

The quantitative analysis was performed by means of LSC analysis of the separated bands (spots) on the TLC plate.

Additionally, for the analysis of standard solutions, purity checks of application solutions and for isolation and verification of degradation products in leachates, the HPLC analysis was performed. It was carried out using HP 1090 work station equipped with DAD (UV) and Ramona 4 (LSC) detectors. The chromatographic separation was performed on LiChrosorb RP 18, 250 • 4 mm, 5 μm , chromatographic column. In the study report it was stated that more detailed information on the HPLC analysis was provided in the raw data.

Results and their discussion:

The long-term weather characteristic of the test site is presented below on figure B.8.1.3.3._CA-6 (the frame-table copied from the study report). The values marked with an asterisk (*) are the mean of those recorded by the Experimental Farm's wether station in years 1966 – 1995, while those marked with (#) are the mean of the measurables recorded in years 1968 – 1995. The weather conditions – air temperature, soil temperature, wind speed, radiant heat, precipitation and irrigation, recorded at the test site during the experiment are presented in the table B.8.1.3.3._CA-3. The table provides monthly mean values. The air temperature, soil temperature at different depths, with exception of that at the depth of 20 cm, radiant heat, wind speed and precipitation are the weather data recorded by the weather station located 1 km apart from the lysimeter site. The soil temperature at 20-cm depth was measured at spot, in Lysimeter #15. Additionally the sum curve of precipitation and irrigation during study is presented on figure B.8.1.3.3._CA-7, immediately below the table B.8.1.3.3._CA-3.

Table 2: Long-term weather characteristics of test location

Annual rainfall (*):	745 mm
Max. / min. monthly rainfall (*):	June (78.1 mm) / February (42.7 mm)
Annual relative humidity of the air (*):	73%
Annual air temperature at 2 m above ground level (*):	10.0°C
Max. / min. monthly air temperature at 2 m above ground level (*):	July (18.4 °C) / January (2.6 °C)
Annual soil temperature (-10 cm) (#):	9.5°C
Annual soil temperature (-30 cm) (#):	10.3°C
Annual soil temperature (-50 cm) (#):	10.7°C
Annual soil temperature (-100 cm) (#):	10.6°C
Annual wind velocity (*):	2.5 m/sec
Annual radiant heat (#):	29.1 kJ/cm ²
Max. / min. monthly radiant heat (#):	July (53.1 kJ/cm ²) / Dec. (5.8 kJ/cm ²)

Figure B.8.1.3.3._CA-6: The table presenting long-term weather characteristic at the lysimeter test site (copied from the study report).

Table B.8.1.3.3._CA-3: The monthly weather data recorded at the test site during the experiment.

Time period		Mean air temperature 2 metres above the ground [°C]	Mean soil temperature [°C] at the depth						Mean monthly radiant heat [kJ/cm ²]	Wind speed [m/s.]	Precipitation (P) and Irrigation (I) [mm]	
Year of experiment	Calendar date (month and year)		0 cm	10 cm	20 cm	30 cm	50 cm	100 cm			P	I
1 st	05/93	15.4	14.1	14.9	15.2	16.1	16.4	14.8	52.5	1.9	51.2	5.0
	06/93	17.0	16.4	17.0	17.3	18.2	18.7	17.4	51.5	1.8	43.6	21.0
	07/93	17.3	16.3	17.6	16.7	18.6	19.2	18.1	43.7	2.0	110.2	0.0
	08/93	16.3	14.5	16.1	15.5	17.8	18.7	18.1	41.5	1.9	24.7	20.0
	09/93	13.6	11.6	13.6	13.2	14.9	15.8	15.8	25.3	2.2	127.3	0.0
	10/93	9.1	7.1	9.2	9.7	10.7	12.0	12.8	14.5	1.8	113.3	0.0
	11/93	2.6	1.2	3.3	3.8	4.8	6.3	7.9	9.0	2.0	35.1	0.0
	12/93	5.5	2.6	3.6	3.7	4.1	4.8	5.4	3.6	2.9	148.2	0.0
	01/94	5.1	2.4	3.7	3.8	4.3	5.0	5.4	6.1	2.8	86.2	0.0
	02/94	2.4	-0.5	1.4	1.7	2.4	3.4	4.2	13.2	2.3	25.7	0.0
2 nd	03/94	8.1	4.4	5.7	5.9	6.2	6.5	5.9	22.5	3.1	86.5	0.0
	04/94	9.4	6.5	7.8	7.9	8.8	9.4	8.7	36.2	2.6	45.1	0.0
	05/94	13.6	12.1	12.9	13.0	13.9	14.4	13.2	44.1	2.0	50.0	5.0
	06/94	17.2	16.0	16.2	16.0	17.1	17.4	15.8	54.7	2.4	66.6	0.0
	07/94	22.6	20.9	21.5	20.6	22.6	22.9	20.7	58.9	1.9	20.5	65.0
	08/94	18.5	17.1	18.4	18.0	19.7	20.5	19.7	41.3	2.1	67.4	25.0
	09/94	14.1	11.4	13.7	14.0	15.1	16.1	16.3	22.0	1.7	90.0	0.0
	10/94	10.0	5.6	8.8	9.7	10.7	11.9	12.6	23.0	1.9	56.4	0.0
	11/94	10.1	7.9	9.5	9.5	10.1	10.9	11.1	8.4	2.1	59.2	0.0
	12/94	6.1	3.6	5.4	5.5	6.1	7.1	8.0	6.0	2.6	68.1	0.0
3 rd	01/95	3.3	1.3	2.7	2.7	3.3	4.1	4.9	7.5	3.5	126.8	0.0
	02/95	6.7	3.8	5.2	5.1	5.5	6.1	6.2	10.9	2.8	90.1	0.0
	03/95	4.7	2.0	4.0	4.0	5.1	6.0	6.1	26.1	3.1	77.4	0.0
	04/95	9.6	7.3	8.6	8.2	9.0	9.3	8.5	30.4	2.6	41.4	5.0
	05/95	13.3	12.5	13.3	13.9	14.1	14.4	13.1	50.5	1.6	49.4	3.0
	06/95	15.4	15.7	16.0	14.8	16.7	17.0	15.7	48.1	1.5	70.4	12.0
	07/95	21.9	20.2	20.9	19.5	21.9	22.2	20.1	56.7	1.5	70.0	56.0
	08/95	20.6	18.5	20.0	19.7	21.9	22.6	21.3	50.7	1.9	19.4	33.0
	09/95	14.2	11.9	13.7	14.8	15.4	16.5	16.8	23.0	2.2	86.1	0.0
	10/95	13.4	10.3	12.1	13.4	13.4	14.4	14.6	21.3	1.8	29.9	0.0
	11/95	6.3	5.3	6.6	6.1	7.6	8.7	10.0	10.3	2.2	40.7	0.0
	12/95	0.1	-0.4	1.6	-0.6	3.0	4.4	5.9	5.9	2.2	50.4	0.0
	01/96	0.9	-1.0	0.6	-0.7	1.3	2.3	3.3	9.3	3.5	7.4	0.0
	02/96	1.0	-1.1	0.3	-0.7	0.8	1.5	2.2	11.9	2.6	45.9	0.0
	03/96	3.7	1.0	2.8	0.6	3.5	4.1	4.1	26.7	2.5	17.7	0.0
	04/96	10.5	6.0	7.5	5.8	8.8	9.2	8.1	50.0	2.0	8.8	0.0

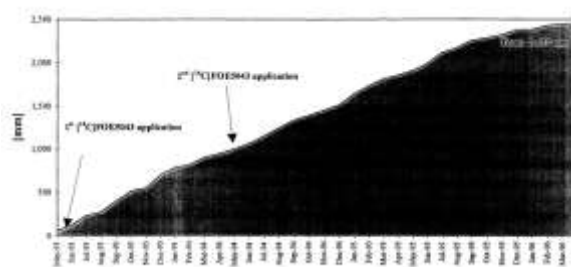


Figure B.8.1.3.3_CA-7: The sum curve of precipitation and irrigation [mm] recorded during the study (copied from the study report).

The total 1st-year precipitation was 897.1 mm and irrigation was 46.0 mm. Therefore the amount of water received by each lysimeter during that experimental year as precipitation and irrigation was 943.1 mm, 143.1 mm more than the BBA Guideline requirement – 800 mm.

The total 2nd-year precipitation was 814.2 mm and irrigation was 100.0 mm. Therefore the amount of water received by each lysimeter that experimental year as precipitation and irrigation was 914.2 mm, 114.2 mm more than the BBA Guideline requirement – 800 mm.

The total 3rd-year precipitation was 496.1 mm and irrigation was 104.0 mm. Therefore the amount of water received by each lysimeter that experimental year as precipitation and irrigation was 600.1 mm, 199.9 mm less than the BBA Guideline requirement – 800 mm.

The total precipitation and irrigation during the study was 2457 mm, what gave average annual precipitation at the level of 819 mm – 19 mm higher than the regulatory requirement.

The weight of the lysimeters during the study is presented below, in graphical form, on figure B.8.1.3.3_CA-8.

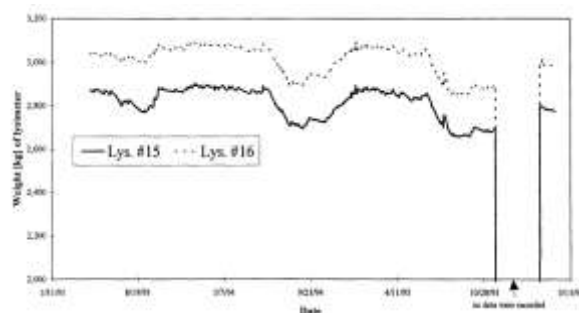


Figure B.8.1.3.3_CA-8: The weight of the lysimeters recorded during the study (copied from the study report).

The leachate from Lysimeter #15 was collected during the 1st experimental year 22 times – on weeks of experiment: 0, 11, 21, 22, 23, 24, 27, 30, 31, 32, 33 (twice), 35, 36, 37, 38, 41, 43, 45, 46, 47 and 50. The total volume of leachate collected during that period was ~350 L. During the 2nd year of experiment the leachates from that lysimeter were collected 17 times – on weeks of experiment 55, 58, 79, 85, 87, 88, 89 (twice), 90, 91, 92, 93, 94, 96, 96, 100 and 103. The total volume of leachate collected during that period was ~318 L. On the 3rd experimental year the leachate from that lysimeter was collected only once – on week 115 of the experiment. Its volume was 13.0 L. Therefore the total, exact, volume of leachate collected from that lysimeter during the experimental period of 3 years was 680.4 L, of which 667.4 L were collected during the first two years. The total number of sampling points during the experiment for that lysimeter was 40. The leachate collected on week 0 is the leachate collected before the application of the test compound.

The leachate from Lysimeter #16 was collected during the 1st experimental year 23 times – on weeks of experiment: 0, 1, 11, 21, 22, 23, 24, 27, 30, 31, 32, 33 (twice), 35, 36, 37, 38, 41, 43, 45, 46, 47 and 50. The total

volume of leachate collected during that period was ~402 L. During the 2nd year of experiment the leachates from that lysimeter were collected 16 times – on weeks of experiment 55, 58, 79, 85, 87, 88, 89, 90, 91, 92, 93, 94, 96, 96, 100 and 103. The total volume of leachate collected during that period was ~300 L. On the 3rd experimental year the leachate from that lysimeter was collected only once – on week 115 of the experiment. Its volume was 17.0 L. Therefore the total, exact, volume of leachate collected from that lysimeter during the experimental period of 3 years was 719.3 L, of which 702.3 L were collected during the first two years. The total number of sampling points during the experiment for that lysimeter was 40. The leachate collected on week 0 is the leachate collected before the application of the test compound.

The detailed information on the collection dates and volumes of individual leachates are presented below in table B.8.1.3.3._CA-4.

Table B.8.1.3.3._CA-4: The sampling time and volume of the individual leachate samples collected during the experiment.

Lysimeter # 15				Lysimeter #16			
Experimental period	Sampling time		Volume of leachate [L]	Experimental period	Sampling time		Volume of leachate [L]
	Date	Week of experiment			Date	Week of experiment	
1 st year	12/05/1993	0	12.0	1 st year	12/05/1993	0	13.0
	29/07/1993	11	0.2		24/05/1993	1	1.7
	08/10/1993	21	7.6		29/07/1993	11	2.1
	15/10/1993	22	11.7		08/10/1993	21	40.0
	22/10/1993	23	13.2		15/10/1993	22	12.8
	29/10/1993	24	3.7		22/10/1993	23	16.5
	19/11/1993	27	10.1		29/10/1993	24	4.7
	09/12/1993	30	9.6		19/11/1993	27	14.3
	15/12/1993	31	13.8		09/12/1993	30	10.0
	23/12/1993	32	40.5		15/12/1993	31	11.9
	29/12/1993	33	22.0		23/12/1993	32	39.5
	04/01/1994	33	44.1		29/12/1993	33	21.5
	12/01/1994	35	21.8		04/01/1994	33	43.7
	19/01/1994	36	13.9		12/01/1994	35	21.5
	28/01/1994	37	17.2		19/01/1994	36	17.5
	04/02/1994	38	22.0		28/01/1994	37	17.8
	24/02/1994	41	15.5		04/02/1994	38	21.4
	14/03/1994	43	19.0		24/02/1994	41	16.4
	24/03/1994	45	22.0		14/03/1994	43	21.1
	31/03/1994	46	16.5		24/03/1994	45	21.5
	11/04/1994	47	11.5		31/03/1994	46	18.8
	29/04/1994	50	13.9		11/04/1994	47	15.5
2 nd year	06/06/1994	55	20.0	2 nd year	29/04/1994	50	13.9
	27/06/1994	58	19.7		06/06/1994	55	19.2
	18/11/1994	79	3.3		27/06/1994	58	20.4
	03/01/1995	85	7.5		18/11/1994	79	3.6
	13/01/1995	87	21.2		03/01/1995	85	12.5
	24/01/1995	88	21.8		13/01/1995	87	19.8
	26/01/1995	89	21.2		24/01/1995	88	21.4
	30/01/1995	89	38.2		30/01/1995	89	30.6
	03/02/1995	90	19.9		03/02/1995	90	20.9
	14/02/1995	91	7.0		14/02/1995	91	16.0
	20/02/1995	92	21.6		20/02/1995	92	21.3
	24/02/1995	93	16.5		24/02/1995	93	19.6
	03/03/1995	94	21.8		03/03/1995	94	21.4
	17/03/1995	96	21.2		17/03/1995	96	17.3
	31/03/1995	98	15.7		31/03/1995	98	13.7
	18/04/1995	100	21.7		18/04/1995	100	21.3
05/05/1995	103	19.2	05/05/1995	103	20.9		
3 rd year	26/07/1996	115	13.0	3 rd year	26/07/1996	115	17.0

The results of the determination of radioactivity in leachates – the amounts of radioactivity recovered, are presented below in two tables – B.8.1.3.3._CA-5 for the Lysimeter #15 and B.8.1.3.3._CA-6 for the Lysimeter #16. Additionally the same results are presented in graphical form on figure B.8.1.3.3._CA-9.

In the study report it was stated that “During and shortly after the application an accidental run-off event down to the leachate containers (soil and run-off water from the top soil layer) was recognised in case of lysimeter #16. This artificial contamination occurred through two holes in the stainless steel container located

quite in the area of the treated soil. The holes resulting from the installation procedure were observed on 25 May 1993 and were closed, immediately. Meanwhile, some radioactivity had been translocated by means of irrigation and/or rainwater outside the soil monolith down to the gravel layer and into the leachate containers. Therefore the leachates of the early period after application could be evaluated from lysimeter #15 only. The leachates of week 0, 1 and 11 were excluded from preparation of AL (93/94) of lysimeter #16 and from residue calculations.”. That event is also marked on the figure B.8.1.3.3._CA-9. As a result RMS decided to mark the results of concern in the table B.8.1.3.3._CA-6 with italics.

TableB.8.1.3.3._CA-5: The total radioactivity recovered in the leachates from Lysimeter #15.

Experimental period	Sampling time		Volume of leachate [L]	Total Radioactivity Recovered (TRR)	
	Date	Week of experiment		Net TRR [$\mu\text{g a. i. equiv./L}$]	Net total TRR/leachate [$\mu\text{g a. i. equiv.}$]
1 st year	12/05/1993	0	12.0	background	background
	29/07/1993	11	0.2	0.024	0.005
	08/10/1993	21	7.6	0.117	0.889
	15/10/1993	22	11.7	0.166	1.936
	22/10/1993	23	13.2	0.220	2.897
	29/10/1993	24	3.7	0.256	0.945
	19/11/1993	27	10.1	0.246	2.485
	09/12/1993	30	9.6	0.229	2.198
	15/12/1993	31	13.8	0.355	4.899
	23/12/1993	32	40.5	0.309	12.515
	29/12/1993	33	22.0	0.410	9.020
	04/01/1994	33	44.1	0.854	37.661
	12/01/1994	35	21.8	1.866	40.668
	19/01/1994	36	13.9	2.223	30.893
	28/01/1994	37	17.2	2.350	40.411
	04/02/1994	38	22.0	2.211	48.642
	24/02/1994	41	15.5	2.044	31.674
	14/03/1994	43	19.0	1.720	32.680
	24/03/1994	45	22.0	1.464	32.197
	31/03/1994	46	16.5	1.121	18.497
	11/04/1994	47	11.5	0.850	9.775
	29/04/1994	50	13.9	0.759	10.543
	Total		349.8	----	371.43
	Mean		----	1.062	----
2 nd year	06/06/1994	55	20.0	0.439	8.780
	27/06/1994	58	19.7	0.425	8.363
	18/11/1994	79	3.3	0.332	1.094
	03/01/1995	85	7.5	0.413	3.094
	13/01/1995	87	21.2	0.421	8.915
	24/01/1995	88	21.8	0.681	14.846
	26/01/1995	89	21.2	0.617	13.070
	30/01/1995	89	38.2	1.011	38.702
	03/02/1995	90	19.9	1.048	20.855
	14/02/1995	91	7.0	1.073	7.508
	20/02/1995	92	21.6	1.122	24.224
	24/02/1995	93	16.5	0.996	16.434
	03/03/1995	94	21.8	0.947	20.645
	17/03/1995	96	21.2	0.840	17.797
	31/03/1995	98	15.7	0.712	11.171
	18/04/1995	100	21.7	0.673	14.604
	05/05/1995	103	19.2	0.561	10.771
	Total		317.6	----	240.87
	Mean		----	0.7581	----
3 rd year	26/07/1996	115	13.0	0.432	5.616
	Total		13.0	----	5.62
	Mean		----	0.432	----

For the further, TLC analysis, aimed on the identification and quantitation of the individual constituents of leachates, the following leachates were taken:

- 24th week leachate, collected on 29 October 1993, representing the 1st-year's early leachate;
- 37th week leachate, collected on 28 January 1994, representing the 1st-year's leachate with maximum TRR;

- 47th week leachate, collected on 11 April 1994, representing the 1st-year's late leachate;
- 1st-year annual leachate;
- 2nd-year annual leachate.

TableB.8.1.3.3_CA-6: The total radioactivity recovered in the leachates from Lysimeter #16.

Experimental period	Sampling time		Volume of leachate [L]	Total Radioactivity Recovered (TRR)	
	Date	Week of experiment		Net TRR [$\mu\text{g a. i. equiv./L}$]	Net total TRR/leachate [$\mu\text{g a. i. equiv.}$]
1 st year	12/05/1993	0	13.0	0.668 ¹⁾	8.678 ¹⁾
	24/05/1993	1	1.7	3.982 ¹⁾	6.928 ¹⁾
	29/07/1993	11	2.1	1.276 ^{1, 2)}	2.731 ^{1, 2)}
	08/10/1993	21	40.0	0.188	7.520
	15/10/1993	22	12.8	0.221	2.829
	22/10/1993	23	16.5	0.205	3.383
	29/10/1993	24	4.7	0.221	1.036
	19/11/1993	27	14.3	0.221	3.160
	09/12/1993	30	10.0	0.178	1.780
	15/12/1993	31	11.9	0.270	3.207
	23/12/1993	32	39.5	0.322	12.719
	29/12/1993	33	21.5	0.691	14.846
	04/01/1994	33	43.7	1.390	60.721
	12/01/1994	35	21.5	1.989	42.764
	19/01/1994	36	17.5	1.852	32.410
	28/01/1994	37	17.8	1.657	29.495
	04/02/1994	38	21.4	1.788	38.253
	24/02/1994	41	16.4	1.570	25.740
	14/03/1994	43	21.1	1.345	28.380
	24/03/1994	45	21.5	1.161	24.951
	31/03/1994	46	18.8	1.003	18.856
	11/04/1994	47	15.5	0.798	12.369
	29/04/1994	50	13.9	0.672	9.341
	Total		402.4	----	375.54
	Mean		----	0.931	----
2 nd year	06/06/1994	55	19.2	0.405	7.776
	27/06/1994	58	20.4	0.454	9.251
	18/11/1994	79	3.6	0.300	1.080
	03/01/1995	85	12.5	0.262	3.269
	13/01/1995	87	19.8	0.238	4.703
	24/01/1995	88	21.4	0.344	7.362
	30/01/1995	89	30.6	0.577	17.656
	03/02/1995	90	20.9	0.725	15.153
	14/02/1995	91	16.0	0.730	11.672
	20/02/1995	92	21.3	0.687	14.622
	24/02/1995	93	19.6	0.664	13.005
	03/03/1995	94	21.4	0.644	13.782
	17/03/1995	96	17.3	0.585	10.121
	31/03/1995	98	13.7	0.496	6.795
	18/04/1995	100	21.3	0.436	9.287
	05/05/1995	103	20.9	0.434	9.071
	Total		299.9	----	154.60
	Mean		----	0.516	----
3 rd year	26/07/1995	115	17.0	0.353	6.001
	Total		17.0	----	----
	Mean		----	0.353	6.00

Footnotes to the table:

- 1) Value resulting from the contamination, not further considered in calculations;
 2) The corresponding value obtained in Lysimeter #15 used instead;

For the further, TLC analysis, aimed on the identification and quantitation of the individual constituents of leachates, the following leachates were taken:

- 24th week leachate, collected on 29 October 1993, representing the 1st-year's early leachate;
- 35th week leachate, collected on 28 January 1994, representing the 1st-year's leachate with maximum TRR;
- 47th week leachate, collected on 11 April 1994, representing the 1st-year's late leachate;
- 1st-year annual leachate;
- 2nd-year annual leachate.

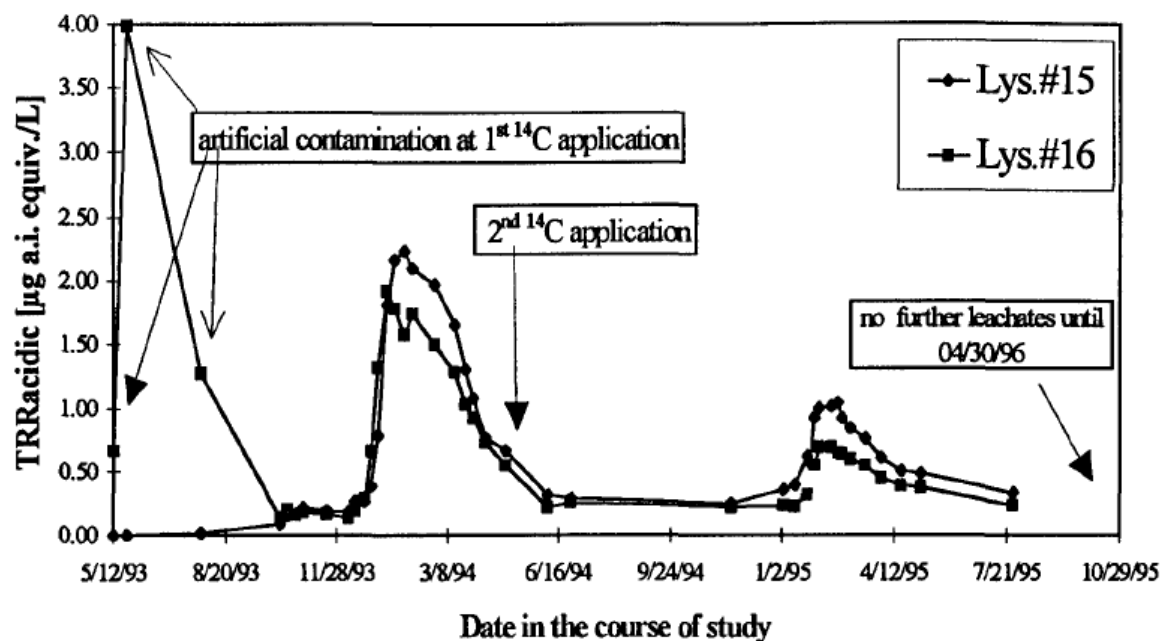


Figure B.8.1.3.3_CA-9: The graphical results of the determination of the total radioactivity recovered (TRR) in leachates from the two lysimeters (copied from the study report).

The detailed results of the characterisation of leachates – measured pH, the concentration of the total (alkaline) TRR and acidic TRR, as well as the content of ¹⁴CO₂ (expressed as % of TRR) are presented below, individually for each lysimeter, in two tables – Table B.8.1.3.3_CA-7 for Lysimeter #15 and Table B.8.1.3.3_CA-8 for Lysimeter #16. For the completeness of the results also was provided the volume of each leachate collected.

Table B.8.1.3.3_CA-7: The detailed results of the examination of the leachates from Lysimeter #15.

Experimental period	Sampling time		Volume of leachate [L]	pH of leachate	Radioactivity recovered (TRR)		
	Date	Week of experiment			Net TRR (alkaline) [µg a. i. equiv./L]	Acidic TRR [µg a. i. equiv./L]	¹⁴ CO ₂ [%]
1 st year	12/05/1993	0	12.0	----	background		
	29/07/1993	11	0.2	7.7	0.024	0.017	29.17
	08/10/1993	21	7.6	7.6	0.117	0.085	27.35
	15/10/1993	22	11.7	7.8	0.166	0.152	8.16
	22/10/1993	23	13.2	7.8	0.220	0.162	26.20
	29/10/1993	24	3.7	7.6	0.256	0.218	14.87
	19/11/1993	27	10.1	7.5	0.246	0.191	22.36
	09/12/1993	30	9.6	7.8	0.229	0.185	19.21
	15/12/1993	31	13.8	7.6	0.355	0.263	25.92
	23/12/1993	32	40.5	7.4	0.309	0.264	14.72
	29/12/1993	33	22.0	7.6	0.410	0.386	5.85
	04/01/1994	33	44.1	7.4	0.854	0.790	7.49
	12/01/1994	35	21.8	7.4	1.866	1.813	2.84
	19/01/1994	36	13.9	7.6	2.223	2.163	2.70
	28/01/1994	37	17.2	7.6	2.350	2.228	5.19
	04/02/1994	38	22.0	7.5	2.211	2.098	5.13
	24/02/1994	41	15.5	7.8	2.044	1.971	3.57
	14/03/1994	43	19.0	7.4	1.720	1.651	4.01
	24/03/1994	45	22.0	7.3	1.464	1.311	10.42
	31/03/1994	46	16.5	7.8	1.121	1.082	3.52
	11/04/1994	47	11.5	7.7	0.850	0.767	9.82
	29/04/1994	50	13.9	7.4	0.759	0.666	12.20
	Total		349.8	----	----	----	----
	Mean		----	7.6	1.062	0.99	6.47
2 nd year	06/06/1994	55	20.0	7.5	0.439	0.314	28.59
	27/06/1994	58	19.7	7.1	0.425	0.291	31.57
	18/11/1994	79	3.3	7.7	0.332	0.246	25.94
	03/01/1995	85	7.5	7.0	0.413	0.356	13.70
	13/01/1995	87	21.2	7.2	0.421	0.398	5.47
	24/01/1995	88	21.8	7.5	0.681	0.622	8.66
	26/01/1995	89	21.2	7.4	0.617	0.571	7.38
	30/01/1995	89	38.2	7.5	1.011	0.927	8.26
	03/02/1995	90	19.9	7.4	1.048	0.999	4.68
	14/02/1995	91	7.0	7.5	1.073	1.018	5.08
	20/02/1995	92	21.6	7.3	1.122	1.042	7.09
	24/02/1995	93	16.5	7.6	0.996	0.922	7.43
	03/03/1995	94	21.8	7.3	0.947	0.844	10.93
	17/03/1995	96	21.2	7.5	0.840	0.763	9.11
	31/03/1995	98	15.7	7.4	0.712	0.613	13.84
	18/04/1995	100	21.7	7.5	0.673	0.503	25.33
	05/05/1995	103	19.2	7.4	0.561	0.482	14.17
	Total		317.6	----	----	----	----
	Mean		----	7.4	0.758	0.670	11.10
3 rd year	26/07/1996	115	13.0	7.7	0.432	0.334	22.80
	Total		13.0	----	----	----	----
	Mean		----	7.7	0.432	0.334	22.80
Total study period	Total		680.4	----	----	----	----
	Mean		----	7.5	0.906	0.83	8.42

Table B.8.1.3.3._CA-8: The detailed results of the examination of the leachates from Lysimeter #16.

Experimental period	Sampling time		Volume of leachate [L]	pH of leachate	Radioactivity recovered (TRR)		
	Date	Week of experiment			Net TRR (alkaline) [µg a. i. equiv./L]	Acidic TRR [µg a. i. equiv./L]	¹⁴ CO ₂ [%]
1 st year	12/05/1993	0	13.0	----	0.668 ¹⁾	0.666 ¹⁾	0.22 ¹⁾
	24/05/1993	1	1.7	----	3.982 ¹⁾	3.986 ¹⁾	0.00
	29/07/1993	11	2.1	7.3	1.276 ¹⁾	1.276 ¹⁾	0.00
	08/10/1993	21	40.0	7.6	0.188	0.140	25.80
	15/10/1993	22	12.8	7.8	0.221	0.199	10.18
	22/10/1993	23	16.5	7.8	0.205	0.155	24.63
	29/10/1993	24	4.7	7.8	0.221	0.183	17.23
	19/11/1993	27	14.3	7.6	0.221	0.165	25.57
	09/12/1993	30	10.0	7.7	0.178	0.140	21.63
	15/12/1993	31	11.9	7.7	0.270	0.192	28.94
	23/12/1993	32	39.5	7.5	0.322	0.284	13.30
	29/12/1993	33	21.5	7.7	0.691	0.661	4.34
	04/01/1994	33	43.7	7.5	1.390	1.324	4.71
	12/01/1994	35	21.5	7.3	1.989	1.915	3.72
	19/01/1994	36	17.5	7.7	1.852	1.781	3.86
	28/01/1994	37	17.8	7.7	1.657	1.574	5.01
	04/02/1994	38	21.4	7.5	1.788	1.736	2.91
	24/02/1994	41	16.4	8.0	1.570	1.498	4.59
	14/03/1994	43	21.1	7.7	1.345	1.283	4.61
	24/03/1994	45	21.5	7.3	1.161	1.033	11.03
	31/03/1994	46	18.8	7.9	1.003	0.923	7.98
	11/04/1994	47	15.5	7.9	0.798	0.732	8.27
	29/04/1994	50	13.9	7.9	0.672	0.550	18.23
	Total		402.4	----	----	----	----
	Mean		----	7.7	0.931	0.87	6.82
2 nd year	06/06/1994	55	19.2	7.4	0.405	0.219	45.93
	27/06/1994	58	20.4	7.2	0.454	0.253	44.21
	18/11/1994	79	3.6	7.8	0.300	0.219	27.17
	03/01/1995	85	12.5	7.2	0.262	0.231	11.66
	13/01/1995	87	19.8	7.3	0.238	0.224	5.68
	24/01/1995	88	21.4	7.5	0.344	0.314	8.87
	30/01/1995	89	30.6	7.6	0.577	0.548	5.11
	03/02/1995	90	20.9	7.7	0.725	0.694	4.34
	14/02/1995	91	16.0	7.6	0.730	0.693	5.07
	20/02/1995	92	21.3	7.6	0.687	0.648	5.61
	24/02/1995	93	19.6	7.6	0.664	0.638	3.92
	03/03/1995	94	21.4	7.6	0.644	0.600	6.83
	17/03/1995	96	17.3	7.7	0.585	0.549	6.15
	31/03/1995	98	13.7	7.5	0.496	0.445	10.38
	18/04/1995	100	21.3	7.6	0.436	0.388	11.12
	05/05/1995	103	20.9	7.4	0.434	0.374	13.94
	Total		299.9	----	----	----	----
	Mean		----	7.5	0.516	0.46	11.19
3 rd year	26/07/1995	115	17.0	7.8	0.353	0.231	8.12
	Total		17.0	----	----	----	----
	Mean		----	7.8	0.353	0.23	34.56
Total study period	Total		719.3	----	----	----	----
	Mean		----	7.6	0.742	0.68	8.39

Footnotes to the table:

1) Value resulting from the contamination, not further considered in calculations.

The results of the profiling of single leachates collected during the 1st year of the study and the pooled 1st-year and 2nd-year leachates showed that they contained, apart from detectable amounts of Flufenacet, also FOE Alcohol, FOE Oxalate, FOE Sulfonic acid and FOE Thioglycolate sulfoxide. Additionally a fraction further called unknown “Unknown 1” was found using both TLC methods in all analysed leachates. In case of the 3rd-year leachates the TRR (total radioactivity recovered) was attributed totally to FOE Sulfonic acid. The detailed results of the profiling of the leachates collected from Lysimeter #15 are presented in the table B.8.1.3.3._CA-9. In the next table – B.8.1.3.3._CA-10 are presented the results of the profiling of the leachates collected from the Lysimeter # 16. Finally, in the table B.8.1.3.3._CA-11 are presented the results of the quantitation of the selected

constituents of the annual leachates collected from the Lysimeter #15 and the Lysimeter #16. The results of the profiling of individual and annual leachates showed that the leaching to groundwater recharge in amounts $> 0.1 \mu\text{g/L}$ occurred only for FOE Sulfonic acid. It shall be also indicated that in leachates was also detected, and in quantifiable amounts, FOE Thioglycolate sulfoxide (FOE TGS) – the soil degradation product of Flufenacet identified in the experiments examining route and rate of degradation of Flufenacet in soil only as a minor compound and hence not covered by the modelling exposure assessment for the groundwater compartment. These results may indicate that under unfavourable conditions FOE Thioglycolate sulfoxide might become a compound of concern, although the identity of that compound was not fully confirmed in the study.

Table B.8.1.3.3._CA-9: Results of the profiling of the leachates collected from the Lysimeter # 15.

Type of leachate	Sampling time		Content [$\mu\text{g/L}$] of:					
	Date	Week of experiment	Flufenacet	FOE Alcohol	FOE Oxalate	FOE Sulfonic acid	FOE TGS ¹⁾	Unknown 1 [$\mu\text{g a. i. equiv./L}$]
<i>1st year early leachate</i>	29/10/1993	24	<0.011	< 0.001	0.002	0.065	0.017	0.012
<i>1st year max. TRR leachate</i>	28/01/1994	37	≤ 0.007	0.001	0.007	1.293	0.079	0.052
<i>1st year late leachate</i>	11/04/1994	47	<0.035	0.001	0.012	0.332	0.014	0.029
<i>1st-year annual leachate</i>	29/04/1994	(50)	0.020	< 0.002	0.015	0.589	0.016	0.030
<i>2nd-year annual leachate</i>	05/05/1995	(103)	0.003	0.003	<0.018	0.235	0.020	0.037
<i>3rd-year annual leachate</i>	26/07/1995	(115)	----	----	----	≤ 0.25	----	----

Footnotes to the table:

1) FOE TGS = FOE Thioglycolate sulfoxide;

Table B.8.1.3.3._CA-10: Results of the profiling of the leachates collected from the Lysimeter # 16.

Type of leachate	Sampling time		Content [$\mu\text{g/L}$] of:					
	Date	Week of experiment	Flufenacet	FOE Alcohol	FOE Oxalate	FOE Sulfonic acid	FOE TGS	Unknown 1 [$\mu\text{g a. i. equiv./L}$]
<i>1st year early leachate</i>	29/10/1993	24	<0.014	0.006	0.007	0.025	0.009	0.011
<i>1st year max. TRR leachate</i>	12/01/1994	35	<0.017	0.004	0.041	1.090	0.036	0.052
<i>1st year late leachate</i>	11/04/1994	47	0.005	<0.001	0.031	0.301	0.010	0.044 ²⁾
<i>1st-year annual leachate</i>	29/04/1994	(50)	0.033	0.000	0.004	0.489	0.014	0.033
<i>2nd-year annual leachate</i>	05/05/1995	(103)	0.003	0.005	<0.014	0.149	0.015	0.041
<i>3rd-year annual leachate</i>	26/07/1995	(115)	----	----	----	≤ 0.17	----	----

Footnotes to the table:

1) FOE TGS = FOE Thioglycolate sulfoxide;

2) This is the sum of the “Unknown 1” fraction detected in all leachates and the “Unknown 2” fraction detected only in this leachate.

Table B.8.1.3.3._CA-11: The concentrations of the selected constituents of annual leachates collected from Lysimeter #15 and Lysimeter # 16.

Constituent of the leachate	Concentration in leachates:			
	Lysimeter #15		Lysimeter #16	
	1 st -year annual leachate	2 nd -year annual leachate	1 st -year annual leachate	2 nd -year annual leachate
Cl^- [$\mu\text{g/L}$]	89000	96000	75000	80000
NO_2^- [$\mu\text{g/L}$]	< 100	< 100	< 100	< 100
NO_3^- [$\mu\text{g/L}$]	70300	28600	75600	22200
NH_4^+ [$\mu\text{g/L}$]	< 500	< 500	< 500	< 500
SO_4^{2-} [$\mu\text{g/L}$]	114000	94000	90300	89800
pH	8.0	7.7	7.9	7.9
TOC [$\mu\text{g/L}$]	3000	6000	< 2000	4000
TRR _{acidic} [$\mu\text{g a. i. equiv./L}$]	0.940	0.718	0.814	0.445
Ratio TOC/TRR _{acidic}	3192	8357	< 2457	8989

The results of the determination of the radioactivity in soil monoliths from each lysimeter are presented below in numerical form in the table B.8.1.3.3._CA-12 (together with the results of the determination of fresh weight – FW, and dry weight – DW, of each soil layer) and in graphical form on figure B.8.1.3.3._CA-10 (in [% AR] – left hand-side graph, and in [mg a. i. equivalent/kg soil, fresh weight] – right-hand-side graph). These results show that radioactivity in the soil monoliths was located predominantly in the top 20 cm and below 40-cm depth it accounted for less that 1.0% AR in each of the analysed soil layers.

Table B.8.1.3.3._CA-12: The numerical results of the determination radioactivity in soil monoliths from each lysimeter.

Lysimeter #15					Lysimeter #16				
Soil layer [cm]	Weight of soil layer [g]		Amount of radioactivity determined as:		Soil layer [cm]	Weight of soil layer [g]		Amount of radioactivity determined as:	
	Fresh weight (FW)	Dry weight (DW)	[% AR]	[mg a. i. equiv./kg FW]		Fresh weight (FW)	Dry weight (DW)	[% AR]	[mg a. i. equiv./kg FW]
0 – 10	149800	149000	28.622	0.184	0 – 10	148000	148800	28.782	0.187
10 – 20	153200	152000	9.556	0.060	10 – 20	153000	149800	11.190	0.070
20 – 30	172768	160871	2.110	0.012	20 – 30	169466	157091	1.442	0.008
30 – 40	209176	195170	1.177	0.005	30 – 40	205714	192066	1.040	0.005
40 – 50	199189	185581	0.582	0.003	40 – 50	193618	179095	0.646	0.003
50 – 60	214826	200382	0.336	0.002	50 – 60	218885	203486	0.567	0.002
60 – 70	193936	181084	0.180	0.001	60 – 70	202491	190475	0.394	0.002
70 – 80	205873	191629	0.151	0.001	70 – 80	224774	210290	0.288	0.001
80 – 90	202292	187451	0.108	0.001	80 – 90	200900	186734	0.148	0.001
90 – 100	229350	214229	0.106	0.000	90 – 100	214428	201457	0.193	0.001
100 – 110	223540	207823	0.097	0.000	100 – 110	171296	162662	0.110	0.001
110 – 120	----	380000 ¹⁾	0.066	0.000	110 – 120	2303367	188743	0.082	0.000
120 – 130			0.066	0.000	120 – 130	----	190000 ¹⁾	0.139	0.001
Gravel bed	----	170000 ¹⁾	0.003	0.000	Gravel bed	----	170000 ¹⁾	0.005	0.000

Footnotes to the table:

1) Assumed value.

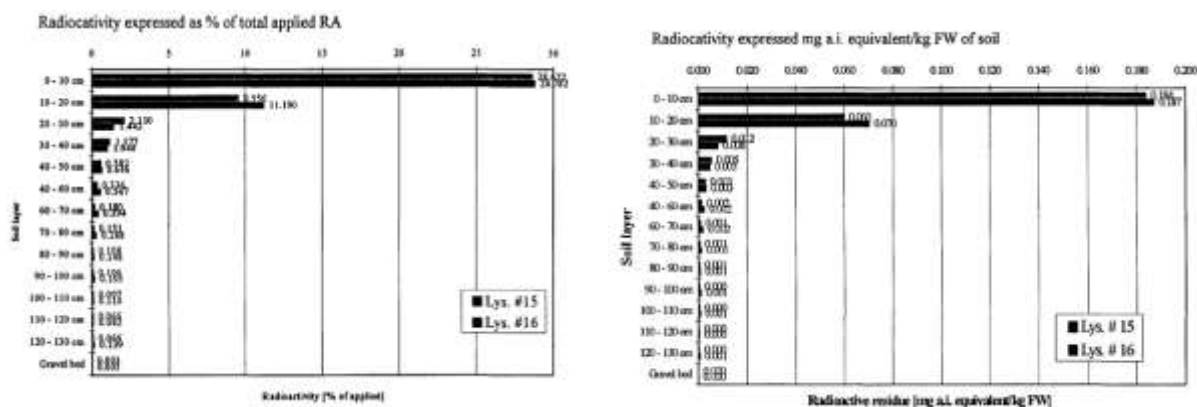
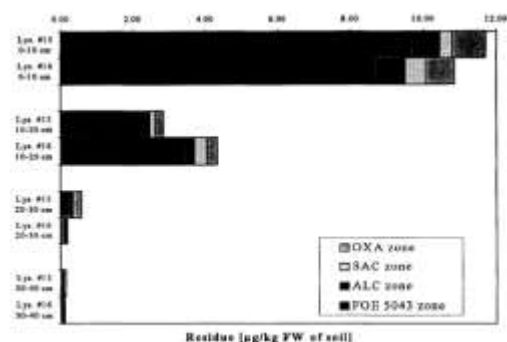


Figure B.8.1.3.3._CA-10: The graphical results of the determination radioactivity in soil monoliths from each lysimeter (copied from the study report).

The 10-cm soil layers sampled down to the depth of 40 cm were further analysed, using TLC for the individual compounds. That analysis enabled the identification and quantitation of the following compounds: Flufenacet, FOE Alcohol, FOE Oxalate and FOE Sulfonic acid. Its detailed results are presented in numerical form below in the table B.8.1.3.3._CA-13 and in graphical form on figure B.8.1.3.3._CA-11. It shall be indicated that in that experiment quite substantial amounts of FOE Alcohol were detected in soil, what stands in some contrast with the results of the examination of route and rate of degradation of Flufenacet in aerobic soil, where FOE Alcohol was demonstrated to be minor degradation product.

Table B.8.1.3.3._CA-13: The numerical results of the profiling of the 10-cm layers of the soil monoliths of the lysimeters sampled down to 40-cm depth.

Results obtained for the Lysimeter #15								
Soil layer [cm]	Amount of Flufenacet expressed in:		Amount of FOE Alcohol expressed in:		Amount of FOE Oxalate expressed in:		Amount of FOE Sulfonic acid expressed in:	
	[µg/soil layer]	[µg/kg soil, FW]	[µg/soil layer]	[µg/kg soil, FW]	[µg/soil layer]	[µg/kg soil, FW]	[µg/soil layer]	[µg/kg soil, FW]
0 – 10	1454.59	9.71	113.34	0.76	136.15	0.91	48.99	0.33
10 – 20	360.00	2.35	19.87	0.13	35.83	0.23	<19.75	<0.13
20 – 30	46.37	0.27	10.28	0.06	40.86	0.24	<2.70	<0.02
30 – 40	<11.84	<0.06	<3.68	<0.02	10.44	0.05	<1.71	<0.01
Results obtained for the Lysimeter #16								
Soil layer [cm]	Amount of Flufenacet expressed in:		Amount of FOE Alcohol expressed in:		Amount of FOE Oxalate expressed in:		Amount of FOE Sulfonic acid expressed in:	
	[µg/soil layer]	[µg/kg soil, FW]	[µg/soil layer]	[µg/kg soil, FW]	[µg/soil layer]	[µg/kg soil, FW]	[µg/soil layer]	[µg/kg soil, FW]
0 – 10	1293.07	8.74	116.26	0.79	117.20	0.79	80.98	0.55
10 – 20	531.66	3.47	36.25	0.24	44.75	0.29	51.31	0.34
20 – 30	<14.95	<0.09	<6.51	<0.04	5.77	0.03	<6.10	<0.04
30 – 40	<11.62	<0.06	<4.36	<0.02	<4.02	0.02	<4.17	<0.02

**Figure B.8.1.3.3._CA-11:** The graphical results of the profiling of the 10-cm layers of the soil monoliths of the lysimeters sampled down to 40-cm depth (copied from the study report).

The results of the analysis of the crops grown on each lysimeter are presented below in the table B.8.1.3.3._CA-14. These results show that the translocation and accumulation of the residues of Flufenacet in crops was minimal – well below 0.1% AR.

Table B.8.1.3.3._CA-14: The results of the analysis of the crops grown on Lysimeters

Lysimeter	Crop	Plant material collected	Yield [dt/ha]	Weight of collected plant material		Radioactivity recovered, expressed as:	
				Fresh weight (FW) [kg]	Dry weight (DW) [g]	[µg a. i. equiv./kg FW]	% applied
#15	1 st year crop – corn	Kernels	88	0.884	817.7	4.38	0.008
		Cobs and huls	32	0.317	290.5	9.18	0.006
	2 nd year crop – corn	Kernels	104	1.039	1025.3	6.40	0.007
		Cobs and huls	77	0.767	577.3	11.70	0.009
	Succeeding crop – sugar beet	Tubers	866	8.66	----	3.01	0.027
		Leaves	508	5.08	----	6.02	0.032
#16	1 st year crop – corn	Kernels	63	0.630	586.3	6.56	0.0086
		Cobs and huls	23	0.231	219.2	12.93	0.0062
	2 nd year crop – corn	Kernels	113	1.131	1127.6	6.50	0.008
		Cobs and huls	56	0.562	455.2	10.89	0.006
	Succeeding crop – sugar beet	Tubers	966	9.66	----	2.25	0.0225
		Leaves	446	4.46	----	8.15	0.0375

Finally, on the basis of the obtained results was determined the mass balance for the applied radioactivity. The results of these calculations are presented below on figure B.8.1.3.3._CA-12, showing the mass balance table provided in the study report. On the basis of these results it can be stated that it was possible to recover from the system 44 – 46% AR of the radioactivity applied, predominantly from soil (43 – 45% AR). The radioactivity recovered from soil profile was located predominantly in the top 30-cm layer. 0.58 – 0.64% AR was found in leachates and only 0.08% AR was uptaken by crops grown on the lysimeters' surface. 54 – 56% AR was lost, and that was attributed to the total mineralization of the test compound – [^{14}C] Flufenacet and the release of the generated [$^{14}\text{CO}_2$] into the air.

Matrix	Lysimeter # 15		Lysimeter # 16		
	[kBq]	% appl.	[kBq]	% appl.	
Harvested crops					
1st (corn, kernels):	7.7	0.008*	8.3	0.009*	*: % of 1st appl., only
1st (corn, cobs & hulls):	5.8	0.006*	6.0	0.006*	
2nd (corn, kernels):	13.3	0.007	14.7	0.008	
2nd (corn, cobs & hulls):	17.9	0.009	12.2	0.006	
3rd (sugar beet tubers):	52.1	0.027	43.3	0.023	
3rd (sugar beet leaves):	61.1	0.032	72.7	0.038	
Crops total:	158	0.08	157	0.08	
Soil monolith					
0-30 cm:	77,501	40.289	79,667	41.414	
30-60 cm:	4,031	2.095	6,017	3.128	
below 60 cm:	1,495	0.777	932	0.485	
Soil total:	83,027	43.16	86,617	45.03	
Leachate:					
1st year:	743	0.772*	784	0.815*	§: incl. artificial contamination of leachate
2nd year:	482	0.250	309	0.161	
3rd year:	11	0.006	12	0.006	
Leachate total:	1,236	0.64	1,11	0.58	
Total recovered RA:	84,420	43.89	87,879	45.68	
Loss (e.g. $^{14}\text{CO}_2$):	107,943	56.11	104,491	54.32	
Applied RA:	192,363	100.00	192,370	100.00	

Figure B.8.1.3.3._CA-12: The results of the determination of mass balance, as presented in the study (table copied from the study report)

Conclusions:

The results of the examination of the leaching behaviour of Flufenacet through two undisturbed soil profiles (two lysimeters filled with soil monoliths consisting of Sandy loam-Loamy sand-Sand soil, having pH in range 6.05 – 6.63 and OC content in the top 30-cm layer of 1.41%) during three consecutive years showed that 44 – 46% of radioactivity applied as [^{14}C]-Flufenacet was recovered. The lost 54-56% AR was attributed to the $^{14}\text{CO}_2$ formed in soil and escaped from there, hence it was stated that such would be the level of the total mineralisation of the test compound.

Of the radioactivity recovered from the test system 0.08% AR (Both Lysimeters) was recovered in collected plant material. 0.58% AR (Lysimeter #16) – 0.64% AR (Lysimeter #15) was recovered in leachates, of which 0.772% AR (Lysimeter #15) – 0.815% AR (Lysimeter #16) in the 1st year annual leachate, 0.161% AR (Lysimeter #15) – 0.250% AR (Lysimeter #16) in the 2nd year annual leachate and only 0.006% AR (both Lysimeters) in the 3rd year annual leachate. That corresponded to:

- for Lysimeter #15:
 - in the 1st year annual leachate to 1.062 [$\mu\text{g a. i. equivalent/L}$] total (alkaline) TRR (TRR = Total Radioactivity Recovered), of which 6.47% was $^{14}\text{CO}_2$ -associated radioactivity, and to 0.990 [$\mu\text{g a. i. equivalent/L}$] acidic TRR subsequently profiled using TLC;
 - in the 2nd year annual leachate to 0.758 [$\mu\text{g a. i. equivalent/L}$] total (alkaline) TRR (TRR = Total Radioactivity Recovered), of which 11.10% was $^{14}\text{CO}_2$ -associated radioactivity, and to 0.670 [$\mu\text{g a. i. equivalent/L}$] acidic TRR subsequently profiled using TLC;
 - in the 3rd year annual leachate to 0.432 [$\mu\text{g a. i. equivalent/L}$] total (alkaline) TRR (TRR = Total Radioactivity Recovered), of which 22.80% was $^{14}\text{CO}_2$ -associated radioactivity, and to 0.334 [$\mu\text{g a. i. equivalent/L}$] acidic TRR not profiled;

- on average in annual leachate to 0.906 [µg a. i. equivalent/L] total (alkaline) TRR (TRR = Total Radioactivity Recovered), of which 8.42% was ¹⁴CO₂-associated radioactivity, and to 0.830 [µg a. i. equivalent/L] acidic TRR.
- for Lysimeter #16:
 - in the 1st year annual leachate to 0.931 [µg a. i. equivalent/L] total (alkaline) TRR (TRR = Total Radioactivity Recovered), of which 6.82% was ¹⁴CO₂-associated radioactivity, and to 0.870 [µg a. i. equivalent/L] acidic TRR subsequently profiled using TLC;
 - in the 2nd year annual leachate to 0.516 [µg a. i. equivalent/L] total (alkaline) TRR (TRR = Total Radioactivity Recovered), of which 11.19% was ¹⁴CO₂-associated radioactivity, and to 0.460 [µg a. i. equivalent/L] acidic TRR subsequently profiled using TLC;
 - in the 3rd year annual leachate to 0.353 [µg a. i. equivalent/L] total (alkaline) TRR (TRR = Total Radioactivity Recovered), of which 35.56% was ¹⁴CO₂-associated radioactivity, and to 0.230 [µg a. i. equivalent/L] acidic TRR not profiled;
 - on average in annual leachate to 0.742 [µg a. i. equivalent/L] total (alkaline) TRR (TRR = Total Radioactivity Recovered), of which 8.39% was ¹⁴CO₂-associated radioactivity, and to 0.680 [µg a. i. equivalent/L] acidic TRR.

The TLC profiling of the leachates (acidic TRR) lead to the identification of its following constituents: Flufenacet, FOE Alcohol, FOE Oxalate, FOE Sulfonic acid and FOE Thioglycolate sulfoxide (FOE TGS). The quantitative analysis gave the following results:

- for Lysimeter #15:
 - the 1st year annual leachate contained 0.020 [µg/L] of Flufenacet, <0.002 [µg/L] of FOE Alcohol, 0.015 [µg/L] of FOE Oxalate, 0.589 [µg/L] of FOE Sulfonic acid, 0.016 [µg/L] of FOE TGS and 0.030 [µg a. i. equivalent/L] of the “Unknown” fraction;
 - the 2nd year annual leachate contained 0.003 [µg/L] of Flufenacet, 0.003 [µg/L] of FOE Alcohol, <0.018 [µg/L] of FOE Oxalate, 0.235 [µg/L] of FOE Sulfonic acid, 0.020 [µg/L] of FOE TGS and 0.039 [µg a. i. equivalent/L] of the “Unknown” fraction;
 - in the 3rd year leachate <0.025 [µg/L] was attributed to FOE Sulfonic acid, no other compounds were taken into consideration.
- for Lysimeter #16:
 - the 1st year annual leachate contained 0.033 [µg/L] of Flufenacet, 0.000 [µg/L] of FOE Alcohol, 0.004 [µg/L] of FOE Oxalate, 0.489 [µg/L] of FOE Sulfonic acid, 0.014 [µg/L] of FOE TGS and 0.033 [µg a. i. equivalent/L] of the “Unknown” fraction;
 - the 2nd year annual leachate contained 0.003 [µg/L] of Flufenacet, 0.005 [µg/L] of FOE Alcohol, <0.014 [µg/L] of FOE Oxalate, 0.149 [µg/L] of FOE Sulfonic acid, 0.015 [µg/L] of FOE TGS and 0.041 [µg a. i. equivalent/L] of the “Unknown” fraction;
 - in the 3rd year leachate <0.017 [µg/L] was attributed to FOE Sulfonic acid, no other compounds were taken into consideration.

The radioactivity determined in the soil monoliths was on the level:

- for Lysimeter #15: 43.16%AR, of which 40.29% AR in the top 30 cm, 2.095% AR in the next 30-60cm layer and the remaining 0.777% AR below that depth, the content of radioactivity decreased with depth being highest - ~28% AR in the top 10-cm section, and below 40 cm not surpassing 1% AR in any of the 10-cm sections;
- for Lysimeter #16: 45.03%AR, of which 41.41% AR in the top 30 cm, 3.128% AR in the next 30-60cm layer and the remaining 0.485% AR below that depth, the content of radioactivity decreased with depth being highest - ~28% AR in the top 10-cm section, and below 40 cm not surpassing 1% AR in any of the 10-cm sections.

The profiling of radioactivity in soil extracts from samples taken from 0-30 cm layer resulted in identification of four compounds: Flufenacet, FOE Alcohol, FOE Oxalate and FOE Sulfonic acid. The RMS calculated their concentrations in that layer using the sumarily weight of soil (Fresh Weight, further denominated FW) within that layer, being 475.768 kg for Lysimeter #15 and 470.466 kg for Lysimeter #16.

The determined amounts and corresponding concentrations of the identified compound were following:

- for Lysimeter #15: content of Flufenacet was 1860.96 µg and its concentration 3.91 [µg/kg soil FW], content of FOE Alcohol was 143.49 µg and its concentration 0.30 [µg/kg soil FW], content of FOE Oxalate was 212.84 µg and its concentration 0.45 [µg/kg soil FW], content of FOE Sulfonic acid was 71.44 µg and its concentration 0.15 [µg/kg soil FW];

- for Lysimeter #16: content of Flufenacet was 1839.68 µg and its concentration 3.91 [µg/kg soil FW], content of FOE Alcohol was 159.02 µg and its concentration 0.34 [µg/kg soil FW], content of FOE Oxalate was 167.72 µg and its concentration 0.36 [µg/kg soil FW], content of FOE Sulfonic acid was 138.39 µg and its concentration 0.29 [µg/kg soil FW].

As a result it may be stated that of all the compounds possible to be identified as originating from Flufenacet radiolabelled in fluorophenyl ring (including Flufenacet itself) only FOE Sulfonic acid was demonstrated to be found in leachates in amounts > 0.1 µg/L, what confirmed the risk to GW associated to that degradation product demonstrated in GW model exposure assessment (for details please refer to the results of calculations presented under the point B.8.5 in the Vol. 3-CP, B.8 of this Renewal Assessment Report).

Neither Flufenacet nor the second major soil degradation product relevant for that radiolabelling position – FOE Oxalate, were detected in leachates in amounts > 0.1 µg/L, what may indicate that they would not pose a threat to the GW compartment.

In soil and leachates FOE Alcohol was detected – the compound determined in the studies examining the route of degradation of Flufenacet in aerobic soil to be minor/transient and therefore not taken into account in the GW model exposure assessment. It shall be indicated however that the would-be risk it may pose to the GW compartment was covered by the calculations carried out for FOE Oxalate – its immediate degradate.

Also detected in leachates was FOE Thioglycolate sulfoxide (FOE TGS), the compound not taken in the model GW exposure assessment into consideration, being identified as minor soil degradation product. It shall be indicated however, that in the study it was determined in leachates in amounts <0.1 µg/L, what may indicate that it would not pose a serious threat to the GW compartment.

It shall be indicated that, due to the fact that in the study was used Flufenacet radiolabelled only in the fluorophenyl ring, the study gave no information of the leaching potential of the degradation products formed from the second moiety present within the molecule of Flufenacet – thiadiazole.

Finally, it shall be indicated that the study, although provides vital information regarding the mobility and leaching behaviour of Flufenacet and some of its soil degradation products within the undisturbed soil profile, and hence the risk posed to the groundwater recharge, is not fully suitable for assessing such risk in case of the present evaluation. The reason is that the test compound, although in higher rate, was applied at spring and not in autumn. Therefore the climatic conditions observed on the test site during the period of the peak concentrations of Flufenacet and its degradation products may not fully reflect those usually occurring in autumn (temperature profile, precipitation), what in turn may influence the degradation in soil (mainly kinetics) and the leaching potential of each detected/quantified compound originating from Flufenacet (including the test compound).

It may be therefore stated that, on the basis of the comparative analysis of the application pattern (crops, application timing and application rates) used in the study and the EU-representative application pattern proposed for the current authorisation of Flufenacet in the EU, the study may be considered as providing supplementary information with regard to the risk posed by Flufenacet and its soil degradation products to the GW compartment, but for the purpose of the decision making it should be considered with care.

Study 1a:

Report: Hellpointner E., (1995): “Lysimeter study on the translocation of *FOE 5043* into the subsoil after 2-year use as pre-emergence herbicide in corn. 1st year of study.”; Bayer AG, Agrochemical Division, Development, Institute for Metabolism Research and Residue analysis; D-51368 Leverkusen, Germany; report No. PF-4024; 09 January 1995; study reference number M-002195-01-1;

Guidelines: The study was performed to comply with the following Guidelines:

- BBA Guidelines for the Testing of Plant Protection Products in Registration Procedure, Part IV, 43- (February 1990) – “Lysimeter tests for the translocation of plant protection products into the subsoil.”.

GLP: Yes;

RMS comments: The study had been evaluated for the previous authorisation of Flufenacet in the EU, by its inclusion into the Annex I of the Directive 91/414/EEC. Its summary can be found under the point B.7.2.4.1., in section B.7 of the Annex B to the Monograph prepared by the RMS – France, for Flufenacet. RMS re-evaluated the study and found it acceptable. It was noticed however, that this is an interim report presenting a part of the results presented in summarised above, as **Study 1**, final report of the same study. RMS compared both reports and stated that they contained the same results, in case of this report limited however to one, 1st, year. Therefore it was not necessary to summarise this study and such summary was not provided in order not to overburden the Renewal Assessment Report. However the RMS

used some of its parts, in particular some figures, in cases they were more clear/better looking than the corresponding figures in the full report.

Summary:

The study report was not summarised because it contained the same data as summarised above, as **Study 1**, full-study report.

Study 1b:

Report: Hellpointner E., (1995): “Lysimeter study on the translocation of *FOE 5043* into the subsoil after 2-year use as pre-emergence herbicide in corn. 2nd year of study.”; Bayer AG, Agrochemical Division, Development, Institute for Metabolism Research and Residue analysis; D-51368 Leverkusen, Germany; report No. PF-4081 (107728); 04 August 1995; study reference number M-002192-01-2;

Guidelines: The study was performed to comply with the following Guidelines:

- BBA Guidelines for the Testing of Plant Protection Products in Registration Procedure, Part IV, 43- (February 1990) – “Lysimeter tests for the translocation of plant protection products into the subsoil.”.

GLP: Yes;

RMS comments: The study had been evaluated for the previous authorisation of Flufenacet in the EU, by its inclusion into the Annex I of the Directive 91/414/EEC. Its summary can be found under the point B.7.2.4.1., in section B.7 of the Annex B to the Monograph prepared by the RMS – France, for Flufenacet. RMS re-evaluated the study and found it acceptable. It was noticed however, that this is an interim report presenting a part of the results presented in summarised above, as **Study 1**, final report of the same study. RMS compared both reports and stated that they contained the same results, in case of this report limited however to one, 2nd, year. Therefore it was not necessary to summarise this study and such summary was not provided in order not to overburden the Renewal Assessment Report. However the RMS used some of its parts, in particular some figures, in cases they were more clear/better looking than the corresponding figures in the full report. It shall also be noted that the same study was probably used for the evaluation of Flufenacet in the USA. It was then submitted by *Bayer Corporation, Agriculture Division, Research and Development Department, P. O. Box 4913, Kansas City, Missouri 64120-0013*, bearing the identification number (for Bayer Report) 107728. However, for the evaluation in the EU the report bore the ID number PF-4081.

Summary:

The study report was not summarised because it contained the same data as summarised above, as **Study 1**, full-study report.

Study 2:

Report: Hellpointner E., (1996): “Lysimeter study on the translocation of *FOE 5043* into the subsoil after use as pre-emergence herbicide in a maize/winter wheat crop rotation.”; Bayer AG, Agrochemical Division, Development, Institute for Metabolism Research and Residue analysis; D-51368 Leverkusen, Germany; report No. PF-4184 (107688); 18 November 1996; study reference number: M-002190-01-2;

Guidelines: The study was performed to comply with the following Guidelines:

- BBA Guidelines for the Testing of Plant Protection Products in Registration Procedure, Part IV, 43- (February 1990) – “Lysimeter tests for the translocation of plant protection products into the subsoil.”.

GLP: Yes;

RMS comments: The study had been evaluated for the previous authorisation of Flufenacet in the EU, by its inclusion into the Annex I of the Directive 91/414/EEC. Its summary can be found under the point B.7.2.4.2., in section B.7 of the Annex B to the Monograph prepared by the RMS – France, for Flufenacet. RMS re-evaluated the study and found it acceptable. It is summarised below. It shall be noted that the same study was probably used for the evaluation of Flufenacet in the USA. It was then submitted by *Bayer Corporation, Agriculture Division, Research and Development Department, P. O. Box 4913, Kansas City, Missouri 64120-0013*, bearing the identification number (for Bayer Report) 107688. However, for the evaluation in the EU the report bore the ID number PF-4184 and under that number it will be presented in the list of references.

Summary:

The aim of the study was to examine, for 2.5 consecutive years, the leaching behaviour of Flufenacet and its degradation products through the undisturbed soil profiles under the climatic and agronomic conditions relevant for Germany. The study was carried out in a way very similar to that described above for *Study 1*. The major differences consisted in:

- the 1st crop was fodder (silage) maize;
- the 2nd crop was Winter cereals sown in autumn of the same year as the 1st crop;
- the test substance – [¹⁴C]-Flufenacet was applied not at the beginning of the Year 1 and Year 2 of the experiment, but both application occurred during the Year 1 of the study – at spring, after maize was sown, and in autumn, shortly after sowing Winter wheat as the 2nd crop;
- the application rates of [¹⁴C]-Flufenacet for the 1st and 2nd applications were different – the 2nd application rate was less than half of that used during the 1st application of the test compound;
- finally the soil monoliths were shallower – they were sampled only down to ~115 cm instead of ~130 cm, as it was in *Study 1*.

The experiment was carried out using two undisturbed soil monoliths having a surface area of 1.0 m² and depth 115 cm. They were taken from the field plot located at the Bayer’s Experimental Farm Laacherhof by pressing a stainless steel cylinder, 100-cm long, 100-cm wide and 115-cm high, into the ground until ~10 cm of the frame remained above the soil surface. The soil monolith was separated from the ground below by pulling the cutting plate under the steel frame. Next, the soil core was placed into 10-cm high steel tray, slightly sloping towards its centre where the outlet was located, half filled with gravel (having particle size 8 – 12 mm). Then the cutting plate was removed and the soil core, now standing on the gravel bed, straightened. The total height of so prepared lysimeter was 120 cm, of which top 115 cm was soil monolith and bottom 5 cm gravel layer.

The design of the lysimeter is presented below on figure B.8.1.3.3._CA-13.

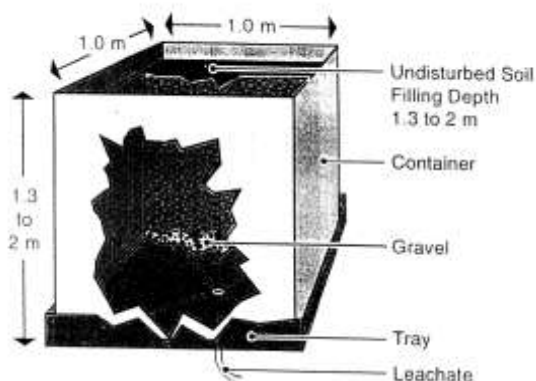


Figure B.8.1.3.3._CA-13: The scheme of the lysimeter used in the study (copied from the study report).

The soil forming soil monolith of the lysimeter was described as brown soil from sand with a low degree of profile differentiation, that originated and then developed from sandy to sandy-loamy sediment overlying the deposits of the lower terrace of the river Rhine. According to German classification it was “Braunerde” from sand and according to FAO – Eutric Cambisol. The detailed characteristic of the soil monolith filling the lysimeter is provided in the table B.8.1.3.3._CA-15. The data are presented only for layers down to the depth of 115, as that was declared target depth for soil core sampling.

Table B.8.1.3.3._CA-15: The characteristic of soil forming the lysimeter’s soil monolith.

Parameter		Soil layer (symbol, depth)			
		A_b , 0 – 30 cm	B_v , 30 – 60 cm	B_v , 60 – 100 cm	B_v , 100 – 115 cm
Soil texture (USDA)		Sandy loam	Sandy loam	Loamy sand	Loamy sand
Particle size distribution	Sand (50 – 2000 μm)	71.8	72.2	79.4	82.7
	Silt (2 – 50 μm)	16.5	16.6	11.0	9.1
	Clay (<2 μm)	11.8	11.2	9.7	8.2
Physico-chemical properties	pH in H_2O	7.04	7.24	7.18	7.46
	pH in CaCl_2	6.05	6.42	6.32	6.61
	OC [%]	1.41	0.34	0.19	0.17
	CEC [meq/100g]	9.61	7.43	7.57	8.52
	Microbial biomass [mg/kg]	235	34	11	13
Physical parameters	Pore volume [vol. %]	44.94	37.97	42.47	42.90
	air capacity AC [vol. % H_2O]	12.49	17.36	24.31	21.64
	field capacity FC [vol. % H_2O]	32.45	20.61	18.16	21.15
	available water capacity AWC [vol. % H_2O]	23.83	13.10	10.46	11.82
	permanent wilting point PWC [vol. % H_2O]	8.83	7.51	7.70	9.43
	saturated hydraulic conductivity K [$\text{cm} \cdot \text{s}^{-1}$]	5.4 E-3	9.8 E-3	7.5 E-3	5.5 E-3
	intrinsic permeability k [cm^2]	5.4 E-8	9.8 E-8	7.5 E-8	5.5 E-8

The lysimeters were transferred to the open-air lysimeter station located in Bayer AG’ Landwirtschaftszentrum, Monheim, Germany (latitude 51°4’ N, longitude 6°55’ E, ~40 m above the sea level), shown on figure B.8.1.3.3._CA-14, and installed in positions #75 and #18. The schematic presentation of the cross-section of the lysimeter station, showing the way the lysimeters were maintained, is presented on figure B.8.1.3.3._CA-15.

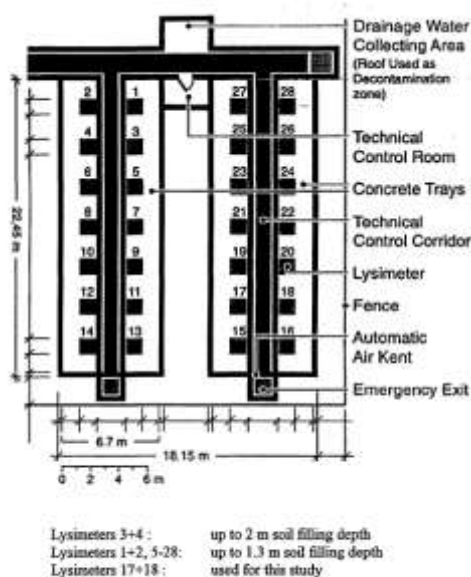


Figure B.8.1.3.3_CA-14: The general view of the lysimeter station of Bayer AG. (copied from the study report).

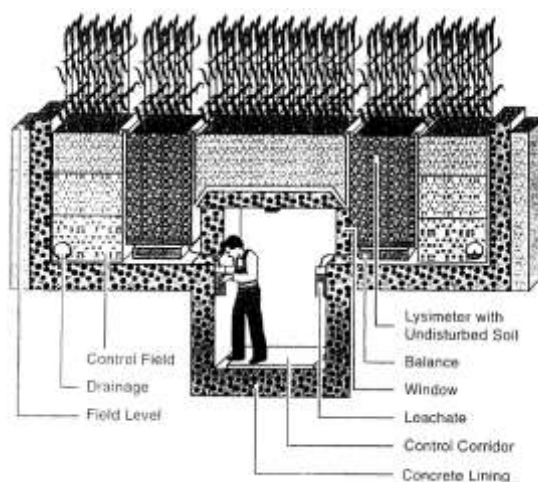


Figure B.8.1.3.3_CA-15: The cross-section general view of the lysimeter station of Bayer AG. (copied from the study report).

The lysimeters were installed in March 1992, then in April 1992 the Inkarnat Clover was sown as a first vegetation after their acquisition. It was broken up and incorporated into top 15 cm. of the soil core in October 1992, then on the 26th November 1992 the Winter wheat var. Orestes was sown. That crop was also incorporated on the lysimeters' top soil on 3rd March 1999 and then the lysimeters were left bare until the preparation of the seed bed for the 1st crop – fodder (silage) maize, variety Mutin, occurred shortly before its sowing on 10th May 1993. The experiment started on the 10th of May 1993 by sowing the 1st target crop – maize and ended in November 1995, when the soil was analysed for the residues of Flufenacet.

During that experimental period the following crops were grown on the lysimeters:

- Maize (fodder) var. Mutin as the 1st, target crop; it was sown on the 10th of May 1993 and harvested on the 28th September 1993, 20 weeks after sowing and 1st application of the test compound;

- Winter wheat, var. Orestis as the 2nd, target crop, it was sown on the 2nd November 1993 and harvested on 3rd August 1994, 64 weeks after 1st application of the test compound and 39 weeks after sowing and 2nd application of the test compound;
- Sugar beet var. Sonja as the 3rd, succeeding crop; it was sown on the 13th April 1995 and harvested on 7th November 1995, 30 weeks after sowing, 130 weeks after the 1st application and 105 weeks after the 2nd application of the test compound;

Maize grown as the 1st crop was sown in two rows 60-cm apart, at seed density 20 grains/m². Shortly after germination, on 25th May 1993 the number of plants was manually reduced to 12 plants/m². Winter wheat, grown as the 2nd crop was sown at seed density 420 grains/m². The 3rd crop – sugar beet, was sown in three rows, 33-cm apart and 17-cm distant from the walls of lysimeter, at seed density 9 seeds/m² (3 seeds per row).

After harvest of the 1st and 2nd crop the plant residues – maize stubble as well as wheat stubble plus 90% of wheat straw, left on the lysimeter were incorporated into the top soil layer (15 cm) as organic fertiliser.

All major crop maintenance measures used during the experiment are presented below in the table B.8.1.3.3._CA-16. In the table, in the columns for crop protection, are also presented the applications of the test compound, marked red. Additionally, when necessary, artificial irrigation was performed as maintenance measure. That was done in order to supply the crops growing on the surface of lysimeters with water in periods of relative drought (in summer, when the level of soil water available to plants is low). The details on that maintenance measure will be provided further down the summary, together with the characteristic of precipitation recorded on site.

The test substance used in the study was [Phenyl-UL-¹⁴C] Flufenacet, having a specific activity of 2.0 MBq/mg (54 µCi/mg) and radiochemical and chemical purity of >99%. Its structural formula is presented below on figure B.8.1.3.3._CA-16. It was used to prepare the application solution.

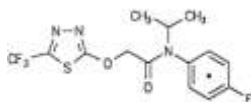


Figure B.8.1.3.3._CA-16: The structural formula of the test compound – the [¹⁴C]-Flufenacet. Asterisk (*) denotes the radiolabelling position (copied from the study report).

It was stated that the test compound should be applied as 60 WG (Water Dispersible Granule) formulation. However, because it was not possible at the time of the experiment to prepare in microscale a representative and homogenous WG formulation containing the radiolabelled active substance, the pure solution of [¹⁴C]-Flufenacet was used instead.

The first application of the test substance took place on the 13th of May 1993, 3 days after the 1st crop – corn, was sown. The assumed application rate was 480 g Flufenacet/ha and the actual was 48.14 mg/m² (+0.29% of the intended amount). For that purpose the whole delivered sample of Flufenacet was dissolved in 4 mL of C₂H₅OH. Next, for the given lysimeter 0.976 mL of that solution was mixed with 100 g of the lysimeter top soil (mixing lasted 1 hour). Then the volume of soil was increased to obtain a final amount of ~4000g of fortified soil. That amount was uniformly distributed onto the lysimeter's surface. The application was terminated by irrigation with 5 mm/m² of water to minimise losses due to wind erosion. The amount of radioactivity introduced that way onto each lysimeter – #17 and #18 was 96273 kBq. The overall loss of radioactivity during application was 27.5 kBq/Lysimeter. That value was taken into account in further calculations.

The second application of the test compound occurred on the 3rd November 1993, 1 day after sowing the 2nd crop – winter wheat. The assumed application rate was 180 g Flufenacet/ha and the actual was 18.02 mg/m² (+0.11% of the intended amount). For that purpose the whole delivered sample of Flufenacet was dissolved in 5 mL of C₂H₅OH. Next, for the given lysimeter 2.21 mL of that solution was mixed with 100 g of the lysimeter top soil (mixing lasted 1 hour). Then the volume of soil was increased to obtain a final amount of ~4000g of fortified soil. That amount was uniformly distributed onto the lysimeter's surface. The application was terminated by irrigation with 5 mm/m² of water to minimise losses due to wind erosion. The amount of radioactivity introduced that way onto each lysimeter – #17 and #18 was 34044 kBq. The overall loss of radioactivity during application was 106.4 kBq/Lysimeter. That value was taken into account in further calculations.

Table B.8.1.3.3._CA-16: Major crop maintenance measures used during the experiment.

Fertilisation			Crop Protection			Other measures	
Date	Fertiliser used	Dose rate	Date	Crop protection measure	Dose rate	Date	Measure
April 1992	Thomas phosphate potash	1500 kg/ha	1992	----	----	April 1992	Sowing of Inkarnat Clover
						October 1992	Digging up and incorporation of residues of clover into the top soil layers (~15 cm)
						26 November 1992	Sowing of Winter wheat var. Orestis
19 March 1993	Thomas phosphate potash	1500 kg/ha	10 May 1993	Maize seeds treated with TMTD	not specified	03 March 1993	Digging up and incorporation of residues of Winter wheat into the top soil layers (~15 cm)
	Lime ammonium salpetre	540 kg/ha					
03 June 1993	Basfoliar	8 L/ha	13 May 1993	1 st application of the test compound – [¹⁴ C] Flufenacet	48.14 mg/ha (480 g/ha)	10 May 1993	Digging up the top soil layer, tilling, crumbling and seed bed preparation for maize; sowing of the 1 st crop
08 June 1993	Nitrophoska permanent	400 kg/ha					
18 June 1993	Basfoliar	8 L/ha				25 May 1993	Manual reduction of the number of growing corn plants
24 June 1993	Basfoliar	10 L/ha					
30 September 1993	Organic fertilisation (corn stubble)	----	02 June 1993	E605 combi	0.1%	28 September 1993	Harvest of the 1 st crop
						30 September 1993	Incorporation of the maize stubble into the top soil layer
			02 November 1993	Winter wheat treated with Baytan univ.	not specified	02 November 1993	Digging up the top soil layer, tilling, crumbling and seed bed preparation Winter wheat; sowing of the 2nd crop
			03 November 1993	2 nd application of the test compound – [¹⁴ C] Flufenacet	18.02 mg/ha (180 g/ha)		
18 February 1994	Lime ammonium salpetre	254 kg/ha	15 April 1994	Tolkan Fox	3.5 L/ha	03 August 1994	Harvest of the 2nd crop
18 May 1994	Lime ammonium salpetre	220 kg/ha	10 May 1994	Sportak Alpha	1.5 L/ha		
23 August 1994	Lime	500 kg/ha		Colt	1.0 L/ha		
11 August 1994	Organic fertilisation (wheat stubble and straw)	----	30 May 1994	Metasystox R	0.125%	11 August 1994	Cutting up and incorporation of residues of Winter wheat (stubbles and 90% straw) into the top soil layers (~15 cm)
				E605 forte	0.05%		
			13 June 1994	E605 forte	0.05%		
				Matador	1.0 L/ha		
				Dyrene	2.0 L/ha		
13 March 1995	Lime ammonium salpetre	660 kg/ha	13 april 1995	Sugar beet seeds treated with TMTD, Hymexazole and Imidachloprid 90 FS 600	----	13 April 1995	Digging up the top soil layer, tilling, crumbling and seed bed preparation for sugar beet; sowing of sugar beet – 3 rd crop
	Thomas phosphate potash	1500 kg/ha					
23 June 1995	Lime ammonium salpetre	280 kg/ha	25 August 1995	Bardos	1.0 L/ha	07 November 1995	Harvest of the 3 rd crop – sugar beet
			22 September 1995	Bardos	1.0 L/ha		

The experiment lasted for two and a half consecutive years, from May 1993, when the 1st crop was sown and first application of the test compound occurred, until November 1995, when soil monolith filling the lysimeter was analysed for the amount and nature of the residues of Flufenacet (active substance and its degradation products) retained within it.

During that whole period the weather conditions on the experimental site, such as air temperature, soil temperature at various depths, duration of sunshine, wind velocity, rainfall air humidity, were constantly monitored and daily recorded by weather station of the experimental facility, located within 1 km from the test site. At the test site the soil temperature at the depth of 20 cm was measured continuously in one of the lysimeters. The collected data were processed to obtain monthly and yearly averages, presented in section **Results and their discussion** of this summary. The weights of each lysimeter were continuously recorded. They will be presented, in graphical form, also in section **Results and their discussion** of this summary.

The leachates from each lysimeter were collected in two replacable 20-L steel containers attached in sequence to the lysimeter's outlet. The collected leachates were taken for analysis in 2-week intervals, or shorter if necessary. To do that the containers were emptied, the volume of the collected leachates determined gravimetrically and their pH measured.

The gross radioactivity in the fresh leachate was determined by LSC using 10-mL aliquots. For that purpose three 10-mL aliquots were mixed with 0.1 mL of 1M NaOH. Next to each of them 10 mL of Quickszint 401 LS cocktail was added and the samples were analysed by LSC. The results represented the content of radioactive residues adjusted to alkaline pH.

Another three aliquots were mixed with 0.1 mL of 18% HCl_{aq}, ultrasonicated in open vessels for ~30 minutes in order to release of ¹⁴CO₂ possibly forming in sample and analysed by LSC after addition of 10 mL of Quickszint 401 LS cocktail. The results represented the content of radioactive residues adjusted to acidic pH.

10% of leachates collected at each sampling were stored combined in the container for annual leachate sample. That container was stored in the deep-freeze storage room. Another 10% of each leachate was stored as a separate sample in the deep-freeze storage room.

The deep-frozen leachates were stored for up to 13 months between collection and analysis. The selected leachates obtained from each lysimeter – 1st-year early leachate, 1st-year leachate with the highest radioactivity content, 1st-year late leachate, annual 1st-year leachate and annual 2nd-year leachate were analysed qualitatively and quantitatively TLC. The profiling of radioactivity in leachates soil – identification and quantitation of Flufenacet and its degradation products, was performed in processed leachates. In case of 1st-year leachates the processing started by concentrating 500 mL of leachate under vacuum to the volume of 50 mL. Its 10-mL aliquot was passed through SPE cartridge. The eluate was discarded and the residue eluted from the SPE column using 5 mL of CH₃CN + 0.4% CH₃COOH (9:1) solution. That eluate was collected and analysed by TLC.

The processing of the 2nd-year annual leachate began with concentrating its 100 mL aliquot to 10 mL. Then the procedure was the same as described above for the 1st-year leachates.

Annual leachates were also analysed for pH, TOC, and content of Cl⁻, SO₄²⁻, NO₂⁻, NO₃⁻ and NH₄⁺.

The plant material collected at harvest for 1st target crop – maize, were above-ground parts – “silage material”, while stubbs were left at spot, in line with agricultural practice, and then incorporated into lysimeter's topsoil as organic fertilizer. In case of the 2nd target crop – Winter wheat the collected plant material were also above-ground parts - kernels, hulls and straw. The stubs were left at spot to be subsequently, together with 90% of the collected straw, incorporated into lysimeter's topsoil as organic fertilizer, in line with agricultural practice

The plant material collected at harvest for the 3rd (succeeding) crop – sugar beets, were tubers and leaves. The harvested fresh plant material was homogenised under liquid nitrogen, dried at T = 50°C and its aliquots were analysed, after combustion, for radioactivity content.

After harvest of the 3rd crop the surface of the lysimeters was left bare, covered by a protective plastic plate until being processed.

On the 14th November 1995 three top 10-cm layers were removed from the Lysimeter #17, followed by the next 10-cm layer sampled two days later – on the 16th November 1995. Each collected layer was weighed to determine its fresh weight.

Next the soil from each layer was air-dried in greenhouse, mixed thoroughly and divided into 9 subsamples the weight of which was determined. Three aliquots of each subsample were taken for the determination of the content of radioactivity by LSC after combustion.

For the deeper layers – from 40 to 100 (120) cm depth five soil cores were taken using an electric soil corer, each having the diameter of 8 cm². The cores were sampled on the 13th December 1995. The distribution of the sampling points is presented below on figure B.8.1.3.3._CA-17.

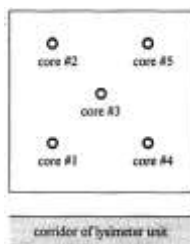


Figure B.8.1.3.3_CA-17: The sampling scheme for the soil cores taken from the lysimeters (copied from the study report).

The obtained 20-cm segments were cut into two 10-cm sections. These 10-cm sections from each core were combined and their total fresh weight recorded. Next the soil was let to dry for 12 days, homogenised and 3 aliquots of so prepared soil samples analysed for radioactivity content using LSC.

The deepest layers were not reached by the corer. Therefore the individual soil sample representing them was taken after the lysimeter was removed from the frame. It was analysed for the radioactivity content using LSC.

Also the gravel filling the bottom of the lysimeter was sampled to determine the amount of radioactivity it retained. For that purpose two 500-g aliquots of gravel were extracted for two hours with 200 mL $\text{CH}_3\text{CN}/0.1\text{M}$ HCl 1:1 (v/v) solution. The extract was analysed for radioactivity content.

In case of the Lysimeter #18 the top layers were not removed, but from the whole soil monolith 5 soil cores were taken on the 13th December 1995 and processed using the same procedure as described above for sampling soil cores from Lysimeter #17.

The profiling of radioactivity in soil – identification and quantitation of Flufenacet and its degradation products, was performed down to the depth of 40 cm. For that purpose two 30-g aliquots of each layer (0-10 cm, 10-20 cm, 20-30 cm and 30-40 cm) from each lysimeter were extracted with two 100-mL portions of $\text{CH}_3\text{CN}/0.1\text{M}$ HCl 1:1 (v/v) solution. Each extraction step lasted 1 hour and was followed by 20-minutes centrifugation. The extracts were filtered through paper filter, combined and their volume recorded. Next they were analysed for radioactivity content by LSC.

The LSC analysys of the liquid samples was carried out using one of the following LS counters: PW 4700, Wallac 1410, Rackbeta 1219, Beckman LS 6000 LL or Beckman LS 6500.

In case of non-processed leachates their 10-mL aliquots were used mixed with 10 mL of Quickszint 401 LS cocktail. The minimum sensitivity of LSC analysis for those samples was $3.1 \text{ E-}7$ ppm. It corresponded to 58 cpm when expressed as Lowest Acceptable Gross Count Rate (LAGC) and 29 cpm for Lowest Acceptable Net Count Rate (LANC), assuming Average Background (BCGK) of 29 cpm ($\text{LAGC} = 2 \times \text{BCGK}$ and $\text{LANC} = \text{LAGC} - \text{BCGK}$). The greatest probable error $\text{GPE} = 5.61\%$.

In case of the organic extracts their 0.1 – 2 mL aliquots were used mixed with 7 mL of Instant Scint Gel or 2 mL of Quicksafe A LS cocktails. The minimum sensitivity of LSC analysis for those samples was $1.5 \text{ E-}6$ ppm. It corresponded to 58 cpm when expressed as Lowest Acceptable Gross Count Rate (LAGC) and 29 cpm for Lowest Acceptable Net Count Rate (LANC), assuming Average Background (BCGK) of 29 cpm ($\text{LAGC} = 2 \times \text{BCGK}$ and $\text{LANC} = \text{LAGC} - \text{BCGK}$). The greatest probable error $\text{GPE} = 5.61\%$.

The radioactivity in the solid samples was determined after their combustion in an oxidiser (Oxidiser 306 Tri-Carb or OX 300). The generated $^{14}\text{CO}_2$ was absorbed in the LS cocktail (the mixture of 8 mL Carbosorb and 10 mL Permafluor, or 15 mL Oxysolv C 400) and analysed by LSC. The analysis was performed for soil and plant material, using samples weighing 0.055 g.

The TLC analysis was carried out in one of the three following variants:

- 1) on 20 • 20 cm, 0.25 mm thick, silica gel 60 F_{254} TLC plates developed at room temperature in closed glass chamber using following solvent system $\text{CHCl}_3/\text{CH}_3\text{COOC}_2\text{H}_5$ 3:1 (v/v), it was used for identification and quantitation of Flufenacet and FOE Alcohol;
- 2) on 20 • 20 cm, 0.25 mm thick, silica gel 60 F_{254} TLC plates developed at room temperature in closed glass chamber using following solvent system: $\text{CH}_3\text{CN}/(\text{CH}_3)_2\text{CHOH}/\text{CH}_3\text{COOC}_2\text{H}_5/\text{H}_2\text{O}$ 60:9:6:3 (v/v/v/v); it was used for identification and quantitation of Flufenacet, FOE Oxalate, FOE Sulfonic acid and FOE Thioglycolate sulfoxide;
- 3) on 20 • 20 cm, 0.25 mm thick, RP-18 F_{254} TLC plates developed at room temperature in closed glass chamber using following solvent system: $\text{CH}_3\text{CN}/(\text{CH}_3\text{OH}/0.5\% \text{ NaCl}_{\text{aq}})$ 2:2:1 (v/v/v);

The detectors used in the analysis were:

- TLC Scanner CS-930 or UV light chamber for “cold” reference standards;
- Radio-TLC-Scanner RITA 6800 used only in the purity check of the applied parent compound
- Bio-Imaging Analyser BAS 2000 for radiolabelled standard solutions and samples;

The identification was performed by means of the comparison of the R_f values of the constituents of the analysed samples with those of the known reference compounds.

The quantitative analysis was performed by means of LSC analysis of the separated bands (spots) on the TLC plate.

Additionally, for the analysis of standard solutions, purity checks of application solutions and for isolation and verification of degradation products in leachates, the HPLC analysis was performed. It was carried out using HP 1090 work station equipped with DAD (UV) and Ramona 4 (LSC) detectors. The chromatographic separation was performed on LiChrosorb RP 18, 250 • 4 mm, 5 μ m, chromatographic column. In the study report it was stated that more detailed information on the HPLC analysis was provided in the raw data.

Results and their discussion:

The long-term weather characteristic of the test site is presented below on figure B.8.1.3.3._CA-18 (the frame-table copied from the study report). The values marked with an asterisk (*) are the mean of those recorded by the Experimental Farm’s wether station in years 1966 – 1995, while those marked with (#) are the mean of the the measurables recorded in years 1968 – 1995. The weather conditions – air temperature, soil temperature, wind speed, radiant heat, precipitation and irrigation, recorded at the test site during the experiment are presented in the table B.8.1.3.3._CA-17. The table provides monthly mean values. The air temperature, soil temperature at different depths, with exception of that at the depth of 20 cm, radiant heat, wind speed and precipitation are the weather data recorded by the weather station located 1 km apart from the lysimeter site. The soil temperature at 20-cm depth was measured at spot, in Lysimeter #17. Additionally the sum curve of precipitation and irrigation during study is presented on figure B.8.1.3.3._CA-19, immediately below the table B.8.1.3.3._CA-17.

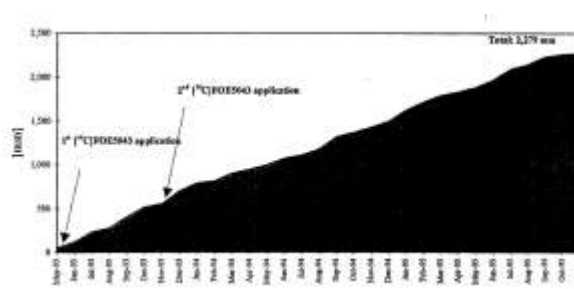
Table 2: Long-term weather characteristics of test location

Annual rainfall (*):	745 mm
Max. / min. monthly rainfall (*):	June (78.1 mm) / February (42.7 mm)
Annual relative humidity of the air (*):	73%
Annual air temperature at 2 m above ground level (*):	10.0°C
Max. / min. monthly air temperature at 2 m above ground level (*):	July (18.4 °C) / January (2.6 °C)
Annual soil temperature (-10 cm) (#):	9.5°C
Annual soil temperature (-30 cm) (#):	10.3°C
Annual soil temperature (-50 cm) (#):	10.7°C
Annual soil temperature (-100 cm) (#):	10.6°C
Annual wind velocity (*):	2.5 m/sec
Annual radiant heat (#):	29.1 kJ/cm ²
Max. / min. monthly radiant heat (#):	July (53.1 kJ/cm ²) / Dec. (5.8 kJ/cm ²)

Figure B.8.1.3.3._CA-18: The table presenting long-term weather characteristic at the lysimeter test site (copied from the study report).

Table B.8.1.3.3._CA-17: The monthly weather data recorded at the test site during the experiment.

Time period		Mean air temperature 2 metres above the ground [°C]	Mean soil temperature [°C] at the depth						Mean monthly radiant heat [kJ/cm ²]	Wind speed [m/s.]	Precipitation (P) and Irrigation (I) [mm]	
Year of experiment	Calendar date (month and year)		0 cm	10 cm	20 cm	30 cm	50 cm	100 cm			P	I
1 st	05/93	15.4	14.1	14.9	14.8	16.1	16.4	14.8	52.5	1.9	51.2	5.0
	06/93	17.0	16.4	17.0	17.4	18.2	18.7	17.4	51.5	1.8	43.6	21.0
	07/93	17.3	16.3	17.6	16.7	18.6	19.2	18.1	43.7	2.0	110.2	0.0
	08/93	16.3	14.5	16.1	15.7	17.8	18.7	18.1	41.5	1.9	24.7	20.0
	09/93	13.6	11.6	13.6	13.1	14.9	15.8	15.8	25.3	2.2	127.3	0.0
	10/93	9.1	7.1	9.2	8.8	10.7	12.0	12.8	14.5	1.8	113.3	0.0
	11/93	2.6	1.2	3.3	3.1	4.8	6.3	7.9	9.0	2.0	35.1	0.0
	12/93	5.5	2.6	3.6	3.3	4.1	4.8	5.4	3.6	2.9	148.2	0.0
	01/94	5.1	2.4	3.7	3.5	4.3	5.0	5.4	6.1	2.8	86.2	0.0
	02/94	2.4	-0.5	1.4	1.3	2.4	3.4	4.2	13.2	2.3	25.7	0.0
2 nd	03/94	8.1	4.4	5.7	5.8	6.2	6.5	5.9	22.5	3.1	86.5	0.0
	04/94	9.4	6.5	7.8	7.6	8.8	9.4	8.7	36.2	2.6	45.1	0.0
	05/94	13.6	12.1	12.9	12.1	13.9	14.4	13.2	44.1	2.0	50.0	0.0
	06/94	17.2	16.0	16.2	14.7	17.1	17.4	15.8	54.7	2.4	66.6	0.0
	07/94	22.6	20.9	21.5	18.0	22.6	22.9	20.7	58.9	1.9	20.5	10.0
	08/94	18.5	17.1	18.4	19.0	19.7	20.5	19.7	41.3	2.1	67.4	0.0
	09/94	14.1	11.4	13.7	16.4	15.1	16.1	16.3	22.0	1.7	90.0	50.0
	10/94	10.0	5.6	8.8	13.4	10.7	11.9	12.6	23.0	1.9	56.4	0.0
	11/94	10.1	7.9	9.5	11.8	10.1	10.9	11.1	8.4	2.1	59.2	0.0
	12/94	6.1	3.6	5.4	9.0	6.1	7.1	8.0	6.0	2.6	68.1	0.0
3 rd	01/95	3.3	1.3	2.7	5.8	3.3	4.1	4.9	7.5	3.5	126.8	0.0
	02/95	6.7	3.8	5.2	6.1	5.5	6.1	6.2	10.9	2.8	90.1	0.0
	03/95	4.7	2.0	4.0	5.8	5.1	6.0	6.1	26.1	3.1	77.4	0.0
	04/95	9.6	7.3	8.6	8.1	9.0	9.3	8.5	30.4	2.6	41.4	0.0
	05/95	13.3	12.5	13.3	11.5	14.1	14.4	13.1	50.5	1.6	49.4	3.0
	06/95	15.4	15.7	16.0	13.6	16.7	17.0	15.7	48.1	1.5	70.4	12.0
	07/95	21.9	20.2	20.9	18.3	21.9	22.2	20.1	56.7	1.5	70.0	56.0
	08/95	20.6	18.5	20.0	20.8	21.9	22.6	21.3	50.7	1.9	19.4	33.0
	09/95	14.2	11.9	13.7	16.5	15.4	16.5	16.8	23.0	2.2	86.1	0.0
	10/95	13.4	10.3	12.1	14.5	13.4	14.4	14.6	21.3	1.8	29.9	0.0
	11/95	6.3	5.3	6.6	10.0	7.6	8.7	10.0	10.3	2.2	12.3	0.0

**Figure B.8.1.3.3._CA-19:** The sum curve of precipitation and irrigation [mm] recorded during the study (copied from the study report).

The total 1st-year precipitation was 897.1 mm and irrigation was 51.0 mm. Therefore the amount of water received by each lysimeter that experimental year as precipitation and irrigation was 948.1 mm, 148.1 mm more than the BBA Guideline requirement – 800 mm.

The total 2nd-year precipitation was 813.9 mm and irrigation was 75.0 mm. Therefore the amount of water received by each lysimeter that experimental year as precipitation and irrigation was 888.9 mm, 88.9 mm more than the BBA Guideline requirement – 800 mm.

The total 3rd-year precipitation was 338 mm and irrigation was 104.0 mm. Therefore the amount of water received by each lysimeter that experimental year as precipitation and irrigation was 442.0 mm, 358 mm less than the BBA Guideline requirement – 800 mm.

The total precipitation and irrigation during the study was 2279 mm, what gave the average annual precipitation at the level of 912 mm – 112 mm higher than the regulatory requirement.

The weight of the lysimeters during the study is presented below, in graphical form, on figure B.8.1.3.3._CA-20.

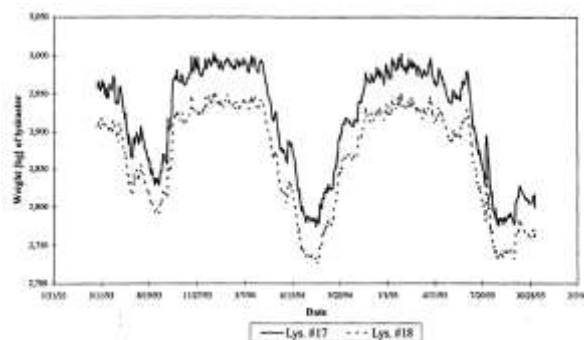


Figure B.8.1.3.3._CA-20: The weight of the lysimeters recorded during the study (copied from the study report).

The leachate from Lysimeter #17 was collected during the 1st experimental year 22 times – on weeks of experiment: 0, 2, 11, 22, 23, 24, 27, 30, 31, 32, 33 (twice), 35, 36, 37, 38, 41, 43, 45, 46, 47 and 50. The total volume of leachate collected during that period was 399.1 L. During the 2nd year of experiment the leachates from that lysimeter were collected 19 times – on weeks of experiment 55, 79, 82, 83, 84, 85, 87, 88, 89 (twice), 90, 91, 92, 93, 94, 96, 96, 100 and 103. The total volume of leachate collected during that period was 365.4 L. On the 3rd experimental year the leachate from that lysimeter was collected only once – on week 115 of the experiment. Its volume was 17.5 L. Therefore the total, exact, volume of leachate collected from that lysimeter during the experimental period of 2.5 years was 781.0 L, of which 764.5 L were collected during the first two years. The total number of sampling points during the experiment for that lysimeter was 41. The leachate collected on week 0 is the leachate collected before the application of the test compound.

The leachate from Lysimeter #16 was collected during the 1st experimental year 22 times – on weeks of experiment: 0, 2, 11, 22, 23, 24, 27, 30, 31, 32, 33 (twice), 35, 36, 37, 38, 41, 43, 45, 46, 47 and 50. The total volume of leachate collected during that period was 383.1 L. During the 2nd year of experiment the leachates from that lysimeter were collected 19 times – on weeks of experiment 55, 79, 82, 83, 84, 85, 87, 88, 89 (twice), 90, 91, 92, 93, 94, 96, 96, 100 and 103. The total volume of leachate collected during that period was 368.9 L. On the 3rd experimental year the leachate from that lysimeter was collected only one – on week 115 of the experiment. Its volume was 19.1 L. Therefore the total, exact, volume of leachate collected from that lysimeter during the experimental period of 2.5 years was 771.1 L, of which 752.0 L were collected during the first two years. The total number of sampling points during the experiment for that lysimeter was 41. The leachate collected on week 0 is the leachate collected before the application of the test compound.

The detailed information on the collection dates and volumes of individual leachates are presented below in table B.8.1.3.3._CA-18.

Table B.8.1.3.3._CA-18: The sampling time and volume of the individual leachate samples collected during the experiment.

Lysimeter # 15				Lysimeter #16			
Experimental period	Sampling time		Volume of leachate [L]	Experimental period	Sampling time		Volume of leachate [L]
	Date	Week of experiment			Date	Week of experiment	
1 st year	12/05/1993	0	15.0	1 st year	12/05/1993	0	12.0
	28/05/1993	2	1.7		28/05/1993	2	1.6
	29/07/1993	11	2.1		29/07/1993	11	3.0
	15/10/1993	22	13.8		15/10/1993	22	7.2
	22/10/1993	23	19.7		22/10/1993	23	19.8
	29/10/1993	24	8.2		29/10/1993	24	8.2
	19/11/1993	27	29.8		19/11/1993	27	29.3
	09/12/1993	30	9.9		09/12/1993	30	9.5
	15/12/1993	31	21.0		15/12/1993	31	19.3
	23/12/1993	32	43.0		23/12/1993	32	42.0
	29/12/1993	33	21.0		29/12/1993	33	21.8
	04/01/1994	33	43.5		04/01/1994	33	44.3
	12/01/1994	35	21.4		12/01/1994	35	21.7
	19/01/1994	36	13.4		19/01/1994	36	13.7
	28/01/1994	37	20.3		28/01/1994	37	17.8
	04/02/1994	38	21.3		04/02/1994	38	21.3
	24/02/1994	41	15.0		24/02/1994	41	14.3
	14/03/1994	43	19.5		14/03/1994	43	19.1
	24/03/1994	45	21.5		24/03/1994	45	22.0
	31/03/1994	46	21.0		31/03/1994	46	19.7
	11/04/1994	47	19.4		11/04/1994	47	15.0
	29/04/1994	50	12.6		29/04/1994	50	12.5
2 nd year	06/06/1994	55	2.5	2 nd year	06/06/1994	55	2.0
	18/11/1994	79	10.3		18/11/1994	79	14.1
	09/12/1994	82	21.3		09/12/1994	82	21.6
	15/12/1994	83	20.1		15/12/1994	83	17.8
	22/12/1994	84	10.4		22/12/1994	84	13.1
	03/01/1995	85	21.3		03/01/1995	85	21.3
	13/01/1995	87	21.2		13/01/1995	87	21.8
	24/01/1995	88	21.4		24/01/1995	88	21.5
	26/01/1995	89	21.2		26/01/1995	89	22.0
	30/01/1995	89	43.7		30/01/1995	89	44.7
	03/02/1995	90	18.5		03/02/1995	90	19.0
	14/02/1995	91	15.6		14/02/1995	91	15.3
	20/02/1995	92	21.2		20/02/1995	92	21.9
	24/02/1995	93	20.9		24/02/1995	93	20.5
	03/03/1995	94	21.3		03/03/1995	94	21.1
	17/03/1995	96	17.5		17/03/1995	96	16.6
	31/03/1995	98	15.0		31/03/1995	98	12.4
	18/04/1995	100	21.3		18/04/1995	100	22.0
	04/05/1995	103	20.7		04/05/1995	103	20.2
3 rd year	26/07/1996	115	17.5	3 rd year	26/07/1996	115	19.1

The results of the determination of radioactivity in leachates – the amounts of radioactivity recovered, are presented below in two tables – B.8.1.3.3._CA-19 for the Lysimeter #17 and B.8.1.3.3._CA-20 for the Lysimeter #18. Additionally the same results are presented in graphical form on figure B.8.1.3.3._CA-21.

TableB.8.1.3.3._CA-19: The total radioactivity recovered in the leachates from Lysimeter #17.

Experimental period	Sampling time		Volume of leachate [L]	Total Radioactivity Recovered (TRR)	
	Date	Week of experiment		Net TRR [$\mu\text{g a. i. equiv./L}$]	Net total TRR/leachate [$\mu\text{g a. i. equiv.}$]
<i>1st year</i>	12/05/1993	0	15.0	background	background
	28/05/1993	2	1.7	background	background
	29/07/1993	11	2.1	0.047	0.098
	15/10/1993	22	13.8	0.219	3.022
	22/10/1993	23	19.7	0.413	3.022
	29/10/1993	24	8.2	0.588	4.818
	19/11/1993	27	29.8	0.571	17.016
	09/12/1993	30	9.9	0.694	6.871
	15/12/1993	31	21.0	0.913	19.173
	23/12/1993	32	43.0	0.931	40.012
	29/12/1993	33	21.0	1.226	25.736
	04/01/1994	33	43.5	2.176	94.656
	12/01/1994	35	21.4	3.849	82.358
	19/01/1994	36	13.4	4.304	57.667
	28/01/1994	37	20.3	4.681	95.024
	04/02/1994	38	21.3	5.106	109.908
	24/02/1994	41	15.0	4.905	73.568
	14/03/1994	43	19.5	4.511	87.955
	24/03/1994	45	21.5	3.735	80.303
	31/03/1994	46	21.0	3.233	67.893
	11/04/1994	47	19.4	2.545	49.373
	29/04/1994	50	12.6	2.084	26.258
	Total		399.1	----	949.8
	Mean		----	2.380	----
<i>2nd year</i>	06/06/1994	55	2.5	1.650	4.124
	18/11/1994	79	10.3	0.171	1.761
	09/12/1994	82	21.3	0.190	4.047
	15/12/1994	83	20.1	0.214	4.291
	22/12/1994	84	10.4	0.240	2.491
	03/01/1995	85	21.3	0.225	4.793
	13/01/1995	87	21.2	0.245	5.183
	24/01/1995	88	21.4	0.217	4.633
	26/01/1995	89	21.2	0.214	4.526
	30/01/1995	89	43.7	0.221	9.636
	03/02/1995	90	18.5	0.221	4.089
	14/02/1995	91	15.6	0.213	3.323
	20/02/1995	92	21.2	0.216	4.569
	24/02/1995	93	20.9	0.214	4.462
	03/03/1995	94	21.3	0.210	4.473
	17/03/1995	96	17.5	0.195	3.404
	31/03/1995	98	15.0	0.192	2.873
	18/04/1995	100	21.3	0.189	4.026
	04/05/1995	103	20.7	0.198	4.088
	Total		365.4	----	80.80
	Mean		----	0.221	----
<i>3rd year</i>	26/07/1996	115	17.5	0.239	4.174
	Total		17.5	----	4.17
	Mean		----	0.239	----

For the further, TLC analysis, aimed on the identification and quantitation of the individual constituents of leachates, the following leachates were taken:

- 24th week leachate, collected on 29 October 1993, representing the 1st-year's early leachate;
- 38th week leachate, collected on 04 February 1994, representing the 1st-year's leachate with maximum TRR;
- 47th week leachate, collected on 11 April 1994, representing the 1st-year's late leachate;
- 1st-year annual leachate;
- 2nd-year annual leachate.

TableB.8.1.3.3._CA-20: The total radioactivity recovered in the leachates from Lysimeter #18.

Experimental period	Sampling time		Volume of leachate [L]	Total Radioactivity Recovered (TRR)	
	Date	Week of experiment		Net TRR [$\mu\text{g a. i. equiv./L}$]	Net total TRR/leachate [$\mu\text{g a. i. equiv.}$]
<i>1st year</i>	12/05/1993	0	12.0	background	background
	28/05/1993	2	1.6	background	background
	29/07/1993	11	3.0	0.018	0.054
	15/10/1993	22	7.2	0.358	2.574
	22/10/1993	23	19.8	0.377	7.465
	29/10/1993	24	8.2	0.505	4.141
	19/11/1993	27	29.3	0.587	17.199
	09/12/1993	30	9.5	0.614	5.833
	15/12/1993	31	19.3	0.960	18.518
	23/12/1993	32	42.0	1.282	53.844
	29/12/1993	33	21.8	1.410	30.727
	04/01/1994	33	44.3	2.373	105.102
	12/01/1994	35	21.7	4.144	89.925
	19/01/1994	36	13.7	4.714	64.575
	28/01/1994	37	17.8	5.110	90.958
	04/02/1994	38	21.3	5.455	116.181
	24/02/1994	41	14.3	5.307	75.883
	14/03/1994	43	19.1	5.150	98.355
	24/03/1994	45	22.0	4.487	98.714
	31/03/1994	46	19.7	3.706	73.008
	11/04/1994	47	15.0	3.102	46.523
	29/04/1994	50	12.5	2.756	34.450
<i>2nd year</i>	Total		383.1	----	1034.00
	Mean		----	2.699	----
	06/06/1994	55	2.0	2.407	4.813
	18/11/1994	79	14.1	0.246	3.469
	09/12/1994	82	21.6	0.250	5.400
	15/12/1994	83	17.8	0.287	5.100
	22/12/1994	84	13.1	0.296	3.871
	03/01/1995	85	21.3	0.307	6.539
	13/01/1995	87	21.8	0.291	6.344
	24/01/1995	88	21.5	0.258	5.536
	26/01/1995	89	22.0	0.257	5.654
	30/01/1995	89	44.7	0.267	11.913
	03/02/1995	90	19.0	0.258	4.902
	14/02/1995	91	15.3	0.254	3.879
	20/02/1995	92	21.9	0.252	5.508
	24/02/1995	93	20.5	0.249	5.094
	03/03/1995	94	21.1	0.243	5.127
	17/03/1995	96	16.6	0.221	3.669
	31/03/1995	98	12.4	0.221	2.734
	18/04/1995	100	22.0	0.225	4.950
	04/05/1995	103	20.2	0.238	4.798
<i>3rd year</i>	Total		368.9	----	99.30
	Mean		----	0.269	----
	Mean		----	0.238	----
<i>3rd year</i>	26/07/1996	115	19.1	0.238	4.536
	Total		19.1	----	4.54
	Mean		----	0.238	----

For the further, TLC analysis, aimed on the identification and quantitation of the individual constituents of leachates, the following leachates were taken:

- 24th week leachate, collected on 29 October 1993, representing the 1st-year's early leachate;
- 38th week leachate, collected on 04 February 1994, representing the 1st-year's leachate with maximum TRR;
- 47th week leachate, collected on 11 April 1994, representing the 1st-year's late leachate;
- 1st-year annual leachate;
- 2nd-year annual leachate.

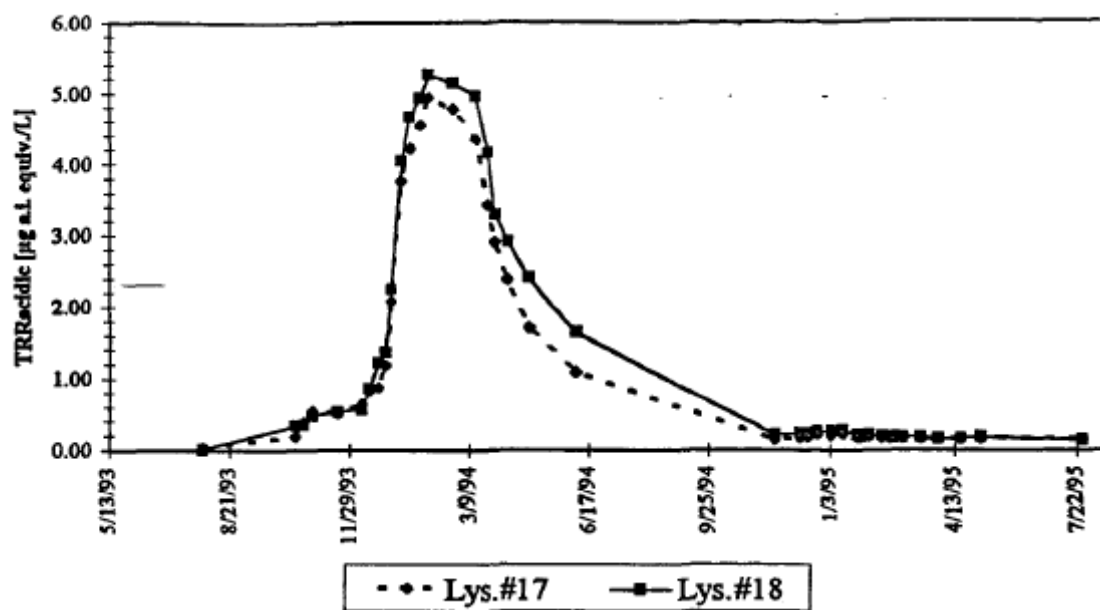


Figure B.8.1.3.3._CA-21: The graphical results of the determination of the total radioactivity recovered (TRR) in leachates from the two lysimeters (copied from the study report).

The detailed results of the characterisation of leachates – measured pH, the concentration of the total (alkaline) TRR and acidic TRR, as well as the content of $^{14}\text{CO}_2$ (expressed as % of TRR) are presented below, individually for each lysimeter, in two tables – Table B.8.1.3.3._CA-21 for Lysimeter #17 and Table B.8.1.3.3._CA-22 for Lysimeter #18. For the completeness of the results also was provided the volume of each leachate collected.

Table B.8.1.3.3._CA-21: The detailed results of the examination of the leachates from Lysimeter #17.

Experimental period	Sampling time		Volume of leachate [L]	pH of leachate	Radioactivity recovered (TRR)		
	Date	Week of experiment			Net TRR (alkaline) [µg a. i. equiv./L]	Acidic TRR [µg a. i. equiv./L]	¹⁴ CO ₂ [%]
1 st year	12/05/1993	0	15.0	----	background		
	28/05/1993	2	1.7	----	background		
	29/07/1993	11	2.1	7.9	0.047	0.035	25.81
	15/10/1993	22	13.8	7.9	0.219	0.196	10.73
	22/10/1993	23	19.7	7.8	0.413	0.382	7.51
	29/10/1993	24	8.2	7.9	0.588	0.539	8.34
	19/11/1993	27	29.8	7.7	0.571	0.520	9.02
	09/12/1993	30	9.9	7.9	0.694	0.643	7.42
	15/12/1993	31	21.0	7.8	0.913	0.830	9.15
	23/12/1993	32	43.0	7.7	0.931	0.880	5.48
	29/12/1993	33	21.0	7.6	1.226	1.188	3.49
	04/01/1994	33	43.5	7.5	2.176	2.086	4.16
	12/01/1994	35	21.4	7.6	3.849	3.772	1.99
	19/01/1994	36	13.4	7.8	4.304	4.218	2.00
	28/01/1994	37	20.3	7.8	4.681	4.551	2.79
	04/02/1994	38	21.3	7.6	5.106	4.940	4.26
	24/02/1994	41	15.0	7.9	4.905	4.780	2.54
	14/03/1994	43	19.5	7.7	4.511	4.353	3.49
	24/03/1994	45	21.5	7.9	3.735	3.444	7.79
	31/03/1994	46	21.0	7.6	3.233	2.913	9.90
	11/04/1994	47	19.4	8.0	2.545	2.389	6.13
	29/04/1994	50	12.6	8.0	2.084	1.715	17.73
	Total		399.1	7.8	----	----	----
	Mean		----	----	2.380	2.26	5.31
2 nd year	06/06/1994	55	2.5	8.0	1.650	1.088	34.04
	18/11/1994	79	10.3	7.7	0.171	0.145	15.50
	09/12/1994	82	21.3	7.4	0.190	0.175	7.89
	15/12/1994	83	20.1	7.0	0.214	0.189	11.48
	22/12/1994	84	10.4	7.2	0.240	0.218	9.19
	03/01/1995	85	21.3	7.3	0.225	0.201	10.89
	13/01/1995	87	21.2	7.4	0.245	0.232	5.11
	24/01/1995	88	21.4	7.6	0.217	0.187	13.63
	26/01/1995	89	21.2	7.6	0.214	0.188	11.94
	30/01/1995	89	43.7	7.7	0.221	0.189	14.29
	03/02/1995	90	18.5	7.7	0.221	0.192	13.35
	14/02/1995	91	15.6	7.6	0.213	0.184	13.85
	20/02/1995	92	21.2	7.7	0.216	0.177	17.87
	24/02/1995	93	20.9	7.6	0.214	0.175	18.03
	03/03/1995	94	21.3	7.7	0.210	0.174	17.38
	17/03/1995	96	17.5	7.6	0.195	0.169	13.37
	31/03/1995	98	15.0	7.6	0.192	0.157	18.02
	18/04/1995	100	21.3	7.7	0.189	0.156	17.46
	04/05/1995	103	20.7	7.5	0.198	0.167	15.70
	Total		365.4	----	----	----	----
	Mean		----	7.6	0.221	0.19	17.06
3 rd year	26/07/1996	115	17.5	7.8	0.239	0.155	35.22
	Total		17.5	----	----	----	----
	Mean		----	7.8	0.239	0.15	35.22
Total study period	Total		782.0	----	----	----	----
	Mean		----	7.7	1.310	1.25	6.28

Table B.8.1.3.3._CA-22 The detailed results of the examination of the leachates from Lysimeter #18.

Experimental period	Sampling time		Volume of leachate [L]	pH of leachate	Radioactivity recovered (TRR)		
	Date	Week of experiment			Net TRR (alkaline) [µg a. i. equiv./L]	Acidic TRR [µg a. i. equiv./L]	¹⁴ CO ₂ [%]
1 st year	12/05/1993	0	12.0	----	background		
	28/05/1993	2	1.6	----	background		
	29/07/1993	11	3.0	7.6	0.018	0.015	19.44
	15/10/1993	22	7.2	8.0	0.358	0.340	4.90
	22/10/1993	23	19.8	7.8	0.377	0.351	6.90
	29/10/1993	24	8.2	8.0	0.505	0.477	5.64
	19/11/1993	27	29.3	7.6	0.587	0.533	9.28
	09/12/1993	30	9.5	7.8	0.614	0.570	7.25
	15/12/1993	31	19.3	7.8	0.960	0.853	11.10
	23/12/1993	32	42.0	7.8	1.282	1.217	5.07
	29/12/1993	33	21.8	7.8	1.410	1.360	3.89
	04/01/1994	33	44.3	7.6	2.373	2.251	5.14
	12/01/1994	35	21.7	7.7	4.144	4.046	2.38
	19/01/1994	36	13.7	7.6	4.714	4.665	1.04
	28/01/1994	37	17.8	7.8	5.110	4.928	3.56
	04/02/1994	38	21.3	7.9	5.455	5.255	3.58
	24/02/1994	41	14.3	7.6	5.307	5.145	3.04
	14/03/1994	43	19.1	7.7	5.150	4.956	3.77
	24/03/1994	45	22.0	7.9	4.487	4.167	7.13
	31/03/1994	46	19.7	7.9	3.706	3.303	10.87
	11/04/1994	47	15.0	7.9	3.102	2.916	6.00
	29/04/1994	50	12.5	----	2.756	2.415	12.39
	Total		383.1	7.8	----	----	----
	Mean		----	----	2.699	2.56	5.35
2 nd year	06/06/1994	55	2.0	8.0	2.407	1.644	31.69
	18/11/1994	79	14.1	7.7	0.246	0.213	13.62
	09/12/1994	82	21.6	7.4	0.250	0.231	7.60
	15/12/1994	83	17.8	7.3	0.287	0.235	17.98
	22/12/1994	84	13.1	7.3	0.296	0.255	13.71
	03/01/1995	85	21.3	7.4	0.307	0.266	13.52
	13/01/1995	87	21.8	7.4	0.291	0.272	6.53
	24/01/1995	88	21.5	7.7	0.258	0.213	17.28
	26/01/1995	89	22.0	7.6	0.257	0.215	16.54
	30/01/1995	89	44.7	7.5	0.267	0.214	19.70
	03/02/1995	90	19.0	7.8	0.258	0.213	17.44
	14/02/1995	91	15.3	7.8	0.254	0.201	20.71
	20/02/1995	92	21.9	7.5	0.252	0.193	23.26
	24/02/1995	93	20.5	7.6	0.249	0.190	23.54
	03/03/1995	94	21.1	7.7	0.243	0.178	26.75
	17/03/1995	96	16.6	7.8	0.221	0.180	18.55
	31/03/1995	98	12.4	7.5	0.221	0.163	26.30
	18/04/1995	100	22.0	7.7	0.225	0.168	26.33
	04/05/1995	103	20.2	7.5	0.238	0.187	21.47
	Total		368.9	----	----	----	----
	Mean		----	7.6	0.269	0.22	23.03
3 rd year	26/07/1996	115	19.1	7.8	0.238	0.141	40.88
	Total		19.1	----	----	----	----
	Mean		----	7.8	0.238	0.14	40.88
Total study period	Total		771.1	----	----	----	----
	Mean		----	7.7	1.492	1.38	6.85

The results of the profiling of single leachates collected during the 1st year of the study and the pooled 1st-year and 2nd-year leachates showed that they contained, apart from detectable amounts of Flufenacet, also FOE Alcohol, FOE Oxalate, FOE Sulfonic acid and FOE Thioglycolate sulfoxide. Additionally a fraction further called unknown “Unknown 1” was found using both TLC methods in all analysed leachates. In case of the 3rd-year leachates the TRR (total radioactivity recovered) was not further analysed, because it was stated that it was approaching the qualitative background level. The detailed results of the profiling of the leachates collected from Lysimeter #17 are presented in the table B.8.1.3.3._CA-23. In the next table – B.8.1.3.3._CA-24 are presented the results of the profiling of the leachates collected from the Lysimeter # 18. Finally, in the table B.8.1.3.3._CA-25 are presented the results of the quantitation of the selected constituents of the annual leachates

collected from the Lysimeter #17 and the Lysimeter #18. The results of the profiling of individual and annual leachates showed that the leaching to groundwater recharge in amounts > 0.1 µg/L occurred only for FOE Sulfonic acid. It shall be also indicated that in leachates was also detected, and in quantifiable amounts, FOE Thioglycolate sulfoxide – the soil degradation product of Flufenacet identified in the experiments examining route and rate of degradation of Flufenacet in soil only as a minor compound and hence not covered by the modeling exposure assessment for the groundwater compartment. These results may indicate that under unfavourable conditions FOE Thioglycolate sulfoxide might become a compound of concern, although the identity of that compound was not fully confirmed in the study.

Table B.8.1.3.3._CA-23: Results of the profiling of the leachates collected from the Lysimeter # 17.

Type of leachate	Sampling time		Content [µg/L] of:					
	Date	Week of experiment	Flufenacet	FOE Alcohol	FOE Oxalate	FOE Sulfonic acid	FOE TGS ¹⁾	Unknown 1 [µg a. i. equiv./L]
<i>1st year early leachate</i>	29/10/1993	24	0.006	0.002	<0.001	0.225	0.015	0.027
<i>1st year max. TRR leachate</i>	04/02/1994	38	<0.011	0.006	0.005	3.375	0.017	0.065
<i>1st year late leachate</i>	11/04/1994	47	0.002	0.008	0.026	1.302	0.005	0.080
<i>1st-year annual leachate</i>	29/04/1994	(50)	0.004	0.034	0.017	1.355	0.030	0.035
<i>2nd-year annual leachate</i>	05/05/1995	(103)	0.002	0.001	0.009	0.013	0.022	0.007

Footnotes to the table:

1) FOE TGS = FOE Thioglycolate sulfoxide.

Table B.8.1.3.3._CA-24: Results of the profiling of the leachates collected from the Lysimeter # 18.

Type of leachate	Sampling time		Content [µg/L] of:					
	Date	Week of experiment	Flufenacet	FOE Alcohol	FOE Oxalate	FOE Sulfonic acid	FOE TGS ¹⁾	Unknown 1 [µg a. i. equiv./L]
<i>1st year early leachate</i>	29/10/1993	24	<0.005	0.095	0.005	0.182	0.027	0.065 ²⁾
<i>1st year max. TRR leachate</i>	04/02/1994	38	<0.001	0.044	0.036	3.682	0.028	0.041
<i>1st year late leachate</i>	11/04/1994	47	0.002	0.041	0.017	1.920	0.012	0.026
<i>1st-year annual leachate</i>	29/04/1994	(50)	0.005	0.016	0.006	1.616	0.027	0.045
<i>2nd-year annual leachate</i>	05/05/1995	(103)	0.005	0.004	0.006	0.016	0.019	0.008

Footnotes to the table:

1) FOE TGS = FOE Thioglycolate sulfoxide;

2) The sum of “Unknown 1”, commonly found in leachates, and “Unknown 2”, detected solely in this leachate.

Table B.8.1.3.3._CA-25: The concentrations of the selected constituents of annual leachates collected from Lysimeter #15 and Lysimeter # 16.

Constituent of the leachate	Concentration in leachates:			
	<i>Lysimeter #17</i>		<i>Lysimeter #18</i>	
	1 st -year annual leachate	2 nd -year annual leachate	1 st -year annual leachate	2 nd -year annual leachate
Cl ⁻ [µg/L]	43000	<10000	44000	<10000
NO ₂ ⁻ [µg/L]	<100	<100	<100	<100
NO ₃ ⁻ [µg/L]	33300	28100	36400	31100
NH ₄ ⁺ [µg/L]	<500	<500	<500	<500
SO ₄ ²⁻ [µg/L]	92600	60800	99300	62500
pH	8.0	7.9	7.9	7.8
TOC [µg/L]	4000	4000	4000	5000
TRR [µg a. i. equiv./L]	2.24	0.22	2.57	0.26
Ratio TOC/TRR _{acidic}	1786	18182	1556	19231

The results of the determination of the radioactivity in soil monoliths from each lysimeter, expressed as the % of applied radioactivity – [%AR], are presented below in graphical form on figure B.8.1.3.3._CA-22 (for the Lysimeter #17 on the left hand-side graph, and for the Lysimeter #18 on the right-hand-side graph). These results show that radioactivity in the soil monoliths was located predominantly in the top 20 cm and below 40-cm depth it accounted for less that 1.0% AR in each of the analysed soil layers.

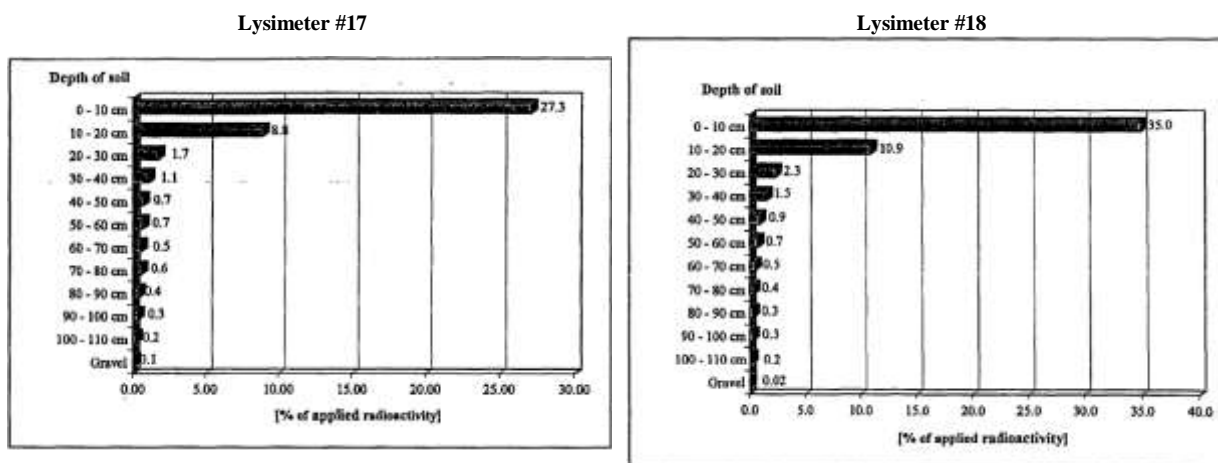


Figure B.8.1.3.3._CA-22: The graphical results of the determination radioactivity in soil monoliths from each lysimeter (copied from the study report).

The 10-cm soil layers sampled down to the depth of 40 cm were further analysed, using TLC for the individual compounds. That analysis enabled the identification and quantitation of the following compounds: Flufenacet, FOE Alcohol, FOE Oxalate and FOE Sulfonic acid. Its detailed results are presented in numerical form below in the table B.8.1.3.3._CA-26 and in graphical form on figure B.8.1.3.3._CA-23. It shall be indicated that in that experiment quite substantial amounts of FOE Alcohol were detected in soil, what stands in some contrast with the results of the examination of route and rate of degradation of Flufenacet in aerobic soil, where FOE Alcohol was demonstrated to be minor degradation product.

Table B.8.1.3.3._CA-26: The numerical results of the profiling of the 10-cm layers of the soil monoliths of the lysimeters sampled down to 40-cm depth.

Results obtained for the Lysimeter #17								
Soil layer [cm]	Amount of Flufenacet expressed in:		Amount of FOE Alcohol expressed in:		Amount of FOE Oxalate expressed in:		Amount of FOE Sulfonic acid expressed in:	
	[µg/soil layer]	[µg/kg soil, FW]	[µg/soil layer]	[µg/kg soil, FW]	[µg/soil layer]	[µg/kg soil, FW]	[µg/soil layer]	[µg/kg soil, FW]
0 – 10	264.65	2.68	44.34	0.33	21.26	0.16	<33.44	0.25
10 – 20	81.52	0.58	<12.99	0.09	<41.3	0.03	<8.83	0.06
20 – 30	<4.59	<0.03	<2.67	<0.02	<2.84	<0.02	<3.47	<0.02
30 – 40	<4.59	<0.03	<2.67	<0.02	<2.84	<0.02	<3.47	<0.02
Results obtained for the Lysimeter #18								
Soil layer [cm]	Amount of Flufenacet expressed in:		Amount of FOE Alcohol expressed in:		Amount of FOE Oxalate expressed in:		Amount of FOE Sulfonic acid expressed in:	
	[µg/soil layer]	[µg/kg soil, FW]	[µg/soil layer]	[µg/kg soil, FW]	[µg/soil layer]	[µg/kg soil, FW]	[µg/soil layer]	[µg/kg soil, FW]
0 – 10	449.54	2.94	66.62	0.44	<47.83	<0.31	<32.45	<0.21
10 – 20	70.98	0.41	<19.39	<0.11	<14.13	<0.08	<8.81	<0.05
20 – 30	<7.96	<0.05	<1.66	<0.01	<1.78	<0.01	<2.16	<0.01
30 – 40	<1.40	<0.01	<0.81	<0.005	<0.87	<0.005	<1.06	<0.01

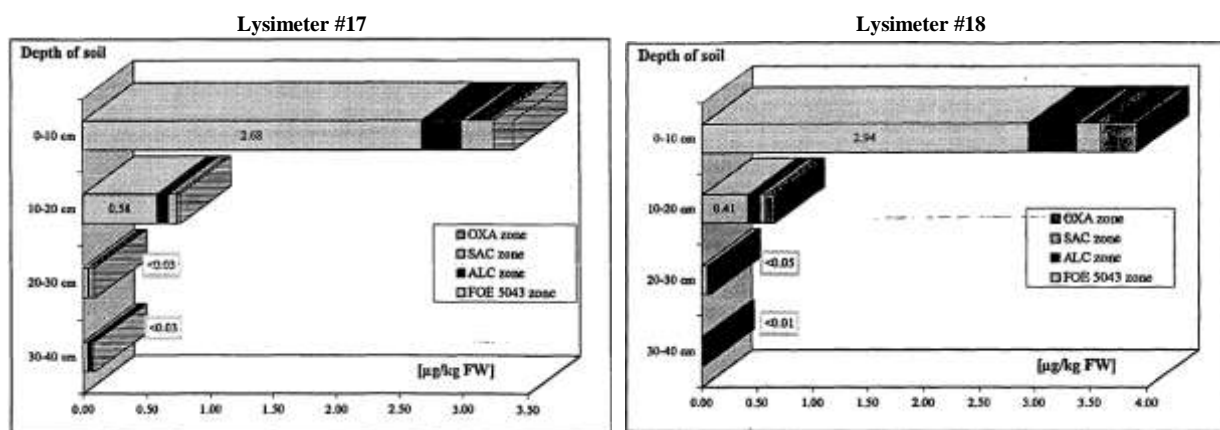


Figure B.8.1.3.3_CA-23: The graphical results of the profiling of the 10-cm layers of the soil monoliths of the lysimeters sampled down to 40-cm depth (copied from the study report).

The results of the analysis of three crops grown on each lysimeter are presented below in the table B.8.1.3.3_CA-27. These results show that the translocation and accumulation of the residues of Flufenacet in crops was not significant – below 1.0% AR.

Table B.8.1.3.3_CA-27: The results of the analysis of the crops grown on Lysimeters

Lysimeter	Crop	Plant material collected	Yield [dt/ha]	Weight of collected plant material		Radioactivity recovered, expressed as:	
				Fresh weight (FW) [kg]	Dry weight (DW) [g]	[µg a. i. equiv./kg FW]	% applied
#17	1 st year crop – fodder maize	Silage material	868	8.682	4175	29.05	0.524
	2 nd year crop – Winter wheat	Kernels	77	0.769	687	20.27	0.02
		Straw and huls	82	0.817	702	130.63	0.15
	Succeeding crop – sugar beet	Tubers	974	9.740	----	1.74	0.026
		Leaves	528	5.280	----	4.71	0.038
#18	1 st year crop – fodder maize	Silage material	911	9.114	2258	28.04	0.531
	2 nd year crop – Winter wheat	Kernels	74	0.739	637	22.05	0.02
		Straw and huls	81	0.807	720	172.47	0.21
	Succeeding crop – sugar beet	Tubers	928	9.280	----	1.32	0.019
		Leaves	537	5.370	----	5.83	0.048

Finally, on the basis of the obtained results was determined the mass balance for the applied radioactivity. The results of these calculations are presented below, on figure B.8.1.3.3_CA-24 showing the mass balance table provided in the study report. On the basis of these results it can be stated that in the experiment on Lysimeter #17 it was possible to recover 44.38% of the applied radioactivity, most of it – 42.33% AR in the soil monolith, 1.56% AR in leachates and the remaining amount – 0.48% AR, in plant material collected from the lysimeter. The lost radioactivity – 55.62% AR was attributed to the ¹⁴CO₂ and, possibly other volatile compounds formed in soil and then escaped to the air compartment, what indicates substantial level of mineralisation of the test compound.

In case of Lysimeter #18 it was possible to recover 55.18% of the applied radioactivity, most of it – 52.96% AR in the soil monolith, 1.72% AR in leachates and the remaining amount – 0.50% AR, in plant material collected from the lysimeter. The lost radioactivity – 44.82% AR was attributed to the ¹⁴CO₂ and, possibly other volatile compounds formed in soil and then escaped to the air compartment, what also indicates substantial level of mineralisation of the test compound.

It was not however explained why the proportions of the radioactivity recovered from the system and that lost were reversed in the Lysimeter #18 in comparison to Lysimeter #17, bearing in mind that the experimental conditions were the same for both lysimeters and other obtained results were quite similar.

Matrix	Lysimeter #17		Lysimeter #18	
	[kBq]	[% applied]*)	[kBq]	[% applied]*)
Harvested crops				
1 st (maize):	504.5	0.38; 0.52§)	511.1	0.39; 0.53§)
2 nd (winter wheat)				
kernels:	31.2	0.02	32.6	0.03
10% straw&hulls:	21.3	0.02	27.8	0.02
3 rd (sugar beet)				
tubers:	33.9	0.03	24.5	0.02
leaves:	49.7	0.04	62.6	0.05
Crops total:	641	0.48	659	0.50
Soil monolith	56,006	42.33	70,080	52.96
Leachates:	2,070	1.56	2,276	1.72
Total:	58,717	44.38	73,015	55.18
Loss (e.g. ¹⁴CO₂):	73,600	55.62	59,302	44.82

*) values in % of total RA application on each lysimeter (100% = 132,317 kBq)
§) values in % of 1st RA application on each lysimeter (100% = 96,273 kBq)

Figure B.8.1.3.3._CA-24 The results of the determination of mass balance, as presented in the study (table copied from the study report)

Conclusions:

The results of the examination of the leaching behaviour of Flufenacet through two undisturbed soil profiles (two lysimeters filled with soil monoliths consisting of Sandy loam-Loamy sand soil, having pH in range 6.05 – 6.63 and OC content in the top 30-cm layer of 1.41%) during three consecutive years showed that:

- in case of Lysimeter #17 44.38% of radioactivity applied as [¹⁴C]-Flufenacet was recovered, of which 42.33% AR in soil monolith, 1.56% AR in leachates and 0.48% in collected plant material; the lost 55.62% AR was attributed to the ¹⁴CO₂ formed in soil and escaped from there, hence it was stated that such would be the level of the total mineralisation of the test compound;
- in case of Lysimeter #18 55.18% of radioactivity applied as [¹⁴C]-Flufenacet was recovered, of which 52.96% AR in soil monolith, 1.72% AR in leachates and 0.50% in collected plant material; the lost 44.82% AR was attributed to the ¹⁴CO₂ formed in soil and escaped from there, hence it was stated that such would be the level of the total mineralisation of the test compound.

In case of the Lysimeter #18

Of the radioactivity recovered within Lysimeter #17 in leachates – 1.56% AR in total, 1.436% AR was recovered in the 1st year annual leachate, 0.122% AR in the 2nd year annual leachate and only 0.006% AR in 3rd year annual leachate. That corresponded to:

- in the 1st year annual leachate to 2.380 [µg a. i. equivalent/L] total (alkaline) TRR (TRR = Total Radioactivity Recovered), of which 5.31% was ¹⁴CO₂-associated radioactivity, and to 2.26 [µg a. i. equivalent/L] acidic TRR subsequently profiled using TLC;
- in the 2nd year annual leachate to 0.221 [µg a. i. equivalent/L] total (alkaline) TRR (TRR = Total Radioactivity Recovered), of which 17.06% was ¹⁴CO₂-associated radioactivity, and to 0.19 [µg a. i. equivalent/L] acidic TRR subsequently profiled using TLC;
- in the 3rd year annual leachate to 0.239 [µg a. i. equivalent/L] total (alkaline) TRR (TRR = Total Radioactivity Recovered), of which 35.22% was ¹⁴CO₂-associated radioactivity, and to 0.15 [µg a. i. equivalent/L] acidic TRR not profiled;
- on average in annual leachate to 1.310 [µg a. i. equivalent/L] total (alkaline) TRR (TRR = Total Radioactivity Recovered), of which 6.28% was ¹⁴CO₂-associated radioactivity, and to 1.25 [µg a. i. equivalent/L] acidic TRR.

Of the radioactivity recovered within Lysimeter #18 in leachates – 1.72% AR in total, 1.563% AR was recovered in the 1st year annual leachate, 0.150% AR in the 2nd year annual leachate and only 0.007% AR in 3rd year annual leachate. That corresponded to:

- in the 1st year annual leachate to 2.699 [µg a. i. equivalent/L] total (alkaline) TRR (TRR = Total Radioactivity Recovered), of which 5.35% was ¹⁴CO₂-associated radioactivity, and to 2.56 [µg a. i. equivalent/L] acidic TRR subsequently profiled using TLC;
- in the 2nd year annual leachate to 0.269 [µg a. i. equivalent/L] total (alkaline) TRR (TRR = Total Radioactivity Recovered), of which 23.02% was ¹⁴CO₂-associated radioactivity, and to 0.22 [µg a. i. equivalent/L] acidic TRR subsequently profiled using TLC;
- in the 3rd year annual leachate to 0.238 [µg a. i. equivalent/L] total (alkaline) TRR (TRR = Total Radioactivity Recovered), of which 40.88% was ¹⁴CO₂-associated radioactivity, and to 0.14 [µg a. i. equivalent/L] acidic TRR not profiled;
- on average in annual leachate to 1.492 [µg a. i. equivalent/L] total (alkaline) TRR (TRR = Total Radioactivity Recovered), of which 6.85% was ¹⁴CO₂-associated radioactivity, and to 1.38 [µg a. i. equivalent/L] acidic TRR.

The TLC profiling of the leachates (acidic TRR) led to the identification of its following constituents: Flufenacet, FOE Alcohol, FOE Oxalate, FOE Sulfonic acid and FOE Thioglycolate sulfoxide (FOE TGS). The quantitative analysis gave the following results:

- for Lysimeter #17:
 - the 1st year annual leachate contained 0.004 [µg/L] of Flufenacet, 0.034 [µg/L] of FOE Alcohol, 0.017 [µg/L] of FOE Oxalate, 1.355 [µg/L] of FOE Sulfonic acid, 0.030 [µg/L] of FOE TGS and 0.035 [µg a. i. equivalent/L] of the “Unknown” fraction;
 - the 2nd year annual leachate contained 0.002 [µg/L] of Flufenacet, 0.001 [µg/L] of FOE Alcohol, 0.009 [µg/L] of FOE Oxalate, 0.013 [µg/L] of FOE Sulfonic acid, 0.022 [µg/L] of FOE TGS and 0.007 [µg a. i. equivalent/L] of the “Unknown” fraction;
 - the 3rd year leachate was not profiled.
- for Lysimeter #18
 - the 1st year annual leachate contained 0.005 [µg/L] of Flufenacet, 0.016 [µg/L] of FOE Alcohol, 0.006 [µg/L] of FOE Oxalate, 1.616 [µg/L] of FOE Sulfonic acid, 0.027 [µg/L] of FOE TGS and 0.045 [µg a. i. equivalent/L] of the “Unknown” fraction;
 - the 2nd year annual leachate contained 0.005 [µg/L] of Flufenacet, 0.004 [µg/L] of FOE Alcohol, 0.006 [µg/L] of FOE Oxalate, 0.016 [µg/L] of FOE Sulfonic acid, 0.019 [µg/L] of FOE TGS and 0.008 [µg a. i. equivalent/L] of the “Unknown” fraction;
 - the 3rd year leachate was not profiled.

The radioactivity determined in the soil monoliths was on the level:

- for Lysimeter #17: 42.33% AR, of which 37.80% AR in the top 30 cm, 2.46% AR in the next 30-60cm layer and the remaining ~2.00% AR below that depth, the content of radioactivity decreased with depth being highest – 27.26% AR in the top 10-cm section, and below 40 cm not surpassing 1% AR in any of the 10-cm sections;
- for Lysimeter #18: 52.96% AR, of which ~48.2% AR in the top 30 cm, ~3.1% AR in the next 30-60cm layer and the remaining ~1.7% AR below that depth, the content of radioactivity decreased with depth being highest - ~35% AR in the top 10-cm section, and below 40 cm not surpassing 1% AR in any of the 10-cm sections.

The profiling of radioactivity in soil extracts from samples taken from 0-30 cm layer resulted in identification of four compounds: Flufenacet, FOE Alcohol, FOE Oxalate and FOE Sulfonic acid. The RMS calculated their concentrations in that layer using the sumarily weight of soil (Fresh Weight, further denominated FW) within that layer, being 418.40 kg for Lysimeter #17 and 498.71 kg for Lysimeter #18.

The determined amounts and corresponding concentrations of the identified compound were following:

- for Lysimeter #17: content of Flufenacet was 450.75 µg and its concentration 1.07 [µg/kg soil FW], content of FOE Alcohol was 60.09 µg and its concentration 0.14 [µg/kg soil FW], content of FOE Oxalate was 28.23 µg and its concentration 0.07 [µg/kg soil FW], content of FOE Sulfonic acid was 45.74 µg and its concentration 0.11 [µg/kg soil FW];
- for Lysimeter #18: content of Flufenacet was 528.48 µg and its concentration 1.06 [µg/kg soil FW], content of FOE Alcohol was 87.67 µg and its concentration 0.18 [µg/kg soil FW], content of FOE Oxalate was 63.74 µg and its concentration 0.13 [µg/kg soil FW], content of FOE Sulfonic acid was 43.42 µg and its concentration 0.09 [µg/kg soil FW].

It may be stated that of all the compounds possible to be identified as originating from Flufenacet radiolabelled in fluorophenyl ring (including Flufenacet itself) only FOE Sulfonic acid was demonstrated to be found in leachates in amounts > 0.1 µg/L, although only in the 1st-year leachates (individual and annual) and not in the 2nd-year one, what confirmed the risk to GW associated to that degradation product demonstrated in GW model exposure assessment (for details please refer to the results of calculations presented under the point B.8.5 in the Vol. 3-CP, B.8 of this Renewal Assessment Report).

Neither Flufenacet nor the second major soil degradation product relevant for that radiolabelling position – FOE Oxalate, were detected in leachates in amounts > 0.1 µg/L, what may indicate that they would not pose a threat to the GW compartment.

In soil and leachates FOE Alcohol was detected – the compound determined in the studies examining the route of degradation of Flufenacet in aerobic soil to be minor/transient and therefore not taken into account in the GW model exposure assessment. It shall be indicated however that the would-be risk it may pose to the GW compartment was covered by the calculations carried out for FOE Oxalate – its immediate degradate.

Also detected in leachates was FOE Thioglycolate sulfoxide (FOE TGS), the compound not taken in the model GW exposure assessment into consideration, being identified as minor soil degradation product. It shall be indicated however, that in the study it was determined in leachates in amounts <0.1 µg/L, what may indicate that it would not pose a serious threat to the GW compartment.

Finally, it shall be indicated that, due to the fact that in the study was used Flufenacet radiolabelled only in the fluorophenyl ring, the study gave no information of the laching potential of the degradation products formed from the second moiety present within the molecule of Flufenacet – thiadiazole.

The comparative analysis of the application pattern (crops, application timing and application rates) used in the study and the EU-representative application pattern proposed for the current authorisation of Flufenacet in the EU showed that the study may be considered as providing supplementary information with regard to the risk posed by Flufenacet and its soil degradation products to the GW compartment, but for the purpose of the decision making should be considered with care.

Study 2a:

Report: Report: Hellpointner E., (1995): “Lysimeter study on the translocation of *FOE 5043* into the subsoil after use as pre-emergence herbicide in a maize/winter wheat crop rotation. 1st year of study.”; Bayer AG, Agrochemical Division, Development, Institute for Metabolism Research and Residue analysis; D-51368 Leverkusen, Germany; report No. PF-4025 (107688); 09 January 1995; study reference number M-002194-01-1;

Guidelines: The study was performed to comply with the following Guidelines:

- BBA Guidelines for the Testing of Plant Protection Products in Registration Procedure, Part IV, 43- (February 1990) – “Lysimeter tests for the translocation of plant protection products into the subsoil.”.

GLP: Yes;

RMS comments: The study had been evaluated for the previous authorisation of Flufenacet in the EU, by its inclusion into the Annex I of the Directive 91/414/EEC. Its summary can be found under the point B.7.2.4.2., in section B.7 of the Annex B to the Monograph prepared by the RMS – France, for Flufenacet. RMS re-evaluated the study and found it acceptable. It was noticed however, that this is an interim report presenting a part of the results presented in summarised above, as **Study 2**, final report of the same study. RMS compared both reports and stated that they contained the same results, in case of this report limited however to one, 1st, year. Therefore it was not necessary to summarise this study and such summary was not provided in order not to overburden the Renewal Assessment Report. However the RMS used some of its parts, in particular some figures, in cases they were more clear/better looking than the analogical figures in the full report.

Summary:

The study report was not summarised because it contained the same data as summarised above, as **Study 2**, full-study report.

Study 3:

Report: Schäfer H., (2000): “Comparison of Results of Lysimeter Studies with PEC_{GW} Values Obtained with Simulation Model PESTLA.”; Bayer AG, Crop Protection Business Group, Institute for Metabolism Research and Residue Analysis, 51368 Leverkusen, Germany; report No. MR-378/00; 2000. 08. 14.; study reference number M-060287-01-1;

Guidelines: The study was not declared to be performed in line with any Guidelines. It was however declared to follow the procedures used the Dutch registration process.

GLP: No (modelling study);

RMS comments: This is a newly submitted study, not previously submitted for the evaluation of Flufenacet at the EU level. However, it was probably used to support the registration of the plant protection products containing Flufenacet in The Netherlands, because it contains several references to the Dutch registration process. RMS evaluated the study and stated that its utility in the EU-evaluation procedure is limited for the following reasons:

- the tool used in calculation was PESTLA ver 3.3, the tool not recommended by FOCUS;
- the pedo-climatic scenario used in calculations was the “Dutch standard scenario”, probably then representative for the local Dutch conditions, so of limited relevance for the EU as a whole;
- the application pattern used in calculations was not defined at all;
- of the substance-specific parameters used in calculations only the average DT_{50} and K_{OM} values were reported, and these changed as a result of the currently performed evaluation;

Therefore RMS stated that although some MS states may still find the report relevant for the purpose of their national registration, it cannot be considered such for the purpose of the renewal of authorisation in the EU. For that reason RMS decided not to summarise it in order not to overburden the Assessment Report. The report was also not included in the list of references relied upon nor its findings used in the List of Endpoints.

Summary:

Study was not summarised for the reasons listed above.

Lysimeter studies – a summary:

The leaching behaviour of Flufenacet and its degradation products through the undisturbed soil profiles under the agronomic and climatic conditions relevant for Germany was examined on four outdoor lysimeters. The results of that examination were presented in two study reports submitted by the Applicant for the purpose of the current evaluation. Additionally the Applicant submitted the interim reports of the same experiments, not summarised in the Renewal Assessment Report for Flufenacet, but analysed for their compliance with the adequate final reports. The third study submitted for evaluation was aimed on the validation of the lysimeter studies by comparing their results with those of the modelling exposure assessment carried out for the GW compartment. RMS however decided not to use it, as the modelling tools and scenarios were not those recommended by FOCUS.

The key data and results obtained in the two studies are summarily presented below in tables B.8.1.3.3._CA-28 – B.8.1.3.3._CA-28c. Additionally RMS decided to present the key results in the format recommended for reporting the data in the EU List of EndPoints.

Table B.8.1.3.3._CA-28: The key data and results obtained in the outdoor lysimeter studies.

Parameter				Data for Lysimeter			
				#15	#16	#17	#18
General information	Trial site	Test facility		Lysimeter station of Bayer AG	Lysimeter station of Bayer AG	Lysimeter station of Bayer AG	Lysimeter station of Bayer AG
		Location (town, region, country)		Monheim, NRW, Germany	Monheim, NRW, Germany	Monheim, NRW, Germany	Monheim, NRW, Germany
		Geographic coordinates	Longitude	6° 55' E	6° 55' E	6° 55' E	6° 55' E
			Latitude	51° 4' N	51° 4' N	51° 4' N	51° 4' N
	Long-term weather conditions at trial site (1996 – 1995)	Average rainfall [mm]	Annual	745	745	745	745
			Monthly min. (month)	42.7 (February)	42.7 (February)	42.7 (February)	42.7 (February)
			Monthly max. (month)	78.1 (June)	78.1 (June)	78.1 (June)	78.1 (June)
		Average annual relative air humidity [%]		73	73	73	73
		Average temperature at 2 metres above the ground [°C]	Annual	10.0	10.0	10.0	10.0
			Monthly min. (month)	2.6 (January)	2.6 (January)	2.6 (January)	2.6 (January)
			Monthly max. (month)	18.4 (June)	18.4 (June)	18.4 (June)	18.4 (June)
		Average annual wind velocity [m/s.]		2.5	2.5	2.5	2.5
		Average radiant heat [kJ/cm ²]	Annual	29.1	29.1	29.1	29.1
			Monthly min. (month)	5.8 (December)	5.8 (December)	5.8 (December)	5.8 (December)
			Monthly max. (month)	53.1 (July)	53.1 (July)	53.1 (July)	53.1 (July)
	Duration of the study	Preliminary period	Duration [years]	1	1	1	1
			Beginning	March 1992	March 1992	March 1992	March 1992
			End	May 1993	May 1993	May 1993	May 1993
		Experimental period	Duration [years]	3	3	2.5	2.5
			Beginning	May 1993	May 1993	May 1993	May 1993
Characterisation of lysimeter	Lysimeter depth	Total [cm]		135	135	120	120
		Soil monolith [cm]		130	130	115	115
		Gravel layer [cm]		5	5	5	5
		Soil type (FAO)		Eutric Cambisol	Eutric Cambisol	Eutric Cambisol	Eutric Cambisol
	Characteristic of soil monolith	Soil properties, depth 0 – 30 cm	Soil texture (USDA)	Sandy loam	Sandy loam	Sandy loam	Sandy loam
			pH (CaCl ₂)	7.04	7.04	7.04	7.04
			OC%	1.41	1.41	1.41	1.41
			CEC [meq/100g]	9.61	9.61	9.61	9.61
			Microbial biomass [mg/kg]	235	235	235	235
		Soil properties, depth 30 – 60 cm	Soil texture (USDA)	Sandy loam	Sandy loam	Sandy loam	Sandy loam
			pH (CaCl ₂)	7.24	7.24	7.24	7.24
			OC%	0.34	0.34	0.34	0.34
			CEC [meq/100g]	7.43	7.43	7.43	7.43
			Microbial biomass [mg/kg]	34	34	34	34
		Soil properties, depth 60 – 100 cm	Soil texture (USDA)	Loamy sand	Loamy sand	Loamy sand	Loamy sand
			pH (CaCl ₂)	7.18	7.18	7.18	7.18
			OC%	0.19	0.19	0.19	0.19
			CEC [meq/100g]	7.57	7.57	7.57	7.57
			Microbial biomass [mg/kg]	11	11	11	11
		Soil properties, depth 100 – 115 cm	Soil texture (USDA)	Loamy sand	Loamy sand	Loamy sand	Loamy sand
			pH (CaCl ₂)	7.46	7.46	7.46	7.46
			OC%	0.17	0.17	0.17	0.17
			CEC [meq/100g]	8.52	8.52	8.52	8.52
			Microbial biomass [mg/kg]	13	13	13	13
Maintenance data	Application of the test compound	Test compound		¹⁴ C-Flufenacet	¹⁴ C-Flufenacet	¹⁴ C-Flufenacet	¹⁴ C-Flufenacet
		Number of applications/ experiment		2	2	2	2
		1 st application	Year of experiment	1	1	1	1
			Application date	12/05/1993	12/05/1993	13/05/1993	13/05/1993
			Application rate	48.14 mg/m ² (480 g/ha)	48.14 mg/m ² (480 g/ha)	48.14 mg/m ² (480 g/ha)	48.14 mg/m ² (480 g/ha)
		2 nd application	Year of experiment	2	2	1	1
			Application date	05/05/1994	05/05/1994	03/11/1993	03/11/1993
			Application rate	48.04 mg/m ² (480 g/ha)	48.04 mg/m ² (480 g/ha)	18.02 mg/m ² (180 g/ha)	18.02 mg/m ² (180 g/ha)

Table B.8.1.3.3._CA-28a: The key data and results obtained in the outdoor lysimeter studies (continued).

Parameter				Data for Lysimeter			
				#15	#16	#17	#18
Maintenance data, continued	Crop data	1 st crop, target	Crop	Maize, grain	Maize, grain	Maize, fodder	Maize, fodder
			Year of experiment	1	1	1	1
			Date of sowing	10/05/1993	10/05/1993	10/05/1993	10/05/1993
			Date of harvest	12/11/1993	12/11/1993	28/09/1993	28/09/1993
			Harvested parts	Corncoobs	Corncoobs	Silage material	Silage material
		2 nd crop, target	Crop	Maize, grain	Maize, grain	Winter wheat	Winter wheat
			Year of experiment	2	2	1 – 2	1 – 2
			Date of sowing	05/05/1994	05/05/1994	02/11/1993	02/11/1993
			Date of harvest	10/05/1994	10/05/1994	03/08/1994	03/08/1994
			Harvested parts	Corncoobs	Corncoobs	Grain and straw	Grain and straw
		3 rd crop, succeeding	Crop	Sugar beet	Sugar beet	Sugar beet	Sugar beet
			Year of experiment	3	3	3	3
			Date of sowing	13/04/1995	13/04/1995	13/04/1995	13/04/1995
			Date of harvest	07/11/1995	07/11/1995	07/11/1995	07/11/1995
			Harvested parts	Leaves and tubers	Leaves and tubers	Leaves and tubers	Leaves and tubers
	Irrigation and precipitation during experiment	1 st year	Precipitation [mm]	897.1	897.1	897.1	897.1
			Irrigation [mm]	46.0	46.0	51.0	51.0
			Sum [mm]	943.1	943.1	948.1	948.1
		2 nd year	Precipitation [mm]	814.2	814.2	813.9	813.9
			Irrigation [mm]	100.0	100.0	75.0	75.0
			Sum [mm]	914.2	914.2	888.9	888.9
		3 rd year	Precipitation [mm]	496.1	496.1	338.0	338.0
			Irrigation [mm]	104.0	104.0	104.0	104.0
			Sum [mm]	600.1	600.1	442.0	442.0
		Total	Precipitation [mm]	2207.5	2207.5	2049.0	2049.0
			Irrigation [mm]	250	250	250	250
			Sum [mm]	2457	2457	2279.0	2279.0
Radioactivity - recovery	Radioactivity recovered [% AR]	in soil monolith	0- 30 cm	40.289	41.414	37.80	~48.2
			30 – 60 cm	2.095	3.128	2.46	~3.1
			below 60 cm	0.777	0.485	~2.00	~1.7
			total	43.16	45.03	42.33	52.96
		in leachates	1 st year	0.772	0.815	1.436	1.563
			2 nd year	0.250	0.161	0.122	0.150
			3 rd year	0.006	0.006	0.006	0.007
			total	0.64	0.58	~1.56	~1.72
		in crops	1 st crop	0.014	0.015	0.38	0.39
			2 nd crop	0.016	0.014	0.04	0.05
			3 rd crop	0.059	0.061	0.07	0.07
			total	0.08	0.08	0.48	0.50
		Total recovered		43.89	45.68	44.38	55.18
		Lost (eg as ¹⁴ CO ₂) [% AR]		56.11	54.32	55.62	44.82
Radioactivity in soil monoliths	in 0 – 30 cm layer	Total [% AR]		40.29	41.41	37.80	48.2
		identified as Flufenacet	[µg/layer]	1860.96	1839.68	450.75	528.48
		identified as FOE Alcohol	[µg/kg soil FW]	3.91	3.91	1.07	1.06
		identified as FOE Oxalate	[µg/layer]	143.49	159.02	60.09	87.67
		identified as FOE Sulfonic acid	[µg/kg soil FW]	0.30	0.34	0.14	0.18
		identified as FOE Oxalate	[µg/layer]	212.84	167.72	28.23	63.74
		Identified as FOE Sulfonic acid	[µg/kg soil FW]	0.45	0.36	0.07	0.13
		Identified as FOE Sulfonic acid	[µg/layer]	71.44	138.39	45.74	43.42
		Identified as FOE Sulfonic acid	[µg/kg soil FW]	0.15	0.29	0.11	0.09
	in 30 – 60 cm layer	Total [% AR]		2.095	3.128	2.46	3.1
Detailed characterisation of leachates	1 st year early leachate	Collection time	Week of experiment	24	24	24	24
			Collection date	29/10/1993	29/10/1993	29/10/1993	29/10/1993
		Volume of leachate [L]		3.7	4.7	8.2	8.2
		Characterisation of TRR – Total Radioactivity Recovered	Total TRR [µg a. i. equival./L]	0.256	0.221	0.588	0.505
			acidic TRR [µg a. i. equival./L]	0.218	0.183	0.539	0.477
			¹⁴ CO ₂ -associated radioactivity [% total TRR]	14.87	17.23	8.34	5.64
		Characterisation of acidic TRR ¹⁾	Flufenacet [µg /L]	<0.011	<0.014	0.006	<0.005
			FOE ALC [µg /L]	<0.001	0.006	0.002	0.095
			FOE OXA [µg /L]	0.002	0.007	<0.001	0.005
			FOE SA [µg /L]	0.065	0.025	0.225	0.182
			FOE TGS [µg /L]	0.017	0.009	0.015	0.027

Footnotes to the table:

1) Abbreviations used: FOE ALC – FOE Alcohol, FOE OXA – FOE Oxalate, FOE SA – FOE Sulfonic acid, FOE TGS – FOE Thioglycolate sulfoxide.

Table B.8.1.3.3._CA-28b: The key data and results obtained in the outdoor lysimeter studies (continued).

Parameter				Data for Lysimeter			
				#15	#16	#17	#18
Detailed characterisation of leachates - continued	1 st year leachate with max. TRR	Collection time	Week of experiment	37	35	38	38
			Collection date	28/01/1994	12/01/1994	04/02/1994	04/02/1994
		Volume of leachate [L]		17.2	21.5	21.3	21.3
		Characterisation of TRR – Total Radioactivity Recovered	Total TRR [µg a. i. equivalent/L]	2.350	1.989	5.106	5.455
			acidic TRR [µg a. i. equivalent/L]	2.228	1.915	4.940	5.255
			¹⁴ C ₂ -associated radioactivity [% total TRR]	5.19	3.72	4.26	3.58
		Characterisation of acidic TRR ¹⁾	Flufenacet [µg /L]	≤0.007	<0.017	<0.011	<0.001
			FOE ALC [µg /L]	0.001	0.004	0.006	0.044
			FOE OXA [µg /L]	0.007	0.041	0.005	0.036
			FOE SA [µg /L]	1.293	1.090	3.375	3.682
			FOE TGS [µg /L]	0.079	0.036	0.017	0.028
	1 st year late leachate	Collection time	Week of experiment	47	47	47	47
			Collection date	11/04/1994	11/04/1994	11/04/1994	11/04/1994
		Volume of leachate [L]		11.5	15.5	19.4	15.0
		Characterisation of TRR – Total Radioactivity Recovered	Total TRR [µg a. i. equivalent/L]	0.850	0.798	2.545	3.102
			acidic TRR [µg a. i. equivalent/L]	0.767	0.732	1.389	2.916
			¹⁴ C ₂ -associated radioactivity [% total TRR]	9.82	8.27	6.13	6.00
		Characterisation of acidic TRR ¹⁾	Flufenacet [µg /L]	<0.035	0.005	0.002	0.002
			FOE ALC [µg /L]	0.001	<0.001	0.008	0.041
			FOE OXA [µg /L]	0.012	0.031	0.026	0.017
			FOE SA [µg /L]	0.332	0.301	1.302	1.920
			FOE TGS [µg /L]	0.014	0.010	0.005	0.012
	1 st year annual leachate (pooled)	Collection time	Week of experiment	50	50	50	50
			Collection date	29/04/1994	29/04/1994	29/04/1994	29/04/1994
		Volume of leachate [L]		349.8	402.4	399.1	383.1
		Characterisation of TRR – Total Radioactivity Recovered	Total TRR [µg a. i. equivalent/L]	1.062	0.931	2.380	2.699
			acidic TRR [µg a. i. equivalent/L]	0.99	0.87	2.26	2.56
			¹⁴ C ₂ -associated radioactivity [% total TRR]	6.47	6.82	5.31	5.35
		Characterisation of acidic TRR ¹⁾	Flufenacet [µg /L]	0.020	0.033	0.004	0.005
			FOE ALC [µg /L]	<0.002	0.000	0.034	0.016
			FOE OXA [µg /L]	0.015	0.004	0.017	0.006
			FOE SA [µg /L]	0.589	0.489	1.355	1.616
			FOE TGS [µg /L]	0.016	0.014	0.030	0.027
	2 nd year annual leachate (pooled)	Collection time	Week of experiment	103	103	103	103
			Collection date	05/05/1995	05/05/1995	05/05/1995	05/05/1995
		Volume of leachate [L]		317.6	299.9	365.4	368.9
		Characterisation of TRR – Total Radioactivity Recovered	Total TRR [µg a. i. equivalent/L]	0.758	0.516	0.221	0.269
			acidic TRR [µg a. i. equivalent/L]	0.670	0.46	0.19	0.22
			¹⁴ C ₂ -associated radioactivity [% total TRR]	11.10	11.19	17.06	23.02
		Characterisation of acidic TRR ¹⁾	Flufenacet [µg /L]	0.003	0.003	0.002	0.005
			FOE ALC [µg /L]	0.003	0.005	0.001	0.004
			FOE OXA [µg /L]	<0.018	<0.014	0.009	0.006
			FOE SA [µg /L]	0.235	0.149	0.013	0.016
			FOE TGS [µg /L]	0.020	0.015	0.022	0.019

Footnotes to the table:

1) Abbreviations used: FOE ALC – FOE Alcohol, FOE OXA – FOE Oxalate, FOE SA – FOE Sulfonic acid, FOE TGS – FOE Thioglycolate sulfoxide.

Table B.8.1.3.3._CA-28c: The key data and results obtained in the outdoor lysimeter studies (continued).

Parameter				Data for Lysimeter			
				#15	#16	#17	#18
Detailed characterisation of leachates - continued	3 rd year annual leachate (pooled)	Collection time	Week of experiment	115	115	115	115
			Collection date	26/07/1995	26/07/1995	26/07/1995	26/07/1995
		Volume of leachate [L]		13.0	17.0	17.5	19.1
		Characterisation of TRR – Total Radioactivity Recovered	Total TRR [µg a. i. equival./L]	0.432	0.353	0.239	0.238
			acidic TRR [µg a. i. equival./L]	0.334	0.23	0.15	0.14
			¹⁴ C ₂ -associated radioactivity [% total TRR]	22.80	34.56	35.22	40.88
		Characterisation of acidic TRR: compound/concentration [µg/L]		FOE SA ¹⁾ ≤ 0.25	FOE SA ¹⁾ ≤ 0.17	not performed	not performed
	Total leachate	Collection time	Weeks of experiment	115	115	115	115
			Collection dates: beginning/end	12/05/1993 26/07/1995	12/05/1993 26/07/1995	12/05/1993 26/07/1995	12/05/1993 26/07/1995
		Volume of leachate [L] (total)		680.4	719.3	782.0	771.1
		Characterisation of TRR – Total Radioactivity Recovered; average values	Total TRR [µg a. i. equival./L]	0.906	0.742	1.310	1.492
			acidic TRR [µg a. i. equival./L]	0.83	0.68	1.25	1.38
			¹⁴ C ₂ -associated radioactivity [% total TRR]	8.42	8.39	6.28	6.85

Footnotes to the table:

1) Abbreviations used: FOE SA – FOE Sulfonic acid.

It may be stated that of all the compounds possible to be identified as originating from Flufenacet radiolabelled in fluorophenyl ring (including Flufenacet itself) only FOE Sulfonic acid was demonstrated to be found in leachates in amounts > 0.1 µg/L, what conformed the risk to GW associated to that degradation product demonstrated in GW model exposure assessment (for details please refer to the results of calculations presented under the point B.8.5 in the Vol. 3-CP, B.8 of this Renewal Assessment Report).

Neither Flufenacet nor the second major soil degradation product relevant for that radiolabelling position – FOE Oxalate, were detected in leachates in amounts > 0.1 µg/L, what may indicate that they would not pose a threat to the GW compartment.

In soil and leachates FOE Alcohol was detected – the compound determined in the studies examining the route of degradation of Flufenacet in aerobic soil to be minor/transient and therefore not taken into account in the GW model exposure assessment. It shall be indicated however that the would-be risk it may pose to the GW compartment was covered by the calculations carried out for FOE Oxalate – its immediate degradate.

Also detected in leachates was FOE Thioglycolate sulfoxide (FOE TGS), the compound not taken in the model GW exposure assessment into consideration, being identified as minor soil degradation product. It shall be indicated however, that in the study it was determined in leachates in amounts <0.1 µg/L, what may indicate that it would not pose a serious threat to the GW compartment.

Finally, it shall be indicated that, due to the fact that in the experiments was used Flufenacet radiolabelled only in the fluorophenyl ring, they gave no information of the laching potential of the degradation products formed from the second moiety present within the molecule of Flufenacet – thiadiazole.

The comparative analysis of the application pattern (crops, application timing and application rates) used in the experiments and the EU-representative application pattern proposed for the current authorisation of Flufenacet in the EU showed that they may be considered as providing supplementary information with regard to the risk posed by Flufenacet and its soil degradation products to the GW compartment, but for the purpose of the decision making should be considered with care.

Lysimeter / field leaching studies (Regulation (EU) N° 283/2013, Annex Part A, points 7.1.4.2 / 7.1.4.3 and Regulation (EU) N° 284/2013, Annex Part A, points 9.1.2.2 / 9.1.2.3)

Lysimeter/ field leaching studies *Lysimeter #15*

Location: *Experimental lysimeter farm of BAYER AG, Monheim NRW, Germany; 51° 4' N, 6°55' E;*

Study type (e.g. lysimeter, field): *outdoor lysimeter*

Soil properties: *topsoil layer 0 – 30 cm texture: Sandy loam, pH = 7.04, OC= 1.41%, WHC = 32.45 [vol % H₂O] – Field Capacity*

Dates of application : *10/05/1993 – 1st application; 05/05/1994 – 2nd application;*

Crop : */Interception estimated: Grain maize (corn) – 1st, target crop, CI = 0%; Grain maize (corn) – 2nd, target crop, CI = 0%; Sugar beet, 3rd, succeeding, crop, CI not required;*

Number of applications: **2 years (+ one without application), 1 application per year**

Duration. *3 years*

Application rate: **480 g/ha – 1st and 2nd application**

Average annual rainfall (mm): **745 mm** (*long-term value covering period 1966–1995*); *1st experimental year precipitation (rainfall + irrigation): 943.1 mm, 2nd experimental year precipitation (rainfall + irrigation): 914.2 mm, 3rd experimental year precipitation (rainfall + irrigation): 600.1 mm; total: 2457 mm*

Average annual leachate volume (mm): *Volume of leachate collected (total): 1st experimental year: 349.8 L, 2nd experimental year: 317.6 L, 3rd experimental year: 13.0 L, total volume collected: 680.4 L*

% radioactivity in leachate (maximum/year): *1st experimental year: 0.772% AR, 2nd experimental year: 0.250% AR, 3rd experimental year: 0.006% AR, total: 0.64% AR*

Individual annual maximum concentrations (e.g. 1st, 2nd, 3rd yr): *1st experimental year (leachate collected on week 37): total TRR 2.350 [µg a. i. equivalents/L], acidic TRR 2.228 [µg a. i. equivalents/L], ¹⁴CO₂-associated radioactivity 5.19 [% total TRR], Flufenacet ≤0.007 [µg/L], FOE Alcohol 0.001 [µg/L], FOE Oxalate 0.007 [µg/L], FOE Sulfonic acid 1.293 [µg/L], FOE Thioglycolate sulfoxide 0.079 [µg/L] Unidentified radioactivity, no of components: 1, 0.052 µg/L parent equivalents.*

Individual annual average concentrations (e.g. 1st, 2nd, 3rd yr): *1st experimental year annual leachate: total TRR 1.062 [µg a. i. equivalents/L], acidic TRR 0.99 [µg a. i. equivalents/L], ¹⁴CO₂-associated radioactivity 6.47 [% total TRR], Flufenacet 0.020 [µg/L], FOE Alcohol <0.002 [µg/L], FOE Oxalate 0.015 [µg/L], FOE Sulfonic acid 0.589 [µg/L], FOE Thioglycolate sulfoxide 0.016 [µg/L] Unidentified radioactivity, no of components: 1, 0.030 µg/L parent equivalents.*

2nd experimental year annual leachate: total TRR 0.758 [µg a. i. equivalents/L], acidic TRR 0.670 [µg a. i. equivalents/L], ¹⁴CO₂-associated radioactivity 11.10 [% total TRR], Flufenacet 0.003 [µg/L], FOE Alcohol 0.003 [µg/L], FOE Oxalate <0.018 [µg/L], FOE Sulfonic acid 0.235 [µg/L], FOE Thioglycolate sulfoxide 0.020 [µg/L] Unidentified radioactivity, no of components: 1, 0.037 µg/L parent equivalents.

3rd experimental year annual leachate: total TRR 0.432 [µg a. i. equivalents/L], acidic TRR 0.334 [µg a. i. equivalents/L], ¹⁴CO₂-associated radioactivity 22.80 [% total TRR], FOE Sulfonic acid ≤0.25 [µg/L], Unidentified radioactivity: no data.

average annual leachate: total TRR 0.906 [µg a. i. equivalents/L], acidic TRR 0.83 [µg a. i. equivalents/L], ¹⁴CO₂-associated radioactivity 8.42 [% total TRR],

Amount of radioactivity in the soils at the end of the study = *total 43.16 % AR, in top 0-30cm layer 40.289% AR, in 30-60 cm layer 2.095% AR, below 60 cm 0.777% AR, identified in the top 30-cm layer: Flufenacet 1860.96 [µg] (concentration 3.91 [µg/kg]), FOE Alcohol 143.49 [µg] (concentration 0.30 [µg/kg]), FOE Oxalate 212.84 [µg] (concentration 0.45 [µg/kg]), FOE*

Lysimeter/ field leaching studies *Lysimeter #16*

<p><i>Sulfonic acid</i> 71.44 [μg] (concentration 0.15 [$\mu\text{g}/\text{kg}$]).</p> <p>Location: <i>Experimental lysimeter farm of BAYER AG, Monheim NRW, Germany; 51° 4' N, 6°55' E;</i></p> <p>Study type (e.g. lysimeter, field): <i>outdoor lysimeter</i></p> <p>Soil properties: <i>topsoil layer 0 – 30 cm texture: Sandy loam, pH = 7.04, OC= 1.41%, WHC = 32.45 [vol % H₂O] – Field Capacity</i></p> <p>Dates of application : <i>10/05/1993 – 1st application; 05/05/1994 – 2nd application;</i></p> <p>Crop : /Interception estimated: <i>Grain maize (corn) – 1st, target crop, CI = 0%; Grain maize (corn) – 2nd, target crop, CI = 0%; Sugar beet, 3rd, succeeding, crop, CI not required;</i></p> <p>Number of applications: 2 years (+ one without application), 1 application per year</p> <p>Duration. <i>3 years</i></p> <p>Application rate: 480 g/ha – <i>1st and 2nd application</i></p> <p>Average annual rainfall (mm): 745 mm (<i>long-term value covering period 1966 – 1995</i>); <i>1st experimental year precipitation (rainfall + irrigation): 943.1 mm, 2nd experimental year precipitation (rainfall + irrigation): 914.2 mm, 3rd experimental year precipitation (rainfall + irrigation): 600.1 mm, total: 2457 mm</i></p> <p>Average annual leachate volume (mm): <i>Volume of leachate collected (total): 1st experimental year: 402.4 L, 2nd experimental year: 299.9 L, 3rd experimental year: 17.0 L, total volume collected: 719.3 L</i></p> <p>% radioactivity in leachate (maximum/year): <i>1st experimental year: 0.815% AR, 2nd experimental year: 0.161% AR, 3rd experimental year: 0.006% AR, total: 0.58% AR</i></p> <p>Individual annual maximum concentrations (e.g. 1st, 2nd, 3rd yr): <i>1st experimental year (leachate collected on week 35): total TRR 1.989 [μg a. i. equivalents/L], acidic TRR 1.915 [μg a. i. equivalents/L], ¹⁴CO₂-associated radioactivity 3.72 [% total TRR], Flufenacet <0.017 [$\mu\text{g}/\text{L}$], FOE Alcohol 0.004 [$\mu\text{g}/\text{L}$], FOE Oxalate 0.041 [$\mu\text{g}/\text{L}$], FOE Sulfonic acid 1.090 [$\mu\text{g}/\text{L}$], FOE Thioglycolate sulfoxide 0.036 [$\mu\text{g}/\text{L}$] Unidentified radioactivity, no of components: 1, 0.052 $\mu\text{g}/\text{L}$ parent equivalents.</i></p> <p>Individual annual average concentrations (e.g. 1st, 2nd, 3rd yr): <i>1st experimental year annual leachate: total TRR 0.931 [μg a. i. equivalents/L], acidic TRR 0.87 [μg a. i. equivalents/L], ¹⁴CO₂-associated radioactivity 6.82 [% total TRR], Flufenacet 0.033 [$\mu\text{g}/\text{L}$], FOE Alcohol 0.000 [$\mu\text{g}/\text{L}$], FOE Oxalate 0.004 [$\mu\text{g}/\text{L}$], FOE Sulfonic acid 0.489 [$\mu\text{g}/\text{L}$], FOE Thioglycolate sulfoxide 0.014 [$\mu\text{g}/\text{L}$] Unidentified radioactivity, no of components: 1, 0.033 $\mu\text{g}/\text{L}$ parent equivalents.</i></p> <p><i>2nd experimental year annual leachate: total TRR 0.516 [μg a. i. equivalents/L], acidic TRR 0.46 [μg a. i. equivalents/L], ¹⁴CO₂-associated radioactivity 11.19 [% total TRR], Flufenacet 0.003 [$\mu\text{g}/\text{L}$], FOE Alcohol 0.005 [$\mu\text{g}/\text{L}$], FOE Oxalate <0.014 [$\mu\text{g}/\text{L}$], FOE Sulfonic acid 0.149 [$\mu\text{g}/\text{L}$], FOE Thioglycolate sulfoxide 0.015 [$\mu\text{g}/\text{L}$] Unidentified radioactivity, no of components: 1, 0.041 $\mu\text{g}/\text{L}$ parent equivalents.</i></p> <p><i>3rd experimental year annual leachate: total TRR 0.353 [μg a. i. equivalents/L], acidic TRR 0.23 [μg a. i. equivalents/L], ¹⁴CO₂-associated radioactivity 34.56 [% total TRR], FOE Sulfonic acid ≤0.17 [$\mu\text{g}/\text{L}$], Unidentified radioactivity: no data.</i></p> <p><i>average annual leachate: total TRR 0.742 [μg a. i. equivalents/L], acidic TRR 0.68 [μg a. i. equivalents/L], ¹⁴CO₂-associated radioactivity 8.39 [% total TRR],</i></p> <p>Amount of radioactivity in the soils at the end of the study = <i>total 45.03 % AR, in top 0-30cm layer 41.414% AR, in 30-60 cm layer 3.128% AR, below 60 cm 0.485% AR, identified in the top 30-cm layer: Flufenacet 1839.68 [μg] (concentration 3.91 [$\mu\text{g}/\text{kg}$]), FOE Alcohol 159.02 [μg] (concentration 0.34 [$\mu\text{g}/\text{kg}$]), FOE Oxalate 167.72 [μg] (concentration 0.36 [$\mu\text{g}/\text{kg}$]), FOE Sulfonic acid 138.39 [μg] (concentration 0.29 [$\mu\text{g}/\text{kg}$]).</i></p> <p>Location: <i>Experimental lysimeter farm of BAYER AG, Monheim</i></p>
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Lysimeter/ field leaching studies *Lysimeter #17*

NRW, Germany; 51° 4' N, 6° 55' E;

Study type (e.g. lysimeter, field): *outdoor lysimeter*

Soil properties: *topsoil layer 0 – 30 cm texture: Sandy loam, pH = 7.04, OC= 1.41%, WHC = 32.45 [vol % H₂O] – Field Capacity*

Dates of application : *13/05/1993 – 1st application; 03/11/1993 – 2nd application;*

Crop : /Interception estimated: *Fodder maize (for silage) – 1st, target crop, CI = 0%; Winter wheat (corn) – 2nd, target crop, CI = 0%; Sugar beet, 3rd, succeeding, crop, CI not required;*

Number of applications: **1** year (+ 1.5 without application), **2** applications per year

Duration. *2.5 years*

Application rate: **480** g/ha – *1st application, 180 g/ha – 2nd application,*

Average annual rainfall (mm): **745** mm (*long-term value covering period 1966 – 1995; 1st experimental year precipitation (rainfall + irrigation): 948.1 mm, 2nd experimental year precipitation (rainfall + irrigation): 888.9 mm, 3rd experimental year precipitation (rainfall + irrigation): 442.0 mm, total: 2279 mm*

Average annual leachate volume (mm): *Volume of leachate collected (total): 1st experimental year: 399.1 L, 2nd experimental year: 365.4 L, 3rd experimental year: 17.5 L, total volume collected: 782.0 L*

% radioactivity in leachate (maximum/year): *1st experimental year: 1.436% AR, 2nd experimental year: 0.122% AR, 3rd experimental year: 0.006% AR, total: 1.56% AR*

Individual annual maximum concentrations (e.g. 1st, 2nd, 3rd yr): *1st experimental year (leachate collected on week 38): total TRR 5.106 [µg a. i. equivalents/L], acidic TRR 4.940 [µg a. i. equivalents/L], ¹⁴CO₂-associated radioactivity 4.26 [% total TRR], Flufenacet <0.011 [µg/L], FOE Alcohol 0.006 [µg/L], FOE Oxalate 0.005 [µg/L], FOE Sulfonic acid 3.375 [µg/L], FOE Thioglycolate sulfoxide 0.017 [µg/L] Unidentified radioactivity, no of components: 1, 0.065 µg/L parent equivalents.*

Individual annual average concentrations (e.g. 1st, 2nd, 3rd yr): *1st experimental year annual leachate: total TRR 2.380 [µg a. i. equivalents/L], acidic TRR 2.26 [µg a. i. equivalents/L], ¹⁴CO₂-associated radioactivity 5.31 [% total TRR], Flufenacet 0.004 [µg/L], FOE Alcohol 0.034 [µg/L], FOE Oxalate 0.017 [µg/L], FOE Sulfonic acid 1.355 [µg/L], FOE Thioglycolate sulfoxide 0.030 [µg/L] Unidentified radioactivity, no of components: 1, 0.080 µg/L parent equivalents.*

2nd experimental year annual leachate: total TRR 0.221 [µg a. i. equivalents/L], acidic TRR 0.19 [µg a. i. equivalents/L], ¹⁴CO₂-associated radioactivity 17.06 [% total TRR], Flufenacet 0.002 [µg/L], FOE Alcohol 0.001 [µg/L], FOE Oxalate 0.009 [µg/L], FOE Sulfonic acid 0.013 [µg/L], FOE Thioglycolate sulfoxide 0.022 [µg/L] Unidentified radioactivity, no of components: 1, 0.035 µg/L parent equivalents.

3rd experimental year annual leachate: total TRR 0.239 [µg a. i. equivalents/L], acidic TRR 0.15 [µg a. i. equivalents/L], ¹⁴CO₂-associated radioactivity 35.22 [% total TRR], acidic TRR not profiled, Unidentified radioactivity: no data.

average annual leachate: total TRR 1.310 [µg a. i. equivalents/L], acidic TRR 1.25 [µg a. i. equivalents/L], ¹⁴CO₂-associated radioactivity 6.28 [% total TRR],

Amount of radioactivity in the soils at the end of the study = *total 42.33 % AR, in top 0-30cm layer 37.80% AR, in 30-60 cm layer 2.46% AR, below 60 cm 2.00% AR, identified in the top 30-cm layer: Flufenacet 450.75 [µg] (concentration 1.07 [µg/kg]), FOE Alcohol 60.09 [µg] (concentration 0.14 [µg/kg]), FOE Oxalate 28.23 [µg] (concentration 0.07 [µg/kg]), FOE Sulfonic acid 45.74 [µg] (concentration 0.11 [µg/kg]).*

Location: *Experimental lysimeter farm of BAYER AG, Monheim NRW, Germany; 51° 4' N, 6° 55' E;*

Study type (e.g. lysimeter, field): *outdoor lysimeter*

Soil properties: *topsoil layer 0 – 30 cm texture: Sandy loam, pH = 7.04, OC= 1.41%, WHC = 32.45 [vol % H₂O] – Field Capacity*

Dates of application : *13/05/1993 – 1st application; 03/11/1993 – 2nd application;*

Crop : /Interception estimated: *Fodder maize (for silage) – 1st, target crop, CI = 0%; Winter wheat (corn) – 2nd, target crop, CI = 0%; Sugar beet, 3rd, succeeding, crop, CI not required;*

Number of applications: **1** year (+ 1.5 without application), **2** applications per year

Duration. *2.5 years*

Application rate: **480** g/ha – *1st application, 180 g/ha – 2nd application,*

Average annual rainfall (mm): **745** mm (*long-term value covering period 1966 – 1995; 1st experimental year precipitation (rainfall + irrigation): 948.1 mm, 2nd experimental year precipitation (rainfall + irrigation): 888.9 mm, 3rd experimental year precipitation (rainfall + irrigation): 442.0 mm, total: 2279 mm*

Average annual leachate volume (mm): *Volume of leachate collected (total): 1st experimental year: 383.1 L, 2nd experimental year: 368.9 L, 3rd experimental year: 19.1 L, total volume collected: 771.1 L*

% radioactivity in leachate (maximum/year): *1st experimental year: 1.563% AR, 2nd experimental year: 0.150% AR, 3rd experimental year: 0.007% AR, total: 1.72% AR*

Individual annual maximum concentrations (e.g. 1st, 2nd, 3rd yr): *1st experimental year (leachate collected on week 38): total TRR 5.455 [µg a. i. equivalents/L], acidic TRR 5.255 [µg a. i. equivalents/L], ¹⁴CO₂-associated radioactivity 3.58 [% total TRR], Flufenacet <0.001 [µg/L], FOE Alcohol 0.044 [µg/L], FOE Oxalate 0.036 [µg/L], FOE Sulfonic acid 3.682 [µg/L], FOE Thioglycolate sulfoxide 0.028 [µg/L] Unidentified radioactivity, no of components: 1, 0.041 µg/L parent equivalents.*

Individual annual average concentrations (e.g. 1st, 2nd, 3rd yr): *1st experimental year annual leachate: total TRR 2.699 [µg a. i. equivalents/L], acidic TRR 2.56 [µg a. i. equivalents/L], ¹⁴CO₂-associated radioactivity 5.35 [% total TRR], Flufenacet 0.005 [µg/L], FOE Alcohol 0.016 [µg/L], FOE Oxalate 0.006 [µg/L], FOE Sulfonic acid 1.616 [µg/L], FOE Thioglycolate sulfoxide 0.027 [µg/L] Unidentified radioactivity, no of components: 1, 0.045 µg/L parent equivalents.*

2nd experimental year annual leachate: total TRR 0.269 [µg a. i. equivalents/L], acidic TRR 0.22 [µg a. i. equivalents/L], ¹⁴CO₂-associated radioactivity 23.02 [% total TRR], Flufenacet 0.005 [µg/L], FOE Alcohol 0.004 [µg/L], FOE Oxalate 0.006 [µg/L], FOE Sulfonic acid 0.016 [µg/L], FOE Thioglycolate sulfoxide 0.019 [µg/L] Unidentified radioactivity, no of components: 1, 0.008 µg/L parent equivalents.

3rd experimental year annual leachate: total TRR 0.238 [µg a. i. equivalents/L], acidic TRR 0.14 [µg a. i. equivalents/L], ¹⁴CO₂-associated radioactivity 40.88 [% total TRR], acidic TRR not profiled, Unidentified radioactivity: no data.

average annual leachate: total TRR 1.492 [µg a. i. equivalents/L], acidic TRR 1.38 [µg a. i. equivalents/L], ¹⁴CO₂-associated radioactivity 6.85 [% total TRR],

Amount of radioactivity in the soils at the end of the study = *total 52.96% AR, in top 0-30cm layer 48.2% AR, in 30-60 cm layer 3.1% AR, below 60 cm 1.7% AR, identified in the top 30-cm layer: Flufenacet 528.48 [µg] (concentration 1.06 [µg/kg]), FOE Alcohol 87.67 [µg] (concentration 0.18 [µg/kg]), FOE Oxalate 63.74 [µg] (concentration 0.13 [µg/kg]), FOE Sulfonic acid 43.42 [µg] (concentration 0.09 [µg/kg]).*

B.8.1.3.4. – Other studies

The Applicant has submitted four study reports presenting the results of the determination of the Plant Uptake Factor – PUF. Two of them are GLP studies, one is a non-GLP study and one is a position paper prepared in support of the findings of one of the studies.

As these reports present the results related to the mobility in soil RMS decided to present them in the Renewal Assessment Report under that data point as “Other studies”. That was done in line with how they were listed in the Document L submitted by the Applicant.

Study 1:

Report: Schmeling S., Bongartz R., (2012): “Determination of the Plant Uptake Factor of FOE Methylsulfone, FOE Sulfonic acid and Trifluoroethanesulfonic acid in Wheat.”; Bayer Crop Science AG, Development-Environmental Safety-Metabolism/ADME and Environmental Fate, 40789 Monheim am Rhein, Germany; Study ID: M9992073-9, Report No. EnSa-12-260; 2012. 06. 28, updated with Amendment No. 1 on 2013. 02. 19; study reference number: M-434257-02-1;

Guidelines: The study was not declared to be performed in line with any specific Guidelines.

GLP: Yes;

RMS comments: This is a newly submitted study, submitted to provide the values required as input parameters in GW and SW modelling exposure assessment. It does not follow any specific Guideline due to the lack of such. RMS evaluated it for the purpose of the current assessment and found acceptable. It is summarised below.

Summary:

The aim of the study was to determine the plant uptake factors – PUF, for three major soil degradation products of Flufenacet – FOE Sulfonic acid, FOE Methylsulfone and FOE 5043-Trifluoroethanesulfonic acid, in wheat.

The test compounds were:

- FOE Sulfonic acid in form of Na⁺ salt, having a chemical purity 87.6%, delivered as a white powder;
- FOE Methylsulfone, having a chemical purity of 97.2%, delivered as a light yellow powder;
- FOE 5043-Trifluoroethanesulfonic acid in form of Na⁺ salt, having a chemical purity of 99.4%, delivered as a white solid.

They were used to prepare stock solutions having a concentration:

- 120 mg/L for FOE Sulfonic acid,
- 24.5 mg/L for FOE Methylsulfone,
- 52.5 mg/L for FOE 5043-Trifluoroethanesulfonic acid.

The test plant used in the experiment was Wheat, variety Thasos, pre-grown on artificial substrate – vermiculite and the nutrient solution, prepared from a commercial fertiliser solution WUXAL TOP K, characterised below in the table B.8.1.3.4._CA-1, with water to obtain a solution having concentration 0.2%. That was done by adding 7 mL of the fertiliser to 3493 mL of water. The same nutrient solution was used in determination of PUF, to prepare the test solution for each test compound. That was done by adding 1 mL of the respective stock solution to 3500 mL of the nutrient solution to obtain the following concentrations:

- 30 µg/L for FOE Sulfonic acid,
- 7 µg/L for FOE Methylsulfone,
- 15 µg/L for FOE 5043-trifluoroethanesulfonic acid.

The test solutions were prepared individually for each test compound. The concentrations of the given test compound in the relevant test solution were determined by HPLC-MS/MS.

Table B.8.1.3.4._CA-1: The composition of the fertiliser solution “WUXAL TOP K” used to prepare the nutrient solution.

Constituent ¹⁾		Constituent's concentration	
Common name	Formula	[g/L]	[%]
Urea	CH ₄ NO	50.0	4.0
Sodium nitrate	NaNO ₃	12.5	1.0
Phosphoric anhydride	P ₂ O ₅	100.0	8.0
Potassium oxide	K ₂ O	150.0	12.0
Boric acid	B (OH) ₃	0.124	0.01
Copper (EDTA chelate)	Cu	0.049	0.04
Iron (EDTA Chelate)	Fe	0.248	0.02
Manganese (EDTA Chelate)	Mn	0.148	0.012
Molybdenum	Mo	0.012	0.001
Zinc (EDTA Chelate)	Zn	0.049	0.004

Footnotes to the table:

1) Common name and formula of each constituent as presented in the study report, probably taken from the product's label;

The plants were pre-grown in the greenhouse in the conditions similar to the natural conditions of Central Europe: daily temperature $T = 18 - 21^{\circ}\text{C}$, relative humidity of 60% and light conditions – artificial light having intensity of at least 35 kLux from 6 am to 8 pm, until reaching the growth phase BBCH 15. At reaching that stage wheat plants were washed and transferred to brown 1-L glass bottles containing 800 mL of the test solution spiked with the given test compound. The number of the individual plants per bottle was ten. Plants were fixed in the bottle with elastomer foam. Then the bottles were wrapped in aluminium foil to prevent lossess of liquid due to evaporation.

For each test solution four bottles were prepared – three test sample bottles containing the equal number of plants (ten), and one without plants, serving as a control.

The bottles were placed in the greenhouse and kept there for eight days in the same conditions as described above for pre-growing of the test plants.

At pre-defined sampling points – DAT 0 (0 h after the experiment started), DAT 0.15 (4 hours after the experiment started), DAT 1, DAT 4 and DAT 8, single 1-mL samples of liquid were taken from each bottle (test samples and control) for determination of the content of test compound.

At the beginning of the experiment – on DAT 0, and on its end DAT 8, the volume of the test solution in each bottle was determined.

The analysis of the concentration of each test compound in the solution sampled from the given test bottle was performed by HPLC-MS/MS.

The chromatographic analysis was performed using Agilent HP 1200 chromatographic station coupled with Finnigan TQS Vantage MS/MS detector. The chromatographic separation was performed on Nucleodur C8 Gravity 50 • 2 mm, 5 µm chromatographic column working in a gradient mode, placed in chromatographic oven set to the constant temperature $T = 40^{\circ}\text{C}$.

The parameters of chromatographic analysis were following:

- **elution mode:** gradient;
- **composition of the mobile phase:**
 - **Solvent A:** 0.1% HCOOH in water
 - **Solvent B:** 0.1% HCOOH in CH₃CN
- **gradient mode:** individual for each analysed compound, presented in the tabler B.8.1.3.4._CA-2;
- **injection volume:** 5 µL for samples containing FOE Sulfonic acid or FOE Methylsulfone, 20 µL for samples containing FOE 5043-Trifluoroethanesulfonic acid;
- **flow rate:** 0.3 mL/min;
- **elution time:** 6 min.

Table B.8.1.3.4._CA-2: Gradient mode used in the study for each analysed compound.

Gradient mode for:								
FOE Sulfonic acid			FOE Methylsulfone			FOE 5043-Trifluoroethanesulfonic acid		
Time	Composition of mobile phase		Time	Composition of mobile phase		Time	Composition of mobile phase	
	% Solvent A	% Solvent B		% Solvent A	% Solvent B		% Solvent A	% Solvent B
0	95	5	0	80	20	0	100	0
1	95	5	1	80	20	3	100	0
2	50	50	2	60	40	5	80	80
5	40	60	5	40	60	6	5	95
6	5	95	6	5	95			

The key parameters of MS/MS analysis for each test compound are presented below in the table B.8.1.3.4._CA-3.

Table B.8.1.3.4._CA-3: The parameters of MS/MS analysis used in the study.

MS/MS parameters	Compound		
	FOE Sulfonic acid	FOE Methylsulfone	FOE 5043-Trifluoroethanesulfonic acid
Q1 Mass [amu]	276.1	274.1	163.0
Q3 Mass [amu]	234.1	232.1	143.0
Ionisation mode	ESI positive	ESI positive	ESI negative
Ion spray voltage [V]	3000	3000	3000
Collision energy [eV]	15	14	15
Collision gas pressure [mTorr]	1.5	1.5	1.5
Vapouriser temp [°C]	60	60	60
Capillary temp. [°C]	280	280	280

The identification of the test compounds in chromatograms was performed by means of the retention time, which were following:

- for FOE Sulfonic acid $R_t \approx 3.4$ min.;
- for FOE Methylsulfone $R_t \approx 3.5$ min.;
- for FOE 5043-Trifluoroethanesulfonic acid $R_t \approx 1.3$ min.

It was confirmed by the results of MS/MS analysis. The quantitative analysis was carried out using the calibration curves constructed for each of the test compound.

The calculations of PUF were carried out using the equation presented below on figure B.8.1.3.4._CA-1.

$$PUF = \frac{\ln(m_{day0} / m_{day8})}{\ln(V_{day0} / V_{day8})}$$

Legend:

m_{day0} = initial mass of test compound / 800 mL test solution [µg]

m_{day8} = mass of test compound in the test solution after 8 days [µg]

V_{day0} = initial volume of test solution (default 800 mL) [L]

V_{day8} = volume of test solution after 8 days [L]

Figure B.8.1.3.4._CA-1: The equation used to calculate PUF (copied from the study report).

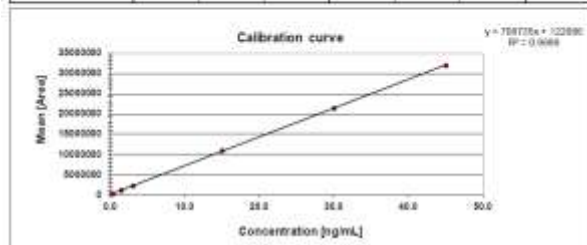
Results and their discussion:

The calibration curves used in the experiment for the quantitative analysis of each of the test compounds are presented below on figure B.8.1.3.4._CA-2.

Calibration curve for FOE Sulfonic acid

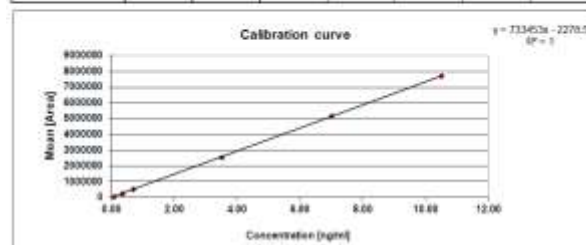
Injection: 5 µL, test compound (AE-0641914) in nutrient solution (0.2% WUXAL TOP K)
Area: (of) the Peak at t_R approx. 3.45 min in the LC-MS-SRM spectra

LC-MS Sample ID	Concentration [µg/mL]	1 st Injection [Area]	2 nd Injection [Area]	3 rd Injection [Area]	Mean [Area]	Standard Deviation	Rel. Standard Deviation [%]
AE05_AL_130_1504	40.0	2177669	2191762	2284860	2191231	13136.30	0.40
AE05_AL_130_1504	30.0	2176669	2175707	2185271	2145231	28126.64	1.12
AE05_AL_130_1504	10.0	1390246	1392280	1076405	1285644	11603.64	1.48
AE05_AL_130_1504	3.0	225417	226346	223346	224036	2564.30	1.14
AE05_AL_13_1504	1.5	114463	115263	113760	113760	1224.35	1.07
AE05_AL_13_1504	0.3	30621	30376	32756	30967	1462.34	3.27

**Calibration curve for FOE Methylsulfone**

Injection: 5 µL, test compound (BCS-CO62475) in nutrient solution (0.2% WUXAL TOP K)
Area: (of) the Peak at t_R approx. 3.5 min in the LC-MS-SRM spectra

LC-MS Sample ID	Concentration [µg/mL]	1 st Injection [Area]	2 nd Injection [Area]	3 rd Injection [Area]	Mean [Area]	Standard Deviation	Rel. Standard Deviation [%]
AE05_CO_130_1505	10.00	1925477	2052270	2092229	1989652	113246.57	4.81
AE05_CO_130_1505	7.00	2265111	2334173	2466271	2335152	227362.30	4.99
AE05_CO_130_1505	3.50	2594822	2642257	2429594	2555558	102165.02	4.07
AE05_CO_130_1505	0.70	107395	509405	482143	118475	17787.89	7.26
AE05_CO_13_1505	0.35	244614	262294	275150	257353	15141.49	5.82
AE05_CO_13_1505	0.07	4862	46227	4662	18632	102.09	1.12

**Calibration curve for FOE 5043-Trifluoroethanesulfonic acid**

Injection: 20 µL, test compound (BCS-CU62474) in nutrient solution (0.2% WUXAL TOP K)
Area: (of) the Peak at t_R approx. 1.3 min in the LC-MS-SRM spectra

LC-MS Sample ID	Concentration [µg/mL]	1 st Injection [Area]	2 nd Injection [Area]	3 rd Injection [Area]	Mean [Area]	Standard Deviation	Rel. Standard Deviation [%]
AE05_CU_130_1506	22.00	1922273	1598000	1474115	1512093	243008.76	2.92
AE05_CU_130_1506	0.00	1000000	920000	1000000	1000000	25400.00	1.26
AE05_CU_130_1506	7.50	5982327	6192726	5482299	5735282	401248.09	2.62
AE05_CU_130_1506	1.50	1078003	1525558	366173	1054882	41864.18	4.86
AE05_CU_13_1506	0.75	521650	426441	401865	449652	16277.14	3.23
AE05_CU_13_1506	0.15	97030	81000	104163	97400	4080.61	0.22

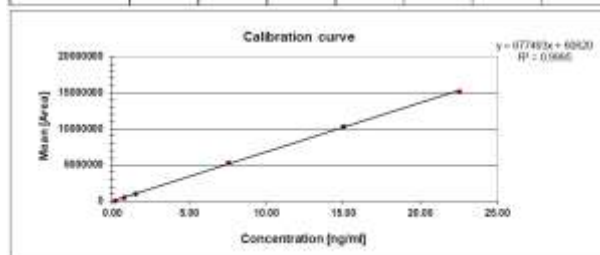


Figure B.8.1.3.4_CA-2: The calibration curves used in the study (copied from the study report).

The initial concentrations of the test compounds in the test solutions were following:

- for FOE Sulfonic acid: 34.44 µg/L;
- for FOE Methylsulfone: 7.86 µg/L;
- for FOE 5043-trifluoroethanesulfonic acid: 15.89 µg/L.

The results of the determination of the volume of the solution at the beginning and the end of experiment for the test with each test compound are presented below in the table B.8.1.3.4_CA-4. In case of the control samples, containing no plants, the changes of the volume were attributed to the losses that resulted from sampling during incubation.

Table B.8.1.3.4._CA-4: The results of the determination of the volume of solution during incubation and its changes.

Sample characteristics			Determined volume [L]		
Test compound	Type of sample	Replicate	Day 0 – V_{day0}	Day 8 – V_{day0}	Amount uptaken by plants – V_{uptake}
FOE Sulfonic acid	Test sample	1	0.80	0.66	0.14
	Test sample	2	0.80	0.67	0.13
	Test sample	3	0.80	0.70	0.10
	Control	----	0.80	0.79	----
FOE Methylsulfone	Test sample	1	0.80	0.69	0.11
	Test sample	2	0.80	0.69	0.11
	Test sample	3	0.80	0.72	0.08
	Control	----	0.80	0.79	----
FOE 5043-Trifluoroethane-sulfonic acid	Test sample	1	0.80	0.69	0.11
	Test sample	2	0.80	0.72	0.08
	Test sample	3	0.80	0.71	0.09
	Control	----	0.80	0.79	----

The results of the determination of concentration of the given test compound in the solution are presented below in the table B.8.1.3.4._CA-5.

Table B.8.1.3.4._CA-5: The results of the determination of the concentration of the given test compound in solution during the experiment.

Test compound	Type of sample		Concentration of the test compound [µg/L] recorded on:				
			DAT 0 (0 hours)	DAT 0.15 (4 hours)	DAT 1	DAT 4	DAT 8
FOE Sulfonic acid	Test sample	Replicate 1	34.27	34.27	34.51	36.20	39.28
	Test sample	Replicate 2	34.58	34.61	34.52	35.94	37.99
	Test sample	Replicate 3	34.47	34.12	34.68	34.95	36.24
	Control		34.47	34.15	34.06	34.11	33.34
FOE Methylsulfone	Test sample	Replicate 1	7.86	7.71	7.78	7.79	7.66
	Test sample	Replicate 2	7.91	7.72	7.78	7.39	7.47
	Test sample	Replicate 3	7.82	7.55	7.58	7.72	7.52
	Control		7.85	7.34	7.79	7.53	7.24
FOE 5043-Trifluoroethane-sulfonic acid	Test sample	Replicate 1	15.78	16.21	15.32	15.22	15.53
	Test sample	Replicate 2	15.94	15.12	16.01	14.94	15.21
	Test sample	Replicate 3	15.96	15.61	15.35	14.86	15.00
	Control		16.05	15.51	15.45	14.94	14.59

The values used in the calculation of PUF for each test compound and the results of these calculations are presented below in the table B.8.1.3.4._CA-6. RMS verified them and found them correct. The calculated mean values reported in that table are the final results of the study.

Table B.8.1.3.4._CA-6: The results of the determination of PUF (as presented in the study report).

Test compound	Type of sample/value		Day-0 results			Day-8 results			PUF
			V_{day0} [L]	C_{day0} [µg/L]	m_{day0} [µg]	V_{day8} [L]	C_{day8} [µg/L]	m_{day8} [µg]	
FOE Sulfonic acid	Test sample	Replicate 1	0.80	34.27	27.42	0.66	39.28	25.92	0.29
	Test sample	Replicate 2	0.80	34.58	27.66	0.67	37.99	25.45	0.47
	Test sample	Replicate 3	0.80	34.47	27.58	0.70	36.24	25.37	0.63
	mean		----	----	----	----	----	----	0.46
FOE Methylsulfone	Test sample	Replicate 1	0.80	7.86	6.29	0.69	7.66	5.29	1.17
	Test sample	Replicate 2	0.80	7.91	6.33	0.69	7.47	5.15	1.39
	Test sample	Replicate 3	0.80	7.82	6.26	0.72	7.52	5.41	1.37
	mean		----	----	----	----	----	----	1.31
FOE 5043-Trifluoroethane-sulfonic acid	Test sample	Replicate 1	0.80	15.78	12.62	0.69	15.53	10.72	1.11
	Test sample	Replicate 2	0.80	15.94	12.75	0.72	15.21	10.95	1.44
	Test sample	Replicate 3	0.80	15.96	12.77	0.71	15.00	10.65	1.52
	mean		----	----	----	----	----	----	1.36

Study 2:

Report: Bongartz R., (2013): “Determination of the Plant Uptake Factor of Trifluoroacetic acid (TFA) in Wheat.”; Bayer Crop Science AG, BCS-D-EnSA-Testing, Monheim, Germany; Study ID: M9992182-0, Report No. EnSa-13-0357; 2013. 06. 05, updated with Amendment No. 1 on 2013. 06. 24 and with Amendment No. 2 on 2013. 07. 25; study reference number: M-456754-03-1.

Guidelines: The study was not performed in line with any specific Guidelines.

GLP: Yes;

RMS comments: This is a newly submitted study, submitted to provide the values required as input parameters in GW and SW modelling exposure assessment. It does not follow any specific Guideline due to the lack of such. RMS evaluated it for the purpose of the current assessment and found acceptable. It is summarised below.

Summary:

The aim of the study was to determine the plant uptake factor – PUF, for a major soil degradation product of Flufenacet – Trifluoroacetic acid (TFA).

The test compounds was Trifluoroacetic acid (TFA), in form of its Na⁺ salt, radiolabelled in C1 position, as shown below on figure B.8.1.3.4._CA-3. It had radiochemical purity of ≥ 98% and specific activity of 4.08 MBq/mg. To the test facility it was delivered as a solid dried under vacuum.

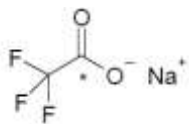


Figure B.8.1.3.4._CA-3: The structural formula of the radiolabelled test compound used in the experiment. The radiolabelling position is indicated by an asterisk – (*)
(copied from the study report).

It was used to prepare the stock solution having a concentration 13.32 µg/mL and specific radioactivity 54.34 kBq/mL, by dissolving its appropriate amount in 100 mL of ultrapure (Milli-Q) water. The stock solution was subsequently used to fortify the test solution to obtain the intended concentration of 70 µg TFA/L. The test solution was a buffer solution consisting of 0.01M 2-morpholino-ethanesulfonic acid (MES) and 0.01M CaCl₂ adjusted to pH = 6.5 with appropriate amount of NaOH_{aq}. 24 mL of the characterised above stock solution of TFA was added to 4.5 L of that buffer solution to obtain the intended concentration of TFA of 70 µg/L.

The test plant used in the experiment was Wheat, variety Thasos, pre-grown in soil until reaching the growth phase BBCH = 15 (five unfolded leaves). The plants were pre-grown in the greenhouse in the conditions similar to the natural conditions of Central Europe: daily temperature T = ~20°C, relative humidity of 60 – 75% and light conditions – artificial light having intensity of at least 35 kLux from 6 am to 8 pm. At reaching the pre-designated growth stage – BBCH 15, wheat plants were removed from growing pots, soil from their root systems was removed by washing with water, and they were transferred to brown 1-L glass bottles containing 800 mL of the test solution spiked with the test compound. The number of the individual plants per bottle was ten. Plants were fixed in the bottle with elastomer foam. Then the bottles were wrapped in aluminium foil to prevent loss of liquid due to evaporation.

Five bottles containing the test solution and equal number of plants (ten) were prepared. Additionally, in the same way, were prepared two bottles containing test plants and buffer solution without test compound. These were used as a control to examine the water uptake by the test plants.

The bottles were placed in the greenhouse and kept there for eight days in the same conditions as described above for pre-growing of the test plants.

At pre-defined sampling points – DAT 0 (0 h after the experiment started), DAT 2, DAT 5 and DAT 8, three 1-mL samples of liquid were taken from each bottle (test samples and control) for determination of the radioactivity content in solution using LSC.

At the beginning of the experiment – on DAT 0, and on its end DAT 8, the volume of the test solution in each bottle was determined.

At the end of the experiment the plant roots from each jar were washed with 200 mL of CH₃CN/H₂O (1:1) solution. The volume of that solution was determined, after what the radioactivity content in it measured using LSC.

Finally, the plants from each jar were weighed, homogenized and combusted to determine the amount of uptaken TFA. That was done by measuring by LSC the amount of ¹⁴CO₂ generated during combustion.

The LSC analysis of liquid samples was carried out using either LKB/Wallac 1219 Spectral scintillation counter or Beckman LS 6500 scintillation counter. The mean measurement efficiency was 89.5%. The counting lasted from few seconds up to 20 minutes. To analyse stock solution of the test compound its 0.020 mL aliquots were mixed with 2 mL of Quicksafe A + 5% water scintillation cocktail. To analyse test solutions their 1-mL samples were mixed with 7 mL of Quicksafe A + 5% water scintillation cocktail.

In case of solid samples the generated ¹⁴CO₂ was absorbed in Oxysolve C400 scintillation cocktail and analysed using LKB/Wallac 1219 Spectral scintillation counter.

Two other analytical methods used in the experiment were radio- HPLC and HPLC-MS. The radio-HPLC was used for checking purity and stability of the test compound – TFA, in stock solution as well as in the DAT-8 test. In the study report it was not specified which samples were analysed using HPLC–MS method.

The radio-HPLC analysis was performed using Agilent HP 1110 chromatographic station equipped with autosampler, gradient pump, chromatographic column oven set to T = 40°C and UV-DAD detector set to λ = 254 nm, coupled with a flow-through Ramona Star radioactivity detector. The chromatographic separation was performed on LiChroCART 250 • 4.6 mm, 5 µm chromatographic column.

The parameters of chromatographic analysis were following:

- **elution mode:** gradient;
- **composition of the mobile phase:**
 - **Solvent A:** HCOOH in water 1:99 (v/v)
 - **Solvent B:** HCOOH in CH₃CN 1:99 (v/v)
- **gradient mode:** presented in the table B.8.1.3.4._CA-7;
- **flow rate:** 1.0 mL/min;
- **elution time:** 70min.

Table B.8.1.3.4._CA-7: Gradient mode used in the study.

Elution time [min]		0	5	55	60	61	70
Composition of mobile phase	% A	100	100	0	0	100	100
	% B	0	0	100	100	0	0

The calculations of PUF were carried out using the equation presented below on figure B.8.1.3.4._CA-4.

$$PUF = \frac{\ln((m_{final} + m_{wash}) / m_{day0})}{\ln(V_{final} / V_{day0})}$$

Legend:
 m_{day0} = initial mass of test compound / 800 mL test solution [µg]
 m_{final} = mass of test compound in the test solution after 8 days [µg]
 m_{wash} = mass of test compound in the wash solution [µg]
 V_{day0} = initial volume of test solution (default 800 mL) [L]
 V_{final} = volume of test solution after 8 days [L]

Figure B.8.1.3.4._CA-4: The equation used to calculate PUF (copied from the study report).

Results and their discussion:

The mean initial concentration of the test compound in the test solution was 75.6 µg/L. Its purity in the stock solution was demonstrated to be 100%. It was demonstrated to be stable within the whole experimental period lasting 8 days.

The results of the determination of the volume of the solution at the beginning and the end of the experiment are presented below in the table B.8.1.3.4._CA-8. The control samples, used to examine the volume of the solution taken by test plants, were blank (not containing the test compound).

Table B.8.1.3.4._CA-8: The results of the determination of the volume of solution during incubation and its changes.

Sample characteristics			Determined volume [L]		
Test compound	Type of sample	Replicate	Day 0 – V_{day0}	Day 8 – V_{day0}	Amount uptaken by plants – V_{uptake}
Trifluoroacetic acid	Test sample	1	0.800	0.260	0.540
	Test sample	2	0.800	0.270	0.530
	Test sample	3	0.800	0.420	0.380
	Test sample	4	0.800	0.280	0.520
	Test sample	5	0.800	0.370	0.430
	Control	1	0.800	0.440	0.360
	Control	2	0.800	0.450	0.350

The results of the determination of concentration of TFA in the solution are presented below in the table B.8.1.3.4._CA-9.

Table B.8.1.3.4._CA-9: The results of the determination of the concentration of TFA in solution during the experiment.

Sampling time	Type of sample		Volume of sample [mL]	Concentration of TFA in solution [$\mu\text{g/L}$]	Mass of TFA in solution [μg]
DAT 0 (0 hours)	Test sample	Replicate 1	800	75.5	60.4
	Test sample	Replicate 2	800	75.3	60.2
	Test sample	Replicate 3	800	75.4	60.3
	Test sample	Replicate 4	800	75.5	60.4
	Test sample	Replicate 5	800	76.5	61.2
DAT 2	Test sample	Replicate 1	Not determined	74.5	Not determined
	Test sample	Replicate 2	Not determined	75.7	Not determined
	Test sample	Replicate 3	Not determined	72.3	Not determined
	Test sample	Replicate 4	Not determined	75.8	Not determined
	Test sample	Replicate 5	Not determined	73.1	Not determined
DAT 5	Test sample	Replicate 1	Not determined	79.7	Not determined
	Test sample	Replicate 2	Not determined	81.4	Not determined
	Test sample	Replicate 3	Not determined	74.7	Not determined
	Test sample	Replicate 4	Not determined	82.7	Not determined
	Test sample	Replicate 5	Not determined	76.4	Not determined
DAT 8	Test sample	Replicate 1	260	100.9	26.2
	Test sample	Replicate 2	270	103.4	27.9
	Test sample	Replicate 3	420	82.2	34.5
	Test sample	Replicate 4	280	105.1	29.4
	Test sample	Replicate 5	370	86.9	32.1
Post-incubation – washing of plant roots	Wash solution	Replicate 1	200	Not determined	6.5
	Wash solution	Replicate 2	200	Not determined	6.5
	Wash solution	Replicate 3	200	Not determined	4.1
	Wash solution	Replicate 4	200	Not determined	5.7
	Wash solution	Replicate 5	200	Not determined	4.5

The values used in the calculation of PUF and the results of these calculations are presented below in the table B.8.1.3.4._CA-10. RMS verified them and found them correct. The calculated mean values reported in that table are the final results of the study. The result of the determination of mass balance showed that the average recovery rate of AR was 92.6%

Table B.8.1.3.4._CA-10: The results of the determination of PUF (as presented in the study report).

Type of sample	Day-0 results			Day-8 results				PUF
	V_{day0} [L]	C_{day0} [$\mu\text{g/L}$]	m_{day0} [μg]	V_{day8} [L]	C_{day8} [$\mu\text{g/L}$]	m_{day8} [μg]	m_{wash} [μg]	
Test sample replicate 1	0.800	75.5	60.4	0.260	100.9	26.2	6.5	0.54
Test sample replicate 2	0.800	75.3	60.2	0.270	103.4	27.9	6.5	0.51
Test sample replicate 3	0.800	75.4	60.3	0.420	82.2	34.5	4.1	0.69
Test sample replicate 4	0.800	75.5	60.4	0.280	105.1	29.4	5.7	0.52
Test sample replicate 5	0.800	76.5	61.2	0.370	86.9	32.1	4.5	0.66
mean	----	----	----	----	----	----	----	0.59

Study 3:

Report: Bongartz R., (2013): “Determination of the Plant Uptake Factor of Trifluoroacetic acid (TFA) in Wheat, Corn and Tomatoes.”; Bayer Crop Science AG, BCS-D-EnSA-Testing, Monheim, Germany; Study ID: M9992182-0, Report No. EnSa-12-0581; 2012. 10. 18; study reference number M-440106-01-1.

Guidelines: The study was not performed in line with any specific Guidelines.

GLP: No;

RMS comments: This is a newly submitted study, submitted to provide the values required as input parameters in GW and SW modelling exposure assessment. It does not follow any specific Guideline due to the lack of such. RMS evaluated it for the purpose of the current assessment and found acceptable, although, being a non-GLP study it can be considered only as a supplementary study. It is summarised below.

Summary:

The aim of the study was to determine the plant uptake factor – PUF, for a major soil degradation product of Flufenacet – Trifluoroacetic acid (TFA).

The test compounds was Trifluoroacetic acid (TFA), in form of Na^+ salt, radiolabelled in C1 position, as shown below on figure B.8.1.3.4._CA-5. It had radiochemical purity of $\geq 98\%$ and specific activity of 3.48 MBq/mg. To the test facility it was delivered as a solid dried under vacuum.

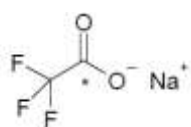


Figure B.8.1.3.4._CA-5: The structural formula of the radiolabelled test compound used in the experiment. The radiolabelling position is indicated by an asterisk – (*)
(copied from the study report).

It was used to prepare two stock solutions. One of them, labelled VG0105D1, had a concentration 1.060 mg TFA/mL (in the study report it was incorrectly reported in g/mL) and specific radioactivity 3.69 MBq/mL. The second one, labelled VG0105D5, had a concentration 1.138 mg TFA/mL (once again in the study report the units were incorrectly reported as [g/mL]) and specific activity of 3.96 MBq/mL. These stock solutions were subsequently used to fortify the 800-mL portions of the nutrient solution to obtain the test solution having the intended concentration of 800 μg TFA/L. The nutrient solution contained 10 mL Hoagland's solution no. 2 and 75 mL 1M KH_2PO_4 aq. The pH of the test solution was 6.

The amount of the stock solution VG0105D1 added to 800 mL of nutrient solution was 0.604 mL and that of the stock solution VG0105D5 – 0.562 mL.

The test plants used in the experiment were:

- Wheat, variety Thasos,

- Corn,
- Tomato.

The test plants were pre-grown in Vermiculite in the greenhouse in the conditions similar to the natural conditions of Central Europe: daily temperature $T = \sim 20^{\circ}\text{C}$, mean relative humidity of $\sim 75\%$ and light conditions – artificial light having intensity of at least 35 kLux from 6 am to 8 pm.

1 day before the beginning of the experiment test plants were removed from growing pots, and Vermiculite removed from their root systems by washing with water.

They were then transferred to brown 1-L glass bottles containing 800 mL of the test solution spiked with the test compound. The number of the individual plants per bottle was:

- ten for the experiment with wheat,
- one for the experiment with corn,
- one for the experiment with tomato.

Plants were fixed in the bottle with elastomer foam. Then the bottles were covered with aluminium foil to prevent loss of liquid due to evaporation.

The experiment with wheat plants was carried out for a single bottle, that for corn using three replicates (bottles) and that with tomato plants using two replicates (bottles). The control samples (bottles) were not prepared.

The bottles were placed in the greenhouse and kept there for eight days in case of experiment with wheat and tomato plants, or for eleven days – in case of the experiment with corn plants, in the same conditions as described above for pre-growing of the test plants.

At pre-defined sampling points three 1-mL samples of liquid were taken from each bottle for determination of the radioactivity content in solution using LSC.

The sampling points were:

- for experiment with wheat: DAT 0 (0 hours after treatment), DAT 0.146 (3.5 hours after treatment), DAT 1 (1 day after treatment), DAT 4 (4 days after treatment) and DAT 8 (8 days after treatment);
- for experiment with corn: DAT 0 (0 hours after treatment), DAT 0.166 (4 hours after treatment), DAT 1 (1 day after treatment), DAT 4 (4 days after treatment), DAT 8 (8 days after treatment) and DAT 11 (11 days after treatment);
- for experiment with tomato: DAT 0 (0 hours after treatment), DAT 0.104 (2.5 hours after treatment), DAT 1 (1 day after treatment), DAT 4 (4 days after treatment) and DAT 8 (8 days after treatment)

The volume of the solution in each bottle was determined at each sampling point specified above.

At the end of the experiment the plant roots from each jar were washed with ~ 50 of H_2O . The volume of that solution was determined, after what the radioactivity content in it measured using LSC.

The LSC analysis of liquid samples was carried out using either LKB/Wallac 1219 Spectral scintillation counter Beckman LS 6600 LL scintillation counter or Beckman LS 6500 scintillation counter. The mean measurement efficiency was 84.3%. The counting lasted from few seconds up to 20 minutes. To analyse stock solutions of the test compound their 0.025 mL aliquots were mixed with 2 mL of Quicksafe A + 5% water scintillation cocktail. To analyse test solutions their 0.1-mL aliquots were mixed with 2 mL of Quicksafe A + 5% water scintillation cocktail.

The calculations of PUF were carried out using the equation presented below on figure B.8.1.3.4._CA-6.

$$PUF = \frac{\ln((m_{\text{final}} + m_{\text{wash}}) / m_{\text{day0}})}{\ln(V_{\text{final}} / V_{\text{day0}})}$$

Legend:
 m_{day0} = initial mass of test compound / 800 mL test solution [μg]
 m_{final} = mass of test compound in the test solution after 8 or 11 days [μg]
 m_{wash} = mass of test compound in the wash solution [μg]
 V_{day0} = initial volume of test solution (default 800 mL) [L]
 V_{final} = volume of test solution after 8 or 11 days [L]

Figure B.8.1.3.4._CA-6: The equation used to calculate PUF (copied from the study report).

Results and their discussion:

The mean initial concentration of the test compound in the test solution was 767.8 $\mu\text{g/L}$ in the experiment with wheat, 769.1 $\mu\text{g/L}$ in the experiment with corn and 711.8 $\mu\text{g/L}$ in the experiment with tomato plants.

The results of the determination of the initial and final volume of the solution for the test with each test compound are presented below in the table B.8.1.3.4._CA-11. The control samples, used to examine the volume of the solution taken by test plants, were blank (not containing the test compound).

Table B.8.1.3.4._CA-11: The results of the determination of the volume of solution during incubation and its changes.

Sample characteristics			Determined volume [L]		
Test plant	Type of sample	Replicate	Day 0 – V_{day0}	Final – V_{final}	Amount uptaken by plants – V_{uptake}
Wheat	Test solution	---	0.800	0.550	0.250
Corn	Test solution	1	0.800	0.640	0.160
	Test solution	2	0.800	0.672	0.128
	Test solution	3	0.800	0.670	0.130
tomato	Test solution	1	0.800	0.535	0.265
	Test solution	2	0.800	0.585	0.215

The results of the determination of concentration of TFA in the solution are presented below, individually for each test plant, in tables: B.8.1.3.4._CA-12 for wheat, B.8.1.3.4._CA-13 for corn and B.8.1.3.4._CA-14 for tomato.

Table B.8.1.3.4._CA-12: The results of the determination of the concentration of TFA in solution during the experiment with wheat.

Sampling time	Type of sample		Volume of sample [mL]	Concentration of TFA in solution [µg/L]	Mass of TFA in solution [µg]
<i>DAT 0 (0 hours)</i>	Test sample	Replicate 1	800	767.8	614.3
<i>DAT 0.146 (3.5 hours)</i>	Test sample	Replicate 1	800	804.5	Not determined
<i>DAT 1</i>	Test sample	Replicate 1	780	758.4	Not determined
<i>DAT 4</i>	Test sample	Replicate 1	675	805.5	Not determined
<i>DAT 11</i>	Test sample	Replicate 1	550	854.1	469.8
<i>Post-incubation – washing of plant roots</i>	Wash solution	Replicate 1	50	Not determined	9.1

Table B.8.1.3.4._CA-13: The results of the determination of the concentration of TFA in solution during the experiment with corn.

Sampling time	Type of sample		Volume of sample [mL]	Concentration of TFA in solution [µg/L]	Mass of TFA in solution [µg]
<i>DAT 0 (0 hours)</i>	Test sample	Replicate 1	800	762.0	609.6
	Test sample	Replicate 2	800	772.6	618.0
	Test sample	Replicate 3	800	772.8	618.2
<i>DAT 0.166 (4 hours)</i>	Test sample	Replicate 1	795	783.6	Not determined
	Test sample	Replicate 2	800	756.8	Not determined
	Test sample	Replicate 3	795	771.1	Not determined
<i>DAT 1</i>	Test sample	Replicate 1	780	776.0	Not determined
	Test sample	Replicate 2	785	770.1	Not determined
	Test sample	Replicate 3	780	779.4	Not determined
<i>DAT 4</i>	Test sample	Replicate 1	740	814.2	Not determined
	Test sample	Replicate 2	750	806.6	Not determined
	Test sample	Replicate 3	750	810.2	Not determined
<i>DAT 8</i>	Test sample	Replicate 1	685	823.8	Not determined
	Test sample	Replicate 2	710	811.2	Not determined
	Test sample	Replicate 3	705	822.5	Not determined
<i>DAT 11</i>	Test sample	Replicate 1	640	750.2	480.1
	Test sample	Replicate 2	672	758.1	509.5
	Test sample	Replicate 3	670	785.9	526.5
<i>Post-incubation – washing of plant roots</i>	Wash solution	Replicate 1	49	Not determined	3.6
	Wash solution	Replicate 2	50	Not determined	4.4
	Wash solution	Replicate 3	48	Not determined	4.3

Table B.8.1.3.4._CA-14: The results of the determination of the concentration of TFA in solution during the experiment with tomato plants.

Sampling time	Type of sample		Volume of sample [mL]	Concentration of TFA in solution [$\mu\text{g/L}$]	Mass of TFA in solution [μg]
<i>DAT 0 (0 hours)</i>	Test sample	Replicate 1	800	600.9	560.7
	Test sample	Replicate 2	800	722.7	578.2
<i>DAT 0.104 (2.5 hours)</i>	Test sample	Replicate 1	800	689.3	Not determined
	Test sample	Replicate 2	800	705.8	Not determined
<i>DAT 1</i>	Test sample	Replicate 1	740	602.8	Not determined
	Test sample	Replicate 2	730	624.1	Not determined
<i>DAT 4</i>	Test sample	Replicate 1	601	728.7	Not determined
	Test sample	Replicate 2	611	710.3	Not determined
<i>DAT 8</i>	Test sample	Replicate 1	535	806.5	431.5
	Test sample	Replicate 2	585	742.2	434.2
<i>Post-incubation – washing of plant roots</i>	Wash solution	Replicate 1	45	Not determined	6.0
	Wash solution	Replicate 2	46	Not determined	7.3

The values used in the calculation of PUF and the results of these calculations are presented below in the table B.8.1.3.4._CA-15. RMS verified them and found them correct. The calculated mean values reported in that table are the final results of the study. RMS however is of the opinion that due to the deficiencies of the study its results – the determined PUF values, should be considered only as indicative and not used as input parameters in modelling.

Table B.8.1.3.4._CA-15: The results of the determination of PUF (as presented in the study report).

Test crop: wheat								
Type of sample	Day-0 results			Final – Day-8 results				PUF
	V_{day0} [L]	C_{day0} [$\mu\text{g/L}$]	m_{day0} [μg]	V_{day8} [L]	C_{day8} [$\mu\text{g/L}$]	m_{day8} [μg]	m_{wash} [μg]	
Test sample replicate 1	0.800	767.8	614.3	0.550	854.1	469.8	9.1	0.66
mean	----	----	----	----	----	----	----	0.66
Test crop: corn								
Type of sample	Day-0 results			Final – Day-11 results				PUF
	V_{day0} [L]	C_{day0} [$\mu\text{g/L}$]	m_{day0} [μg]	V_{day11} [L]	C_{day11} [$\mu\text{g/L}$]	m_{day11} [μg]	m_{wash} [μg]	
Test sample replicate 1	0.800	762.0	609.6	0.640	750.2	480.1	3.6	1.04
Test sample replicate 2	0.800	772.6	618.0	0.672	758.1	509.5	4.4	1.06
Test sample replicate 3	0.800	772.8	618.2	0.670	785.9	526.5	4.3	0.86
mean	----	----	----	----	----	----	----	0.98
Test crop: tomato plants								
Type of sample	Day-0 results			Final – Day-8 results				PUF
	V_{day0} [L]	C_{day0} [$\mu\text{g/L}$]	m_{day0} [μg]	V_{day8} [L]	C_{day8} [$\mu\text{g/L}$]	m_{day8} [μg]	m_{wash} [μg]	
Test sample replicate 1	0.800	700.9	560.7	0.535	806.5	431.5	6.0	0.62
Test sample replicate 2	0.800	722.7	578.2	0.585	742.2	434.2	7.3	0.86
mean	----	----	----	----	----	----	----	0.74

Study 4:

Report: Roepke B., (2013): “Determination of a suitable Plant Uptake Factor (PUF) of Trifluoroacetic acid (TFA) for use in Environmental Fate Models in the Target Crop Wheat.”; Bayer Crop Science AG, Environmental Safety, Alfred Nobel Str. 50, D-40789 Monheim am Rhein, Germany; Report No. EnSa-13-0545; 24. 10. 2013; study reference number M-468684-01-1.

Guidelines: The study is a position paper examining existing experimental data, therefore it was not performed in line with any specific Guidelines.

GLP: No, not applicable – position paper;

RMS comments: This is a newly submitted study, analysing the available data in order to determine the most appropriate PUF value for Trifluoroacetic acid to be used in regulatory GW model exposure assessment. It did not follow any specific Guidelines, as no such Guidelines exist, but it bears references to several EU documents that may be considered as such, e.g. Report of FOCUS Groundwater Scenarios Workgroup ([FOCUS, 2000]) and Report of FOCUS Ground Water Work Group ([FOCUS, 2009]), Scientific Opinion of EFSA PPR Panel on the report of FOCUS groundwater working group ([EFSA Journal, 2013]). RMS evaluated it for the purpose of the current assessment and found acceptable. It shall be indicated however, that it can be considered only as a supplementary study. It is briefly summarised below.

Summary:

The aim of the study was to examine the available experimental data in order to determine the most appropriate value of plant uptake factor – PUF, for Trifluoroacetic acid (TFA), a major soil degradation product of Flufenacet, to be used in the regulatory GW model exposure assessment.

Four studies were selected as a source of data:

- Bongartz [2012], study reference number: M-440106-01-1;
- Bongartz [2013], study reference number: M-456754-03-1;
- Bongartz and Klankers [2012], study reference number: M-443538-01-1;
- Roohi and Buntain [2004], study reference number: M-222225-01-1;

Studies by [Bongartz, 2012] and [Bongartz, 2013] are both laboratory studies that were aimed on the determination of the PUF value for TFA in Wheat (both studies), Corn and Tomato plants. They are summarised in this Renewal Assessment Report, under this point, as **Study 2** and **Study 3**.

The other two studies referred to in the report are crop rotational studies.

First of them – by [Bongartz and Klankers; 2012], was performed in order to examine the metabolism of Flufenacet, precursor of TFA, in confined rotational crops. The test crops used in that experiment were Wheat, Turnip and Swiss chard.

On the basis of the results presented below on figure B.8.1.3.4._CA-7 (table copied from the study report) it was stated that the increase in the concentration of TFA in plants was correlated with its decrease in soil, as well as may be correlated with its formation pattern in soil from Flufenacet. It shall be indicated that in the table are presented the values obtained for Total Radioactive Residues (TRR) measured in rotational crops and expressed as [mg Flufenacet equivalents/kg]. However, their further qualitative analysis showed that >92.5% TRR could be attributed to TFA. To support that statement another table from that study report was presented, showing the results of the qualitative and quantitative analysis of TRR in Wheat of the 1st rotation. These results are presented on figure B.8.1.3.4._CA-8. On their basis it was stated that it may be postulated that the decline of the concentration of TFA in soil may be explained by its uptake by plants and not by its further transformation.

Table 4: Plant Residues in Confined Rotational Crop Matrices (Bongartz & Klankers, 2012)

Total Radioactive Residues (TRRs) in Confined Rotational Crops (mg flufenacet equivalents / kg)			
Matrix	1 st rotation	2 nd rotation	3 rd rotation
wheat forage	1.543	2.318	1.441
wheat hay	3.755	8.225	3.740
wheat straw	4.376	9.335	4.035
wheat grain	3.024	7.673	1.371
turnip leaves	6.792	3.536	0.993
turnip roots	0.601	0.197	0.087
Swiss chard (intermediate)	6.117	1.951	4.784
Swiss chard (at maturity)	3.386	2.950	1.973

Figure B.8.1.3.4._CA-7: The results of the study by [Bongartz and Klankers; 2012] – the TRR in the rotational crops (copied from the study report).**Table 5: Recovery of TFA in matrices of the target crop wheat (Bongartz & Klankers, 2012)**

Distribution of Metabolites in Wheat of the 1 st Rotation								
Metabolite Fraction (Report name, peak ID)	Forage		Hay		Straw		Grain	
	TRR = 1.543 mg/kg		TRR = 3.755 mg/kg		TRR = 4.376 mg/kg		TRR = 3.024 mg/kg	
	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg
TFA (trifluoroacetic acid) (R1)	95.2	1.469	90.7	3.404	92.6	4.054	95.9	2.899
FOE 5043- trifluoroethanesulfonic acid (R1)	3.3	0.50	2.1	0.079	0.5	0.021	n.d.	n.d.
FOE-thiadone-glycoside (R3)	1.3	0.019	3.8	0.142	4.5	0.198	n.d.	n.d.
Total identified	99.7	1.538	96.6	3.625	97.7	4.274	95.9	2.899
unknown (R4)	n.d.	n.d.	0.4	0.016	0.6	0.027	n.d.	n.d.
Total characterised *	n.d.	n.d.	0.4	0.016	0.6	0.027	n.d.	n.d.
Distillate (not analysed)	---	---	---	---	0.2	0.008	3.5	0.106
Total extractable	99.7	1.538	97.0	3.641	98.5	4.309	99.4	3.006
Total bound (PES) **	0.3	0.004	3.0	0.113	1.5	0.067	0.6	0.018
Accountability	100.0	1.543	100.0	3.755	100.0	4.376	100.0	3.024

Figure B.8.1.3.4._CA-8: The results of the study by [Bongartz and Klankers; 2012] – the results of the profiling of TRR in the rotational crops (copied from the study report).

The second study – by [Roohi and Buntain; 2004] was aimed on the determination of the residues flurtamone, a compound also identified as a precursor of TFA, in rotational crop. Due to the fact that in the study was used the active compound other than the compound of interest of the present evaluation – Flurtamone and not Flufenacet, the study is of the limited utility for the current evaluation. However, in the summarised study report it was stated that the results of the study by [Roohi and Buntain; 2004] confirmed the statement that TFA will dissipate from soil throughout its uptake by plants.

On the basis of the performed evaluation it was proposed to consider the PUF = 0.59, determined in the **Study 2** (by [Bongartz; 2013]) as appropriate input value to be used in higher-tier leaching model calculations, in line with recommendations of the EFSA PPR-Panel [EFSA Journal; 2013].

RMS considers that conclusion correctly drawn and therefore valid.

**Summary – the determination of PUF values suitable as input parameter
for GW/SW model exposure assessment**

The PUF – plant uptake factor was determined in three separate experiments – *Study 1*, *Study 2* and *Study 3*, for the following major soil degradation products of Flufenacet: FOE Sulfonic acid, FOE Methylsulfone, FOE 5043-Trifluoroethanesulfonic acid – FOE TFESA (all in *Study 1*), and Trifluoroacetic acid – TFA (in *Study 2* and *Study 3*). The PUF values for FOE Sulfonic acid, FOE Methylsulfone and FOE TFESA were determined for Wheat as the experimental crop, while for TFA the test crops for which the PUF values were determined were Wheat, Corn (Maize) and Tomato.

Additionally was submitted a study, being in fact a position paper, supporting the value of PUF proposed for TFA.

For all four test compounds the experimental PUF values were determined for Wheat, the crop that may be considered representative for all cereals.

The determined values are:

- for FOE Sulfonic acid the PUF in cereals is **0.46**;
- for FOE Methylsulfone the PUF in cereals is **1.31**;
- for FOE 5043-Trifluoroethanesulfonic acid the PUF in cereals is **1.36**;
- for TFA (Trifluoroacetic acid) the PUF in cereals is **0.59**.

The Applicant proposed to use two of these experimentally derived values – PUF for FOE Sulfonic acid and PUF for TFA, as input values for GW model exposure assessment (please also refer to the point B.8.3. in the document Vol. 3_CP – B.8. of this Renewal Assessment Report).

RMS decided to verify the correctness of that selection in light of the recommendations of the current Guidelines. That was done using the *Generic Guidance for Tier 1 FOCUS Ground Water Assessments, Version 2.2, May 2014*, the document, which in paragraph 2.4.4 – *Crop related substance parameters* provides the recommendations with regard to the appropriate selection of the Plant Uptake Factor value. It is stated that the recommended default value for all compounds is 0. However, when a reliable measured K_{OW} value determined for neutral pH is available, the Briggs equation proposed for calculation of TSCF (Transpiration Stream Concentration Factor) may be used. So determined TSCF value may be used as input parameter for PUF in GW model exposure assessment. The Briggs equation for calculating TSCF presented in the cited above Guidance document looks as follows:

$$TSCF = 0.784 \exp \{(-[\text{Log}(K_{OW}) - 1.78]^2 / 2.44)\}$$

RMS decided to use it in order to calculate the TSCF values for Flufenacet and all its major soil degradation products, for which the GW model exposure assessment shall be performed and for which were available the reliable $\text{Log } P_{OW}$ (= $\text{Log } K_{OW}$) presented in section B.2 (Physicochemical properties) of this Renewal Assessment Report. The results of the calculations, together with the input parameters used in them, are presented below in the table B.8.1.3.4._CA-16. As a next step, the calculated values were compared with the proposed in the same Guideline maximum recommended TSCF value – 0.8, and, where available, with the experimental value. That was done in order to determine the suitable value representing TSCF/PUF to be used as input parameter in GW model exposure assessment. These values are also presented in the table B.8.1.3.4._CA-16. The TSCF/PUF values recommended as input for GW/SW modelling are given in **bold**.

Table B.8.1.3.4._CA-16: The results of the determination of TSCF/PUF value suitable for GW/SW model exposure assessment

Compound	Ionisable substance	Experimental values		TSCF		Measured PUF	TSCF/PUF value selected for modelling
		$\text{Log } P_{OW}$	measured at pH	calculated	Regulatory upper limit		
Flufenacet	No	3.5	7.0	0.744	0.8	n. a. ³⁾	0.744
FOE Oxalate	No	2.2	7.0	0.983	0.8	n. a. ³⁾	0.8
FOE Sulfonic acid	Yes	-2.72	7.0	0.133	0.8	0.46	0.46
FOE Methylsulfone	No	1.7	7.0	0.999	0.8	1.31	0.8
FOE Thiadone	No	0.62	7.0	0.874	0.8	n. a. ³⁾	0.8
FOE TFESA ¹⁾	Yes	-2.95	7.0	0.107	0.8	1.36	0.8
TFA ²⁾	Yes	-2.6	7.0	0.148	0.8	0.59	0.59

Footnotes to the table:

1) FOE TFESA = FOE 5043-Trifluoroethanesulfonic acid;

2) TFA = Trifluoroacetic acid;

3) n. a. = value not available (not determined experimentally).

B.8.1.3.5. – Summary of the soil mobility

The examination of the mobility of Flufenacet and its major transformation products in soil covered following issues:

- column leaching,
- aged residue column leaching,
- lysimeter studies,
- determination of the Plant Uptake Factor – PUF, as “Other studies”

The Applicant did not submit any studies covering the issue of the column leaching of Flufenacet. Instead, in the provided justification for the non-submission, stated that it was covered by the results of the examination of sorption in soil at equilibrium (batch sorption studies) and those aimed on the examination of leaching of the aged residues. That justification was found acceptable by the RMS. It shall be indicated however, that the evaluation of the study examining the leaching behaviour of the aged residues of Flufenacet demonstrated that the study was not acceptable.

Two additional open-literature studies found by the RMS, considered supplementary, indicated that under typical EU conditions Flufenacet should not move in the soil profile below the depth of 25 cm. Such statement seems to be confirmed by the results of the field dissipation studies performed for Flufenacet.

Additionally, a study was submitted examining the column leaching of one of the major soil degradation products of Flufenacet – TFA. That study, performed using four European soils, showed that TFA was very mobile in soil. The key results of that study are presented below.

The leaching behaviour of TFA was examined using soil columns filled with one of the following test soils:

- Loamy sand (*Laacherhof AXXa*) test soil, having OC = 1.8% and pH = 6.2;
- Loam (*Dollendorf II*) test soil, having OC = 5.2% and pH = 7.4;
- Silt loam (*Höfchen am Hohenseh*) test soil, having OC = 1.6 and pH = 6.5;
- Sandy loam (*Laacherhof Wurmwielse*) test soil, having OC = 1.9 and pH = 5.3.

The experiment was performed in two variants, denominated **Study design A** and **Study design B**, that may be characterised as follows:

- in **Study design A** leaching lasted 48 hours and was performed with 393 mL of artificial rain (0.01M $\text{CaCl}_{2\text{aq}}$), corresponding to 200 mm of rain;
- in **Study design B** leaching lasted 120 hours and was performed with 984 mL of artificial rain (0.01M $\text{CaCl}_{2\text{aq}}$), corresponding to 502 mm of rain;

In the variant denominated **Study design A** the following results were obtained for TFA:

- amount of TFA in the eluates (mean values of the two replicates), expressed as % AR, was:
 - 95.5% AR for columns filled with Loamy sand (*Laacherhof AXXa*) test soil;
 - 73.2% AR for columns filled with Loam (*Dollendorf II*) test soil;
 - 92.1% AR for columns filled with Silt loam (*Höfchen am Hohenseh*) test soil;
 - 66.2% AR for columns filled with Sandy loam (*Laacherhof Wurmwielse*) test soil.
- the extractable radioactivity retained within soil columns attributed to TFA was (mean values of the two replicates):
 - 5.0% AR for columns filled with Loamy sand (*Laacherhof AXXa*) test soil;
 - 28.3% AR for columns filled with Loam (*Dollendorf II*) test soil;
 - 6.5% of AR for columns filled with Silt loam (*Höfchen am Hohenseh*) test soil;
 - 35.6% AR for columns filled with Sandy loam (*Laacherhof Wurmwielse*) test soil.
- the NER fraction attributed to TFA, expressed as % AR, in the soil columns (mean values of the two replicates) was:
 - 1.2% AR for columns filled with Loamy sand (*Laacherhof AXXa*) test soil;
 - 1.8% AR for columns filled with Loam (*Dollendorf II*) test soil;
 - 0.8% AR for columns filled with Silt loam (*Höfchen am Hohenseh*) test soil;
 - 1.1% AR for columns filled with Sandy loam (*Laacherhof Wurmwielse*) test soil.
- the distribution of residues of TFA in soil was following:
 - for columns filled with Loamy sand (*Laacherhof AXXa*) test soil they were found predominantly in the lowest segment – S5;

- for columns filled with Loam (*Dollendorf II*) test soil the highest concentration of TFA residues was determined in the top section of the column (segments S1 and S2) with the peak amount in segment S2, and it gradually decreased towards the bottom of the soil column;
- for columns filled with Silt loam (*Höfchen am Hohenseh*) test soil they were found predominantly in the lowest segment – S5;
- for columns filled with Sandy loam (*Laacherhof Wurmwielse*) test soil the residues of TFA were generally found in the lower part of the column, with the peak amount in the middle section S3.
- The K_d and K_{dOC} values determined for TFA in this experiment were following:
 - for the test soil Loamy sand (*Laacherhof AXXa*) $K_d = 0.0$ mL/g and $K_{dOC} = 0.0$ mL/g;
 - for the test soil Loam (*Dollendorf II*) $K_d = 0.0$ mL/g and $K_{dOC} = 0.0$ mL/g;
 - for the test soil Silt loam (*Höfchen am Hohenseh*) $K_d = 0.0$ mL/g and $K_{dOC} = 0.0$ mL/g;
 - for the test soil Sandy loam (*Laacherhof Wurmwielse*) $K_d = 0.0$ mL/g and $K_{dOC} = 0.0$ mL/g;
 - mean $K_d = 0.0$ mL/g and $K_{dOC} = 0.0$ mL/g.

In the variant denominated **Study design B** the following results were obtained for TFA:

- amount of TFA in the eluates (mean values of the two replicates), expressed as % AR, was:
 - 101.1% AR for columns filled with Loamy sand (*Laacherhof AXXa*) test soil;
 - 96.3% AR for columns filled with Loam (*Dollendorf II*) test soil;
 - 98.6% AR for columns filled with Silt loam (*Höfchen am Hohenseh*) test soil;
 - 100.9% AR for columns filled with Sandy loam (*Laacherhof Wurmwielse*) test soil.
- the amount of radioactivity retained within soil columns attributed to TFA was not analysed because it was wholly recovered in leachates.
- The K_d and K_{dOC} values determined for TFA in this experiment were following:
 - for the test soil with Loamy sand (*Laacherhof AXXa*) $K_d = 0.1$ mL/g and $K_{dOC} = 4.5$ mL/g;
 - for the test soil Loam (*Dollendorf II*) $K_d = 0.0$ mL/g and $K_{dOC} = 0.0$ mL/g;
 - for the test soil Silt loam (*Höfchen am Hohenseh*) $K_d = 0.2$ mL/g and $K_{dOC} = 11.3$ mL/g;
 - for the test soil Sandy loam (*Laacherhof Wurmwielse*) $K_d = 0.2$ mL/g and $K_{dOC} = 7.1$ mL/g;
 - mean $K_d = 0.2$ mL/g and $K_{dOC} = 9.1$ mL/g.

The aged residues leaching was examined in one study, submitted also for the previous authorisation of Flufenacet in the EU. RMS evaluated that study for its compliance with the current guidelines, in particular the OECD Guideline for testing chemicals No. 312. Several minor deficiencies were stated that had no impact on the validity of the study. However, the thorough examination of the study report showed that there was a significant discrepancy between the application rate declared to be used to treat soil subjected to the ageing procedure and that used in the leaching experiment with aged soil.

Second problem identified in the study report was the fact that the analytical procedure used to characterise quantitatively and qualitatively the residues in soil after ageing was not presented.

As a result, mainly due to the discrepancies in the amount of the radioactivity introduced into soil at the beginning of the ageing period and that used in leaching experiment, introduced with aged soils, RMS decided to consider the study not acceptable because of the significant uncertainty related to the reliability of the obtained results.

The leaching behaviour of Flufenacet and its degradation products through the undisturbed soil profiles under the agronomic and climatic conditions relevant for Germany was examined on four outdoor lysimeters. The results of that examination were presented in two study reports submitted by the Applicant for the purpose of the current evaluation. Additionally the Applicant submitted the interim reports of the same experiments, not summarised in the Renewal Assessment Report for Flufenacet, but analysed for their compliance with the adequate final reports. The third study submitted for evaluation was aimed on the validation of the lysimeter studies by comparing their results with those of the modelling exposure assessment carried out for the GW compartment. RMS however decided not to use it, as the modelling tools and scenarios were not those recommended by FOCUS.

The key data and results obtained in the two studies are summarily presented below in tables B.8.1.3.5._CA-1 – B.8.1.3.5._CA-1c.

Table B.8.1.3.5_ CA-1: The key data and results obtained in the outdoor lysimeter studies.

Parameter				Data for Lysimeter			
				#15	#16	#17	#18
General information	Trial site	Test facility		Lysimeter station of Bayer AG	Lysimeter station of Bayer AG	Lysimeter station of Bayer AG	Lysimeter station of Bayer AG
		Location (town, region, country)		Monheim, NRW, Germany	Monheim, NRW, Germany	Monheim, NRW, Germany	Monheim, NRW, Germany
		Geographic coordinates	Longitude	6° 55' E	6° 55' E	6° 55' E	6° 55' E
			Latitude	51° 4' N	51° 4' N	51° 4' N	51° 4' N
	Long-term weather conditions at trial site (1996 – 1995)	Average rainfall [mm]	Annual	745	745	745	745
			Monthly min. (month)	42.7 (February)	42.7 (February)	42.7 (February)	42.7 (February)
			Monthly max. (month)	78.1 (June)	78.1 (June)	78.1 (June)	78.1 (June)
		Average annual relative air humidity [%]		73	73	73	73
		Average temperature at 2 metres above the ground [°C]	Annual	10.0	10.0	10.0	10.0
			Monthly min. (month)	2.6 (January)	2.6 (January)	2.6 (January)	2.6 (January)
			Monthly max. (month)	18.4 (June)	18.4 (June)	18.4 (June)	18.4 (June)
		Average annual wind velocity [m/s.]		2.5	2.5	2.5	2.5
		Average radiant heat [kJ/cm ²]	Annual	29.1	29.1	29.1	29.1
			Monthly min. (month)	5.8 (December)	5.8 (December)	5.8 (December)	5.8 (December)
			Monthly max. (month)	53.1 (July)	53.1 (July)	53.1 (July)	53.1 (July)
	Duration of the study	Preliminary period	Duration [years]	1	1	1	1
			Beginning	March 1992	March 1992	March 1992	March 1992
			End	May 1993	May 1993	May 1993	May 1993
		Experimental period	Duration [years]	3	3	2.5	2.5
			Beginning	May 1993	May 1993	May 1993	May 1993
			End	April 1996	April 1996	November 1995	November 1995
Characterisation of lysimeter	Lysimeter depth	Total [cm]		135	135	120	120
		Soil monolith [cm]		130	130	115	115
		Gravel layer [cm]		5	5	5	5
		Soil type (FAO)		Eutric Cambisol	Eutric Cambisol	Eutric Cambisol	Eutric Cambisol
	Characteristic of soil monolith	Soil properties, depth 0 – 30 cm	Soil texture (USDA)	Sandy loam	Sandy loam	Sandy loam	Sandy loam
			pH (CaCl ₂)	7.04	7.04	7.04	7.04
			OC%	1.41	1.41	1.41	1.41
			CEC [meq/100g]	9.61	9.61	9.61	9.61
			Microbial biomass [mg/kg]	235	235	235	235
		Soil properties, depth 30 – 60 cm	Soil texture (USDA)	Sandy loam	Sandy loam	Sandy loam	Sandy loam
			pH (CaCl ₂)	7.24	7.24	7.24	7.24
			OC%	0.34	0.34	0.34	0.34
			CEC [meq/100g]	7.43	7.43	7.43	7.43
			Microbial biomass [mg/kg]	34	34	34	34
		Soil properties, depth 60 – 100 cm	Soil texture (USDA)	Loamy sand	Loamy sand	Loamy sand	Loamy sand
			pH (CaCl ₂)	7.18	7.18	7.18	7.18
			OC%	0.19	0.19	0.19	0.19
			CEC [meq/100g]	7.57	7.57	7.57	7.57
			Microbial biomass [mg/kg]	11	11	11	11
		Soil properties, depth 100 – 115 cm	Soil texture (USDA)	Loamy sand	Loamy sand	Loamy sand	Loamy sand
			pH (CaCl ₂)	7.46	7.46	7.46	7.46
			OC%	0.17	0.17	0.17	0.17
			CEC [meq/100g]	8.52	8.52	8.52	8.52
			Microbial biomass [mg/kg]	13	13	13	13
Maintenance data	Application of the test compound	Test compound		¹⁴ C-Flufenacet	¹⁴ C-Flufenacet	¹⁴ C-Flufenacet	¹⁴ C-Flufenacet
		Number of applications/ experiment		2	2	2	2
		1 st application	Year of experiment	1	1	1	1
			Application date	12/05/1993	12/05/1993	13/05/1993	13/05/1993
			Application rate	48.14 mg/m ² (480 g/ha)	48.14 mg/m ² (480 g/ha)	48.14 mg/m ² (480 g/ha)	48.14 mg/m ² (480 g/ha)
		2 nd application	Year of experiment	2	2	1	1
			Application date	05/05/1994	05/05/1994	03/11/1993	03/11/1993
			Application rate	48.04 mg/m ² (480 g/ha)	48.04 mg/m ² (480 g/ha)	18.02 mg/m ² (180 g/ha)	18.02 mg/m ² (180 g/ha)

Table B.8.1.3.5._CA-1a: The key data and results obtained in the outdoor lysimeter studies (continued).

Parameter				Data for Lysimeter			
				#15	#16	#17	#18
Maintenance data, continued	Crop data	1 st crop, target	Crop	Maize, grain	Maize, grain	Maize, fodder	Maize, fodder
			Year of experiment	1	1	1	1
			Date of sowing	10/05/1993	10/05/1993	10/05/1993	10/05/1993
			Date of harvest	12/11/1993	12/11/1993	28/09/1993	28/09/1993
			Harvested parts	Corncoobs	Corncoobs	Silage material	Silage material
		2 nd crop, target	Crop	Maize, grain	Maize, grain	Winter wheat	Winter wheat
			Year of experiment	2	2	1 – 2	1 – 2
			Date of sowing	05/05/1994	05/05/1994	02/11/1993	02/11/1993
			Date of harvest	10/05/1994	10/05/1994	03/08/1994	03/08/1994
			Harvested parts	Corncoobs	Corncoobs	Grain and straw	Grain and straw
		3 rd crop, succeeding	Crop	Sugar beet	Sugar beet	Sugar beet	Sugar beet
			Year of experiment	3	3	3	3
			Date of sowing	13/04/1995	13/04/1995	13/04/1995	13/04/1995
			Date of harvest	07/11/1995	07/11/1995	07/11/1995	07/11/1995
			Harvested parts	Leaves and tubers	Leaves and tubers	Leaves and tubers	Leaves and tubers
	Irrigation and precipitation during experiment	1 st year	Precipitation [mm]	897.1	897.1	897.1	897.1
			Irrigation [mm]	46.0	46.0	51.0	51.0
			Sum [mm]	943.1	943.1	948.1	948.1
		2 nd year	Precipitation [mm]	814.2	814.2	813.9	813.9
			Irrigation [mm]	100.0	100.0	75.0	75.0
			Sum [mm]	914.2	914.2	888.9	888.9
		3 rd year	Precipitation [mm]	496.1	496.1	338.0	338.0
			Irrigation [mm]	104.0	104.0	104.0	104.0
			Sum [mm]	600.1	600.1	442.0	442.0
		Total	Precipitation [mm]	2207.5	2207.5	2049.0	2049.0
			Irrigation [mm]	250	250	250	250
			Sum [mm]	2457	2457	2279.0	2279.0
Radioactivity - recovery	Radioactivity recovered [% AR]	in soil monolith	0- 30 cm	40.289	41.414	37.80	~48.2
			30 – 60 cm	2.095	3.128	2.46	~3.1
			below 60 cm	0.777	0.485	~2.00	~1.7
			total	43.16	45.03	42.33	52.96
		in leachates	1 st year	0.772	0.815	1.436	1.563
			2 nd year	0.250	0.161	0.122	0.150
			3 rd year	0.006	0.006	0.006	0.007
			total	0.64	0.58	~1.56	~1.72
		in crops	1 st crop	0.014	0.015	0.38	0.39
			2 nd crop	0.016	0.014	0.04	0.05
			3 rd crop	0.059	0.061	0.07	0.07
			total	0.08	0.08	0.48	0.50
		Total recovered		43.89	45.68	44.38	55.18
		Lost (eg as ¹⁴ CO ₂) [% AR]		56.11	54.32	55.62	44.82
Radioactivity in soil monoliths	in 0 – 30 cm layer	Total [% AR]		40.29	41.41	37.80	48.2
		identified as Flufenacet	[µg/layer]	1860.96	1839.68	450.75	528.48
		identified as FOE Alcohol	[µg/kg soil FW]	3.91	3.91	1.07	1.06
		identified as FOE Oxalate	[µg/layer]	143.49	159.02	60.09	87.67
		identified as FOE Sulfonic acid	[µg/kg soil FW]	0.30	0.34	0.14	0.18
		identified as FOE Oxalate	[µg/layer]	212.84	167.72	28.23	63.74
		Identified as FOE Sulfonic acid	[µg/kg soil FW]	0.45	0.36	0.07	0.13
		Identified as FOE Sulfonic acid	[µg/layer]	71.44	138.39	45.74	43.42
		Identified as FOE Sulfonic acid	[µg/kg soil FW]	0.15	0.29	0.11	0.09
	in 30 – 60 cm layer	Total [% AR]		2.095	3.128	2.46	3.1
Detailed characterisation of leachates	1 st year early leachate	Collection time	Week of experiment	24	24	24	24
			Collection date	29/10/1993	29/10/1993	29/10/1993	29/10/1993
		Volume of leachate [L]		3.7	4.7	8.2	8.2
		Characterisation of TRR – Total Radioactivity Recovered	Total TRR [µg a. i. equival./L]	0.256	0.221	0.588	0.505
			acidic TRR [µg a. i. equival./L]	0.218	0.183	0.539	0.477
			¹⁴ CO ₂ -associated radioactivity [% total TRR]	14.87	17.23	8.34	5.64
		Characterisation of acidic TRR ¹⁾	Flufenacet [µg /L]	<0.011	<0.014	0.006	<0.005
			FOE ALC [µg /L]	<0.001	0.006	0.002	0.095
			FOE OXA [µg /L]	0.002	0.007	<0.001	0.005
			FOE SA [µg /L]	0.065	0.025	0.225	0.182
			FOE TGS [µg /L]	0.017	0.009	0.015	0.027

Footnotes to the table:

1) Abbreviations used: FOE ALC – FOE Alcohol, FOE OXA – FOE Oxalate, FOE SA – FOE Sulfonic acid, FOE TGS – FOE Thioglycolate sulfonide.

Table B.8.1.3.5._CA-1b: The key data and results obtained in the outdoor lysimeter studies (continued).

Parameter				Data for Lysimeter			
				#15	#16	#17	#18
Detailed characterisation of leachates - continued	1 st year leachate with max. TRR	Collection time	Week of experiment	37	35	38	38
			Collection date	28/01/1994	12/01/1994	04/02/1994	04/02/1994
		Volume of leachate [L]		17.2	21.5	21.3	21.3
		Characterisation of TRR – Total Radioactivity Recovered	Total TRR [µg a. i. equivalent/L]	2.350	1.989	5.106	5.455
			acidic TRR [µg a. i. equivalent/L]	2.228	1.915	4.940	5.255
			¹⁴ CO ₂ -associated radioactivity [% total TRR]	5.19	3.72	4.26	3.58
		Characterisation of acidic TRR ¹⁾	Flufenacet [µg /L]	<0.007	<0.017	<0.011	<0.001
			FOE ALC [µg /L]	0.001	0.004	0.006	0.044
			FOE OXA [µg /L]	0.007	0.041	0.005	0.036
			FOE SA [µg /L]	1.293	1.090	3.375	3.682
			FOE TGS [µg /L]	0.079	0.036	0.017	0.028
	1 st year late leachate	Collection time	Week of experiment	47	47	47	47
			Collection date	11/04/1994	11/04/1994	11/04/1994	11/04/1994
		Volume of leachate [L]		11.5	15.5	19.4	15.0
		Characterisation of TRR – Total Radioactivity Recovered	Total TRR [µg a. i. equivalent/L]	0.850	0.798	2.545	3.102
			acidic TRR [µg a. i. equivalent/L]	0.767	0.732	1.389	2.916
			¹⁴ CO ₂ -associated radioactivity [% total TRR]	9.82	8.27	6.13	6.00
		Characterisation of acidic TRR ¹⁾	Flufenacet [µg /L]	<0.035	0.005	0.002	0.002
			FOE ALC [µg /L]	0.001	<0.001	0.008	0.041
			FOE OXA [µg /L]	0.012	0.031	0.026	0.017
			FOE SA [µg /L]	0.332	0.301	1.302	1.920
			FOE TGS [µg /L]	0.014	0.010	0.005	0.012
	1 st year annual leachate (pooled)	Collection time	Week of experiment	50	50	50	50
			Collection date	29/04/1994	29/04/1994	29/04/1994	29/04/1994
		Volume of leachate [L]		349.8	402.4	399.1	383.1
		Characterisation of TRR – Total Radioactivity Recovered	Total TRR [µg a. i. equivalent/L]	1.062	0.931	2.380	2.699
			acidic TRR [µg a. i. equivalent/L]	0.99	0.87	2.26	2.56
			¹⁴ CO ₂ -associated radioactivity [% total TRR]	6.47	6.82	5.31	5.35
		Characterisation of acidic TRR ¹⁾	Flufenacet [µg /L]	0.020	0.033	0.004	0.005
			FOE ALC [µg /L]	<0.002	0.000	0.034	0.016
			FOE OXA [µg /L]	0.015	0.004	0.017	0.006
			FOE SA [µg /L]	0.589	0.489	1.355	1.616
			FOE TGS [µg /L]	0.016	0.014	0.030	0.027
	2 nd year annual leachate (pooled)	Collection time	Week of experiment	103	103	103	103
			Collection date	05/05/1995	05/05/1995	05/05/1995	05/05/1995
		Volume of leachate [L]		317.6	299.9	365.4	368.9
		Characterisation of TRR – Total Radioactivity Recovered	Total TRR [µg a. i. equivalent/L]	0.758	0.516	0.221	0.269
			acidic TRR [µg a. i. equivalent/L]	0.670	0.46	0.19	0.22
			¹⁴ CO ₂ -associated radioactivity [% total TRR]	11.10	11.19	17.06	23.02
		Characterisation of acidic TRR ¹⁾	Flufenacet [µg /L]	0.003	0.003	0.002	0.005
			FOE ALC [µg /L]	0.003	0.005	0.001	0.004
			FOE OXA [µg /L]	<0.018	<0.014	0.009	0.006
			FOE SA [µg /L]	0.235	0.149	0.013	0.016
			FOE TGS [µg /L]	0.020	0.015	0.022	0.019

Footnotes to the table:

1) Abbreviations used: FOE ALC – FOE Alcohol, FOE OXA – FOE Oxalate, FOE SA – FOE Sulfonic acid, FOE TGS – FOE Thioglycolate sulfoxide.

Table B.8.1.3.5._CA-1c: The key data and results obtained in the outdoor lysimeter studies (continued).

Parameter				Data for Lysimeter			
				#15	#16	#17	#18
Detailed characterisation of leachates - continued	3 rd year annual leachate (pooled)	Collection time	Week of experiment	115	115	115	115
			Collection date	26/07/1995	26/07/1995	26/07/1995	26/07/1995
		Volume of leachate [L]		13.0	17.0	17.5	19.1
		Characterisation of TRR – Total Radioactivity Recovered	Total TRR [µg a. i. equival./L]	0.432	0.353	0.239	0.238
			acidic TRR [µg a. i. equival./L]	0.334	0.23	0.15	0.14
			¹⁴ C ₂ -associated radioactivity [% total TRR]	22.80	34.56	35.22	40.88
		Characterisation of acidic TRR: compound/concentration [µg/L]		FOE SA ¹⁾ ≤ 0.25	FOE SA ¹⁾ ≤ 0.17	not performed	not performed
	Total leachate	Collection time	Weeks of experiment	115	115	115	115
			Collection dates: beginning/end	12/05/1993 26/07/1995	12/05/1993 26/07/1995	12/05/1993 26/07/1995	12/05/1993 26/07/1995
		Volume of leachate [L] (total)		680.4	719.3	782.0	771.1
		Characterisation of TRR – Total Radioactivity Recovered; average values	Total TRR [µg a. i. equival./L]	0.906	0.742	1.310	1.492
			acidic TRR [µg a. i. equival./L]	0.83	0.68	1.25	1.38
			¹⁴ C ₂ -associated radioactivity [% total TRR]	8.42	8.39	6.28	6.85

Footnotes to the table:

1) Abbreviations used: FOE SA – FOE Sulfonic acid.

It may be stated that of all the compounds possible to be identified as originating from Flufenacet radiolabelled in fluorophenyl ring (including Flufenacet itself) only FOE Sulfonic acid was demonstrated to be found in leachates in amounts > 0.1 µg/L, what conformed the risk to GW associated to that degradation product demonstrated in GW model exposure assessment (for details please refer to the results of calculations presented under the point B.8.5 in the Vol. 3-CP, B.8 of this Renewal Assessment Report).

Neither Flufenacet nor the second major soil degradation product relevant for that radiolabelling position – FOE Oxalate, were detected in leachates in amounts > 0.1 µg/L, what may indicate that they would not pose a threat to the GW compartment.

In soil and leachates FOE Alcohol was detected – the compound determined in the studies examining the route of degradation of Flufenacet in aerobic soil to be minor/transient and therefore not taken into account in the GW model exposure assessment. It shall be indicated however that the would-be risk it may pose to the GW compartment was covered by the calculations carried out for FOE Oxalate – its immediate degradate.

Also detected in leachates was FOE Thioglycolate sulfoxide (FOE TGS), the compound not taken in the model GW exposure assessment into consideration, being identified as minor soil degradation product. It shall be indicated however, that in the study it was determined in leachates in amounts <0.1 µg/L, what may indicate that it would not pose a serious threat to the GW compartment.

Finally, it shall be indicated that, due to the fact that in the experiments was used Flufenacet radiolabelled only in the fluorophenyl ring, they gave no information of the laching potential of the degradation products formed from the second moiety present within the molecule of Flufenacet – thiadiazole.

The comparative analysis of the application pattern (crops, application timing and application rates) used in the experiments and the EU-representative application pattern proposed for the current authorisation of Flufenacet in the EU showed that they may be considered as providing supplementary information with regard to the risk posed by Flufenacet and its soil degradation products to the GW compartment, but for the purpose of the decision making should be considered with care.

The PUF – plant uptake factor was determined in three separate experiments for the following major soil degradation products of Flufenacet: FOE Sulfonic acid, FOE Methylsulfone, FOE 5043-Trifluoroethanesulfonic acid – FOE TFESA (for all three in one experiment), and Trifluoroacetic acid – TFA (in two separate experiments). The PUF values for FOE Sulfonic acid, FOE Methylsulfone and FOE TFESA were determined for Wheat as the experimental crop, while for TFA the test crops for which the PUF values were determined were Wheat, Corn (Maize) and Tomato.

Additionally was submitted a study, being in fact a position paper, supporting the value of PUF proposed for TFA.

For all four test compounds the experimental PUF values were determined for Wheat, the crop that may be considered representative for all cereals.

The determined values are:

- for FOE Sulfonic acid the PUF in cereals is **0.46**;
- for FOE Methylsulfone the PUF in cereals is **1.31**;
- for FOE 5043-Trifluoroethanesulfonic acid the PUF in cereals is **1.36**;
- for TFA (Trifluoroacetic acid) the PUF in cereals is **0.59**.

The Applicant proposed to use two of these experimentally derived values – PUF for FOE Sulfonic acid and PUF for TFA, as input values for GW model exposure assessment (please also refer to the point B.8.3. in the document Vol. 3_CP – B.8. of this Renewal Assessment Report).

RMS decided to verify the correctness of that selection in light of the recommendations of the current Guidelines. That was done using the *Generic Guidance for Tier 1 FOCUS Ground Water Assessments, Version 2.2, May 2014*, document, which in paragraph 2.4.4 – *Crop related substance parameters* provides the recommendations with regard to the appropriate selection of the Plant Uptake Factor value. It is stated that the recommended default value for all compounds is 0. However, when a reliable measured K_{OW} value determined for neutral pH is available, the Briggs equation proposed for calculation of TSCF (Transpiration Stream Concentration Factor) may be used and so determined TSCF value used as input parameter for PUF in GW model exposure assessment. The Briggs equation for calculating TSCF presented in the cited above Guidance document looks as follows:

$$TSCF = 0.784 \exp \{(-[\text{Log}(K_{OW}) - 1.78]^2 / 2.44)\}$$

RMS decided to use it in order to calculate the TSCF values for Flufenacet and all its major soil degradation products, for which the GW model exposure assessment shall be performed and for which were available the reliable $\text{Log } P_{OW}$ (= $\text{Log } K_{OW}$) presented in section B.2 (Physicochemical properties) of this Renewal Assessment Report. The results of the calculations, together with the input parameters used in them, are presented below in the table B.8.1.3.5._CA-2. As a next step the calculated values were compared with the proposed in the same Guideline maximum recommended TSCF value – 0.8, and, where available, with the experimental value. That was done in order to determine the suitable value representing TSCF/PUF to be used as input parameter in GW model exposure assessment. These value are also presented in the table B.8.1.3.5._CA-2. The TSCF/PUF values recommended as input for GW/SW modelling are given in **bold**.

Table B.8.1.3.5._CA-2: The results of the determination of TSCF/PUF value suitable for GW/SW model exposure assessment

Compound	Ionisable substance	Experimental values		TSCF		Measured PUF	TSCF/PUF value selected for modelling
		$\text{Log } P_{OW}$	measured at pH	calculated	Regulatory upper limit		
Flufenacet	No	3.5	7.0	0.744	0.8	n. a. ³⁾	0.744
FOE Oxalate	No	2.2	7.0	0.983	0.8	n. a. ³⁾	0.8
FOE Sulfonic acid	Yes	-2.72	7.0	0.133	0.8	0.46	0.46
FOE Methylsulfone	No	1.7	7.0	0.999	0.8	1.31	0.8
FOE Thiadone	No	0.62	7.0	0.874	0.8	n. a. ³⁾	0.8
FOE TFESA ¹⁾	Yes	-2.95	7.0	0.107	0.8	1.36	0.8
TFA ²⁾	Yes	-2.6	7.0	0.148	0.8	0.59	0.59

Footnotes to the table:

1) FOE TFESA = FOE 5043-Trifluoroethanesulfonic acid;

2) TFA = Trifluoroacetic acid;

3) n. a. = value not available (not determined experimentally).

B.8.1.4. – Summary of adsorption, desorption and mobility in soil

The sorption of Flufenacet onto soil at equilibrium was extensively examined in four studies using fourteen test soils. The results of that examination were used to obtain Freundlich sorption isotherms for adsorption and desorption processes and derive Freundlich sorption isotherm parameters. In case of adsorption reliable parameters of Freundlich isotherm were obtained for ten test soils, while for desorption the reliable Freundlich parameters were derived using nine test soils. They are presented below in two tables: B.8.1.4._CA-1 for adsorption and B.8.1.4._CA-2 for desorption. The results obtained for adsorption indicate that Flufenacet is moderately to strongly sorbed onto soil and that the process is not preferential. It was also determined that it was not pH-dependent.

Table B.8.1.4._CA-1: The results of the determination of the adsorption of Flufenacet onto soil at equilibrium – the reliable parameters of the Freundlich adsorption isotherm.

Soil name	Soil properties			Adsorption distribution coefficients		Freundlich adsorption isotherm parameters			
	Soil type (USDA)	pH	OC [%]	K_d [mL/g]	$K_{d oc}$ [mL/g]	K_f [mL/g]	$K_{f oc}$ [mL/g]	1/n	R^2
<i>Stanley (307)</i>	Silt loam	5.9	1.68	----	----	3.18	189.28	0.848	0.9971
<i>Hagerstown (318)</i>	Clay loam	6.4	1.28	----	----	2.81	219.53	0.878	0.9986
<i>Howe (395)</i>	Loamy sand	6.4	0.23	----	----	1.48	643.48	0.894	0.9932
<i>Monheim (3253)</i>	Sandy loam	6.4	1.4	----	----	4.55	325.00	0.920	0.9991
<i>Laacher Hof AXXa (AA)</i>	Loamy sand	5.8	2.2	----	----	3.55	161.6	0.928	0.9991
<i>Hoefchen am Hohenseh (HH)</i>	Silt loam	6.5	1.6	----	----	3.28	205.0	0.926	0.9965
<i>Hanscheider Hof (HN)</i>	Silt loam	5.3	2.7	----	----	5.10	188.9	0.926	0.9992
<i>Dollendorf II (DD)</i>	Loam	7.3	4.4	----	----	7.49	178.5	0.903	0.9994
<i>Wurmweise (WW)</i>	Sandy loam	5.1	1.7	----	----	3.39	195.2	0.980	0.9966
<i>Kamikawa</i>	Loam	4.9	2.1	----	----	8.96	426.5	0.958	0.9984
Geomean (n = 10)						3.89	245.9	----	----
Arithmetic mean (n = 10)						----	----	0.916	----
pH dependence						No			----

Table B.8.1.4._CA-2: The results of the determination of the desorption of Flufenacet onto soil at equilibrium – the reliable parameters of the Freundlich desorption isotherm.

Soil name	Soil properties			Desorption distribution coefficients		Freundlich desorption isotherm parameters			
	Soil type (USDA)	pH	OC [%]	K_d [mL/g]	$K_{d oc}$ [mL/g]	K_f [mL/g]	$K_{f oc}$ [mL/g]	1/n	R^2
<i>Stanley (307)</i>	Silt loam	5.9	1.68	----	----	3.81	226.79	0.864	0.9998
<i>Hagerstown (318)</i>	Clay loam	6.4	1.28	----	----	2.75	214.84	0.893	0.9996
<i>Howe (395)</i>	Loamy sand	6.4	0.23	----	----	2.10	913.04	0.911	0.9992
<i>Monheim (3253)</i>	Sandy loam	6.4	1.4	----	----	5.25	375.00	0.928	0.9993
<i>Laacher Hof AXXa (AA)</i>	Loamy sand	5.8	2.2	----	----	5.58	253.6	0.944	0.9988
<i>Hoefchen am Hohenseh (HH)</i>	Silt loam	6.5	1.6	----	----	5.64	352.3	0.943	0.9980
<i>Hanscheider Hof (HN)</i>	Silt loam	5.3	2.7	----	----	8.49	314.4	0.937	0.9996
<i>Dollendorf II (DD)</i>	Loam	7.3	4.4	----	----	11.71	278.7	0.908	0.9996
<i>Wurmweise (WW)</i>	Sandy loam	5.1	1.7	----	----	5.49	349.4	0.989	0.9967
Geomean (n = 9)						5.01	329.38	----	----
Arithmetic mean (n = 9)						----	----	0.924	----
pH dependence						No			----

The additional information on the soil sorption of Flufenacet at equilibrium were provided by three open-literature scientific papers. The key results obtained in them are presented below in the table B.8.1.4._CA-3. The values reported below may be considered as indicative and should not be used to derive the regulatory endpoints characterising soil sorption of Flufenacet.

Table B.8.1.4._CA-3: The results of the determination of the adsorption of Flufenacet onto soil at equilibrium obtained in the open-source literature scientific papers.

Study	Soil name	Soil properties			Freundlich adsorption isotherm parameters			
		Soil type	pH	OC [%]	K_f [mL/g]	K_{fOC} [mL/g]	1/n	r
<i>Gupta, Gajbhiye & Agnihotri; 2001</i>	<i>Inceptisol</i>	Sandy loam	7.1	0.34	2.26	664.71	0.988	0.99
<i>Gajbhiye & Gupta; 2001</i>	<i>Delhi</i>	Loamy sand	7.69	0.501	2.10	419.16	0.996	0.99
	<i>Ranchi</i>	Sandy clay loam	5.54	0.042	3.62	8619.05	0.981	0.98
	<i>Nagpur</i>	Clay	8.35	0.399	3.20	802.00	1.221	0.99
	<i>Kerala</i>	Sandy clay loam	4.45	0.456	4.39	962.72	1.015	0.99
<i>Rouchaud, Neus, Eelen, Bulcke; 2001</i>	<i>Melle</i>	Sandy loam	7.0	1.51 ¹⁾	16	1802	0.89	----
	<i>Zingem</i>	Loamy sand	6.4	1.60 ¹⁾	43	4602	0.91	----
	<i>Zevekote</i>	Clay loam	6.6	2.1 ¹⁾	15	1231	0.93	----
	<i>Cortil-Noirmont</i>	Silt loam	6.7	1.2 ¹⁾	9	1257	0.94	----

Footnotes to the table:

1) OM content reported, no values for OC content.

In the studies by [Gupta, Gajbhiye and Agnihotri; 2001] and [Gajbhiye and Gupta; 2001] for adsorption of Flufenacet onto test soil the value of the free Gibbs energy of adsorption – ΔG , was determined. It was in range $\Delta G = (-3.27) - (-5.08)$ [Kcal/mol], indicating that adsorption of Flufenacet onto soil was a spontaneous process and mechanistically it was predominantly physisorption. It was also demonstrated, in the study by [Gupta, Gajbhiye and Agnihotri; 2001], that the soil sorption of Flufenacet was strongly positively correlated with soil OC/OM content. As the results obtained in these two studies are in line with those from reliable regulatory studies, that conclusion may be considered to be a general conclusion with regard to the adsorption of Flufenacet onto soil.

Also examined was sorption onto soil at equilibrium of major soil degradation products of Flufenacet: FOE Oxalate, FOE Sulfonic acid, FOE Methylsulfone, FOE Thiadone, FOE 5043-Trifluoroethanesulfonic acid (TFESA) and Trifluoroacetic acid (TFA). The key results – Freundlich sorption parameters, are presented below, individually for each test compound.

For FOE Oxalate the reliable Freundlich isotherm parameters for adsorption were determined in three test soils. The desorption was not examined because of the low level of adsorption onto soil. The results are presented below in the table B.8.1.4._CA-4.

Table B.8.1.4._CA-4: The Freundlich adsorption and desorption parameters determined for FOE Oxalate.

Test soil – USDA type (name)	Key soil properties		Freundlich adsorption isotherm parameters			Freundlich desorption isotherm parameters		
	pH ¹⁾	OC [%]	K_F [mL/g]	K_{FOC} [mL/g]	1/n	K_F [mL/g]	K_{FOC} [mL/g]	1/n
<i>Sandy loam (Shipshe)</i>	6.3	0.75	0.096	12.80	0.933	Not determined		
<i>Silty clay loam (Drummer)</i>	6.6	2.13	0.153	7.18	0.824	Not determined		
<i>Silty clay (Oska-Martin)</i>	6.0	1.21	0.157	12.97	0.978	Not determined		
Geomean (n = 3)			0.132	10.60	----			
Arithmetic mean (n = 3)			----	----	0.912			
pH dependence			No					

Footnotes to the table:

1) Measured in water;

For FOE Sulfonic acid the reliable Freundlich isotherm parameters for adsorption were determined in four test soils. The desorption was not examined because of the low level of adsorption onto soil. The results are presented below in the table B.8.1.4._CA-5.

Table B.8.1.4._CA-5: The Freundlich adsorption and desorption parameters determined for FOE Sulfonic acid.

Test soil – USDA type (name)	Key soil properties		Freundlich adsorption isotherm parameters			Freundlich desorption isotherm parameters		
	pH ¹⁾	OC [%]	K _F [mL/g]	K _{F OC} [mL/g]	1/n	K _F [mL/g]	K _{F OC} [mL/g]	1/n
<i>Sand (Winder)</i>	5.8	0.27	0.051	18.88	0.865	Not determined		
<i>Sandy loam (Shipshe)</i>	6.3	0.75	0.106	14.13	1.002	Not determined		
<i>Silty clay loam (Drummer)</i>	6.6	2.13	0.204	9.58	0.931	Not determined		
<i>Silty clay (Oska-Martin)</i>	6.0	1.21	0.072	5.95	1.183	Not determined		
Geomean (n = 4)			0.094	11.10	----			
Arithmetic mean (n = 4)			----	----	0.995			
pH dependence			No					

Footnotes to the table:

1) Measured in water;

For FOE Methylsulfone reliable Freundlich isotherm parameters for adsorption and desorption were determined in five test soils. The results are presented below in the table B.8.1.4._CA-6.

Table B.8.1.4._CA-6: The of Freundlich adsorption and desorption parameters determined for FOE Methylsulfone.

Test soil – USDA type (name)	Key soil properties		Freundlich adsorption isotherm parameters			Freundlich desorption isotherm parameters		
	pH ¹⁾	OC [%]	K _F [mL/g]	K _{F OC} [mL/g]	1/n	K _F [mL/g]	K _{F OC} [mL/g]	1/n
<i>Loam (Wurmwiess)</i>	5.5	1.8	0.658	37.4	0.892	0.769	43.7	0.898
<i>Silt loam (Hoefchchen am Hohenseh)</i>	6.8	2.4	1.280	52.9	0.888	1.467	60.6	0.893
<i>Clay loam (Dollendorf II)</i>	7.4	4.6	1.569	33.2	0.900	1.820	38.6	0.912
<i>Sandy loam (Guadalupe)</i>	6.8	0.7	0.525	75.0	0.910	0.567	81.0	0.905
<i>Silt loam (Springfield)</i>	7.2	1.7	2.920	171.8	0.860	3.594	211.4	0.883
Geomean (n = 5)			1.152	61.03	----	1.332	70.57	----
Arithmetic mean (n = 5)			----	----	0.860	----	----	0.898
pH dependence			No			No		

Footnotes to the table:

1) Measured in water;

For FOE Thiadone the reliable Freundlich isotherm parameters for adsorption and desorption were determined in four test soils. The results are presented below in the table B.8.1.4._CA-7.

Table B.8.1.4._CA-7: The of Freundlich adsorption and desorption parameters determined for FOE Thiadone.

Test soil – USDA type (name)	Key soil properties		Freundlich adsorption isotherm parameters			Freundlich desorption isotherm parameters		
	pH ¹⁾	OC [%]	K _F [mL/g]	K _{F OC} [mL/g]	1/n	K _F [mL/g]	K _{F OC} [mL/g]	1/n
<i>Sand (Winder)</i>	5.8	0.27	0.115	42.59	0.781	0.467	172.96	0.909
<i>Sandy loam (Shipshe)</i>	6.3	0.75	0.332	44.27	0.806	1.368	182.40	0.867
<i>Silty clay loam (Drummer)</i>	6.6	2.13	0.611	28.68	0.672	1.559	73.91	0.654
<i>Silty clay (Oska-Martin)</i>	6.0	1.21	0.703	58.10	0.796	2.104	173.88	0.887
Geomean (n = 4)			0.358	42.10	----	1.203	141.90	----
Arithmetic mean (n = 4)			----	----	0.764	----	----	0.829
pH dependence			No			No		

Footnotes to the table:

1) Measured in water;

For Trifluoroacetic acid Freundlich isotherm parameters for adsorption were determined in five test soils. The desorption was not examined because of the very low level of adsorption onto soil. The results are presented below in the table B.8.1.4._CA-8.

Table B.8.1.4._CA-8: The of Freundlich adsorption and desorption parameters determined for Trifluoroacetic acid.

Test soil – USDA type (name)	Key soil properties		Freundlich adsorption isotherm parameters			Freundlich desorption isotherm parameters		
	pH ¹⁾	OC [%]	K _F [mL/g]	K _{F OC} [mL/g]	1/n	K _F [mL/g]	K _{F OC} [mL/g]	1/n
<i>Loam (Wurmwiese)</i>	5.5	1.76	0.0	0.0001	1.00	Not determined		
<i>Silt loam (Hoefchen am Hohenseh)</i>	6.8	2.42	0.0	0.0001	1.00	Not determined		
<i>Clay loam (Dollendorf II)</i>	7.4	4.72	0.0	0.0001	1.00	Not determined		
<i>Sandy loam (Guadalupe)</i>	6.8	0.7	0.0	0.0001	1.00	Not determined		
<i>Silt loam (Springfield)</i>	7.2	1.7	0.0	0.0001	1.00	Not determined		
Geomean (n = 5)			0.0	0.0001	----			
Arithmetic mean (n = 5)			----	----	1.00			
pH dependence			No					

Footnotes to the table:

1) Measured in water;

For FOE 5043-Trifluoroethanesulfonic acid reliable Freundlich isotherm parameters for adsorption were determined in five test soils. The desorption was not examined because of the very low level of adsorption onto soil. The results are presented below in the table B.8.1.4._CA-9.

Table B.8.1.4._CA-9: The of Freundlich adsorption and desorption parameters determined for FOE 5043-Trifluoroethanesulfonic acid.

Test soil – USDA type (name)	Key soil properties		Freundlich adsorption isotherm parameters			Freundlich desorption isotherm parameters		
	pH ¹⁾	OC [%]	K _F [mL/g]	K _{F OC} [mL/g]	1/n	K _F [mL/g]	K _{F OC} [mL/g]	1/n
<i>Loamy sand (Laacher Hof AXXa)</i>	6.6	1.8	0.0	0.0001	1.00	Not determined		
<i>Silt loam (Hoefchen am Hohenseh)</i>	6.7	1.7	0.0	0.0001	1.00	Not determined		
<i>Slit loam (Hnascheider Hof)</i>	5.3	2.8	0.0	0.0001	1.00	Not determined		
<i>Loam (Dollendorf II)</i>	7.5	5.0	0.0	0.0001	1.00	Not determined		
<i>Sandy loam (Wurmweise)</i>	5.4	1.9	0.0	0.0001	1.00	Not determined		
Geomean (n = 5)			0.0	0.0001	----			
Arithmetic mean (n = 5)			----	----	1.00			
pH dependence			No					

Footnotes to the table:

1) Measured in water;

The results showed that FOE Methylsulfone and FOE Thiadone were moderately sorbed onto soil. FOE Oxalate and FOE Sulfonic acid were only weakly sorbed onto soil, while FOE 5043-Trifluoroethanesulfonic acid and Trifluoroacetic acid were practically not sorbed onto soil. No pH-dependence of the adsorption was stated for any of the degradation products, but in case of FOE Thiadone, FOE Sulfonic acid and FOE Oxalate that may be due to the limited number of soils used in the experiment as well as their narrow pH range.

Additionally for FOE Methylsulfide – major aquatic degradation product of Flufenacet, the K_{OC} value was estimated using KOCWIN – a part of EPISuite 4.1 modelling tool. The estimated value is **K_{OC} = 598 L/kg** and is recommended to be used as an input value in SW/SED model exposure assessment.

For FOE Sulfonic acid the additional examination of the soil sorption in function of time – time-dependent sorption, was performed. The key results of that examination – adsorption parameters in function of time, are provided below in the table B.8.1.4._CA-10.

Table B.8.1.4._CA-10: The key results of the examination of the time-dependent sorption of FOE Sulfonic acid onto soil.

Results obtained for <i>Laacherhof AXXa</i> test soil					Results obtained for <i>Laacherhof AIII</i> test soil				
Soil key properties		Results			Soil key properties		Results		
Parameter	Value	Time point [DAT]	K _d [mL/g]	K _{d OC} [mL/g]	Parameter	Value	Time point [DAT]	K _d [mL/g]	K _{d OC} [mL/g]
Soil type (USDA)	Sandy loam	0	0.12	8	Soil type (USDA)	Silt loam	0	0.12	13
		3	0.16	11			3	0.14	16
		7	0.16	11			7	0.14	16
OC [%]	1.47	14	0.17	11	OC [%]	0.88	14	0.15	17
		28	0.20	13			28	0.15	17
Soil pH (in H ₂ O)	6.9	56	0.18	12	Soil pH (in H ₂ O)	7.6	56	0.15	18
		100	0.23	16			100	0.18	20
DT ₅₀ [days]	49.8				DT ₅₀ [days]	40.4			

The calculated adsorption coefficient increase factor was **2** for Laacherhof AXXa test soil and **1.5** for Laacherhof AIII test soil, indicating that the compound became more strongly sorbed onto soil with elapsing time. However that increase did not strongly influenced the mobility of FOE Sulfonic acid in soil, which remained very mobile, as indicated K_d and K_{d OC} values.

The examination of the mobility of Flufenacet and its major transformation products in soil covered following issues:

- column leaching,
- aged residue column leaching,
- lysimeter studies,
- determination of the Plant Uptake Factor – PUF, as “Other studies”

The Applicant did not submit any studies covering the issue of the column leaching of Flufenacet. Instead, in the provided justification for the non-submission, stated that it was covered by the results of the examination of sorption in soil at equilibrium (batch sorption studies) and those aimed on the examination of leaching of the aged residues. That justification was found acceptable by the RMS. It shall be indicated however, that the evaluation of the study examining the leaching behaviour of the aged residues of Flufenacet demonstrated that the study was not acceptable.

Two additional open-literature studies found by the RMS, considered supplementary, indicated that under typical EU conditions Flufenacet should not move in the soil profile below the depth of 25 cm. Such statement seems to be confirmed by the results of the field dissipation studies performed for Flufenacet.

Additionally, a study was submitted examining the column leaching of one of the major soil degradation products of Flufenacet – TFA. That study, performed using four European soils, showed that TFA was very mobile in soil. The key results of that study are presented below.

The leaching behaviour of TFA was examined using soil columns filled with one of the following test soils:

- Loamy sand (*Laacherhof AXXa*) test soil, having OC = 1.8% and pH = 6.2;
- Loam (*Dollendorf II*) test soil, having OC = 5.2% and pH = 7.4;
- Silt loam (*Höfchen am Hohenseh*) test soil, having OC = 1.6 and pH = 6.5;
- Sandy loam (*Laacherhof Wurmwiese*) test soil, having OC = 1.9 and pH = 5.3.

The experiment was performed in two variants, denominated **Study design A** and **Study design B**, that may be characterised as follows:

- in **Study design A** leaching lasted 48 hours and was performed with 393 mL of artificial rain (0.01M $\text{CaCl}_{2\text{aq}}$), corresponding to 200 mm of rain;
- in **Study design B** leaching lasted 120 hours and was performed with 984 mL of artificial rain (0.01M $\text{CaCl}_{2\text{aq}}$), corresponding to 502 mm of rain;

In the variant denominated **Study design A** the following results were obtained for TFA:

- amount of TFA in the eluates (mean values of the two replicates), expressed as % AR, was:
 - 95.5% AR for columns filled with Loamy sand (*Laacherhof AXXa*) test soil;
 - 73.2% AR for columns filled with Loam (*Dollendorf II*) test soil;
 - 92.1% AR for columns filled with Silt loam (*Höfchen am Hohenseh*) test soil;
 - 66.2% AR for columns filled with Sandy loam (*Laacherhof Wurmwiese*) test soil.
- the extractable radioactivity retained within soil columns attributed to TFA was (mean values of the two replicates):
 - 5.0% AR for columns filled with Loamy sand (*Laacherhof AXXa*) test soil;
 - 28.3% AR for columns filled with Loam (*Dollendorf II*) test soil;
 - 6.5% of AR for columns filled with Silt loam (*Höfchen am Hohenseh*) test soil;
 - 35.6% AR for columns filled with Sandy loam (*Laacherhof Wurmwiese*) test soil.
- the NER fraction attributed to TFA, expressed as % AR, in the soil columns (mean values of the two replicates) was:
 - 1.2% AR for columns filled with Loamy sand (*Laacherhof AXXa*) test soil;
 - 1.8% AR for columns filled with Loam (*Dollendorf II*) test soil;
 - 0.8% AR for columns filled with Silt loam (*Höfchen am Hohenseh*) test soil;
 - 1.1% AR for columns filled with Sandy loam (*Laacherhof Wurmwiese*) test soil.
- the distribution of residues of TFA in soil was following:
 - for columns filled with Loamy sand (*Laacherhof AXXa*) test soil they were found predominantly in the lowest segment – S5;
 - for columns filled with Loam (*Dollendorf II*) test soil the highest concentration of TFA residues was determined in the top section of the column (segments S1 and S2) with the peak amount in segment S2, and it gradually decreased towards the bottom of the soil column;
 - for columns filled with Silt loam (*Höfchen am Hohenseh*) test soil they were found predominantly in the lowest segment – S5;
 - for columns filled with Sandy loam (*Laacherhof Wurmwiese*) test soil the residues of TFA were generally found in the lower part of the column, with the peak amount in the middle section S3.

- The K_d and K_{dOC} values determined for TFA in this experiment were following:
 - for the test soil Loamy sand (*Laacherhof AXXa*) $K_d = 0.0$ mL/g and $K_{dOC} = 0.0$ mL/g;
 - for the test soil Loam (*Dollendorf II*) $K_d = 0.0$ mL/g and $K_{dOC} = 0.0$ mL/g;
 - for the test soil Silt loam (*Höfchen am Hohenseh*) $K_d = 0.0$ mL/g and $K_{dOC} = 0.0$ mL/g;
 - for the test soil Sandy loam (*Laacherhof Wurmwielse*) $K_d = 0.0$ mL/g and $K_{dOC} = 0.0$ mL/g;
 - mean $K_d = 0.0$ mL/g and $K_{dOC} = 0.0$ mL/g.

In the variant denominated **Study design B** the following results were obtained for TFA:

- amount of TFA in the eluates (mean values of the two replicates), expressed as % AR, was:
 - 101.1% AR for columns filled with Loamy sand (*Laacherhof AXXa*) test soil;
 - 96.3% AR for columns filled with Loam (*Dollendorf II*) test soil;
 - 98.6% AR for columns filled with Silt loam (*Höfchen am Hohenseh*) test soil;
 - 100.9% AR for columns filled with Sandy loam (*Laacherhof Wurmwielse*) test soil.
- the amount of radioactivity retained within soil columns attributed to TFA was not analysed because it was wholly recovered in leachates.
- The K_d and K_{dOC} values determined for TFA in this experiment were following:
 - for the test soil with Loamy sand (*Laacherhof AXXa*) $K_d = 0.1$ mL/g and $K_{dOC} = 4.5$ mL/g;
 - for the test soil Loam (*Dollendorf II*) $K_d = 0.0$ mL/g and $K_{dOC} = 0.0$ mL/g;
 - for the test soil Silt loam (*Höfchen am Hohenseh*) $K_d = 0.2$ mL/g and $K_{dOC} = 11.3$ mL/g;
 - for the test soil Sandy loam (*Laacherhof Wurmwielse*) $K_d = 0.2$ mL/g and $K_{dOC} = 7.1$ mL/g;
 - mean $K_d = 0.2$ mL/g and $K_{dOC} = 9.1$ mL/g.

The aged residues leaching was examined in one study, submitted also for the previous authorisation of Flufenacet in the EU. RMS evaluated that study for its compliance with the current guidelines, in particular the OECD Guideline for testing chemicals No. 312. Several minor deficiencies were stated that had no impact on the validity of the study. However, the thorough examination of the study report showed that there was a significant discrepancy between the application rate declared to be used to treat soil subjected to the ageing procedure and that used in the leaching experiment with aged soil.

Second problem identified in the study report was the fact that the analytical procedure used to characterise quantitatively and qualitatively the residues in soil after ageing was not presented.

As a result, mainly due to the discrepancies in the amount of the radioactivity introduced into soil at the beginning of the ageing period and that used in leaching experiment, introduced with aged soils, RMS decided to consider the study not acceptable because of the significant uncertainty related to the reliability of the obtained results.

The leaching behaviour of Flufenacet and its degradation products through the undisturbed soil profiles under the agronomic and climatic conditions relevant for Germany was examined on four outdoor lysimeters. The results of that examination were presented in two study reports submitted by the Applicant for the purpose of the current evaluation. Additionally the Applicant submitted the interim reports of the same experiments, not summarised in the Renewal Assessment Report for Flufenacet, but analysed for their compliance with the adequate final reports. The third study submitted for evaluation was aimed on the validation of the lysimeter studies by comparing their results with those of the modelling exposure assessment carried out for the GW compartment. RMS however decided not to use it, as the modelling tools and scenarios were not those recommended by FOCUS.

The key data and results obtained in the two studies are summarily presented below in tables B.8.1.4._CA-10 – B.8.1.4._CA-10c.

Table B.8.1.4._CA-10: The key data and results obtained in the outdoor lysimeter studies.

Parameter				Data for Lysimeter			
				#15	#16	#17	#18
General information	Trial site	Test facility		Lysimeter station of Bayer AG	Lysimeter station of Bayer AG	Lysimeter station of Bayer AG	Lysimeter station of Bayer AG
		Location (town, region, country)		Monheim, NRW, Germany	Monheim, NRW, Germany	Monheim, NRW, Germany	Monheim, NRW, Germany
		Geographic coordinates	Longitude	6° 55' E	6° 55' E	6° 55' E	6° 55' E
			Latitude	51° 4' N	51° 4' N	51° 4' N	51° 4' N
	Long-term weather conditions at trial site (1996 – 1995)	Average rainfall [mm]	Annual	745	745	745	745
			Monthly min. (month)	42.7 (February)	42.7 (February)	42.7 (February)	42.7 (February)
			Monthly max. (month)	78.1 (June)	78.1 (June)	78.1 (June)	78.1 (June)
		Average annual relative air humidity [%]		73	73	73	73
		Average temperature at 2 metres above the ground [°C]	Annual	10.0	10.0	10.0	10.0
			Monthly min. (month)	2.6 (January)	2.6 (January)	2.6 (January)	2.6 (January)
			Monthly max. (month)	18.4 (June)	18.4 (June)	18.4 (June)	18.4 (June)
		Average annual wind velocity [m/s.]		2.5	2.5	2.5	2.5
		Average radiant heat [kJ/cm ²]	Annual	29.1	29.1	29.1	29.1
			Monthly min. (month)	5.8 (December)	5.8 (December)	5.8 (December)	5.8 (December)
			Monthly max. (month)	53.1 (July)	53.1 (July)	53.1 (July)	53.1 (July)
	Duration of the study	Preliminary period	Duration [years]	1	1	1	1
			Beginning	March 1992	March 1992	March 1992	March 1992
			End	May 1993	May 1993	May 1993	May 1993
		Experimental period	Duration [years]	3	3	2.5	2.5
			Beginning	May 1993	May 1993	May 1993	May 1993
Characterisation of lysimeter	Lysimeter depth	Total [cm]		135	135	120	120
		Soil monolith [cm]		130	130	115	115
		Gravel layer [cm]		5	5	5	5
		Soil type (FAO)		Eutric Cambisol	Eutric Cambisol	Eutric Cambisol	Eutric Cambisol
	Characteristic of soil monolith	Soil properties, depth 0 – 30 cm	Soil texture (USDA)	Sandy loam	Sandy loam	Sandy loam	Sandy loam
			pH (CaCl ₂)	7.04	7.04	7.04	7.04
			OC%	1.41	1.41	1.41	1.41
			CEC [meq/100g]	9.61	9.61	9.61	9.61
			Microbial biomass [mg/kg]	235	235	235	235
		Soil properties, depth 30 – 60 cm	Soil texture (USDA)	Sandy loam	Sandy loam	Sandy loam	Sandy loam
			pH (CaCl ₂)	7.24	7.24	7.24	7.24
			OC%	0.34	0.34	0.34	0.34
			CEC [meq/100g]	7.43	7.43	7.43	7.43
			Microbial biomass [mg/kg]	34	34	34	34
		Soil properties, depth 60 – 100 cm	Soil texture (USDA)	Loamy sand	Loamy sand	Loamy sand	Loamy sand
			pH (CaCl ₂)	7.18	7.18	7.18	7.18
			OC%	0.19	0.19	0.19	0.19
			CEC [meq/100g]	7.57	7.57	7.57	7.57
			Microbial biomass [mg/kg]	11	11	11	11
		Soil properties, depth 100 – 115 cm	Soil texture (USDA)	Loamy sand	Loamy sand	Loamy sand	Loamy sand
			pH (CaCl ₂)	7.46	7.46	7.46	7.46
			OC%	0.17	0.17	0.17	0.17
			CEC [meq/100g]	8.52	8.52	8.52	8.52
			Microbial biomass [mg/kg]	13	13	13	13
Maintenance data	Application of the test compound	Test compound		¹⁴ C-Flufenacet	¹⁴ C-Flufenacet	¹⁴ C-Flufenacet	¹⁴ C-Flufenacet
		Number of applications/ experiment		2	2	2	2
		1 st application	Year of experiment	1	1	1	1
			Application date	12/05/1993	12/05/1993	13/05/1993	13/05/1993
			Application rate	48.14 mg/m ² (480 g/ha)	48.14 mg/m ² (480 g/ha)	48.14 mg/m ² (480 g/ha)	48.14 mg/m ² (480 g/ha)
		2 nd application	Year of experiment	2	2	1	1
			Application date	05/05/1994	05/05/1994	03/11/1993	03/11/1993
			Application rate	48.04 mg/m ² (480 g/ha)	48.04 mg/m ² (480 g/ha)	18.02 mg/m ² (180 g/ha)	18.02 mg/m ² (180 g/ha)

Table B.8.1.4._CA-10a: The key data and results obtained in the outdoor lysimeter studies (continued).

Parameter				Data for Lysimeter			
				#15	#16	#17	#18
Maintenance data, continued	Crop data	1 st crop, target	Crop	Maize, grain	Maize, grain	Maize, fodder	Maize, fodder
			Year of experiment	1	1	1	1
			Date of sowing	10/05/1993	10/05/1993	10/05/1993	10/05/1993
			Date of harvest	12/11/1993	12/11/1993	28/09/1993	28/09/1993
			Harvested parts	Corncoobs	Corncoobs	Silage material	Silage material
		2 nd crop, target	Crop	Maize, grain	Maize, grain	Winter wheat	Winter wheat
			Year of experiment	2	2	1 – 2	1 – 2
			Date of sowing	05/05/1994	05/05/1994	02/11/1993	02/11/1993
			Date of harvest	10/05/1994	10/05/1994	03/08/1994	03/08/1994
			Harvested parts	Corncoobs	Corncoobs	Grain and straw	Grain and straw
		3 rd crop, succeeding	Crop	Sugar beet	Sugar beet	Sugar beet	Sugar beet
			Year of experiment	3	3	3	3
			Date of sowing	13/04/1995	13/04/1995	13/04/1995	13/04/1995
			Date of harvest	07/11/1995	07/11/1995	07/11/1995	07/11/1995
			Harvested parts	Leaves and tubers	Leaves and tubers	Leaves and tubers	Leaves and tubers
	Irrigation and precipitation during experiment	1 st year	Precipitation [mm]	897.1	897.1	897.1	897.1
			Irrigation [mm]	46.0	46.0	51.0	51.0
			Sum [mm]	943.1	943.1	948.1	948.1
		2 nd year	Precipitation [mm]	814.2	814.2	813.9	813.9
			Irrigation [mm]	100.0	100.0	75.0	75.0
			Sum [mm]	914.2	914.2	888.9	888.9
		3 rd year	Precipitation [mm]	496.1	496.1	338.0	338.0
			Irrigation [mm]	104.0	104.0	104.0	104.0
			Sum [mm]	600.1	600.1	442.0	442.0
		Total	Precipitation [mm]	2207.5	2207.5	2049.0	2049.0
			Irrigation [mm]	250	250	250	250
			Sum [mm]	2457	2457	2279.0	2279.0
Radioactivity - recovery	Radioactivity recovered [% AR]	in soil monolith	0- 30 cm	40.289	41.414	37.80	~48.2
			30 – 60 cm	2.095	3.128	2.46	~3.1
			below 60 cm	0.777	0.485	~2.00	~1.7
			total	43.16	45.03	42.33	52.96
		in leachates	1 st year	0.772	0.815	1.436	1.563
			2 nd year	0.250	0.161	0.122	0.150
			3 rd year	0.006	0.006	0.006	0.007
			total	0.64	0.58	~1.56	~1.72
		in crops	1 st crop	0.014	0.015	0.38	0.39
			2 nd crop	0.016	0.014	0.04	0.05
			3 rd crop	0.059	0.061	0.07	0.07
			total	0.08	0.08	0.48	0.50
		Total recovered		43.89	45.68	44.38	55.18
		Lost (eg as ¹⁴ CO ₂) [% AR]		56.11	54.32	55.62	44.82
Radioactivity in soil monoliths	in 0 – 30 cm layer	Total [% AR]		40.29	41.41	37.80	48.2
		identified as Flufenacet	[µg/layer]	1860.96	1839.68	450.75	528.48
		identified as FOE Alcohol	[µg/kg soil FW]	3.91	3.91	1.07	1.06
		identified as FOE Oxalate	[µg/layer]	143.49	159.02	60.09	87.67
		identified as FOE Sulfonic acid	[µg/kg soil FW]	0.30	0.34	0.14	0.18
		identified as FOE Sulfonic acid	[µg/layer]	212.84	167.72	28.23	63.74
		Identified as FOE Sulfonic acid	[µg/kg soil FW]	0.45	0.36	0.07	0.13
		Identified as FOE Sulfonic acid	[µg/layer]	71.44	138.39	45.74	43.42
		Identified as FOE Sulfonic acid	[µg/kg soil FW]	0.15	0.29	0.11	0.09
	in 30 – 60 cm layer	Total [% AR]		2.095	3.128	2.46	3.1
Detailed characterisation of leachates	1 st year early leachate	Collection time	Week of experiment	24	24	24	24
			Collection date	29/10/1993	29/10/1993	29/10/1993	29/10/1993
		Volume of leachate [L]		3.7	4.7	8.2	8.2
		Characterisation of TRR – Total Radioactivity Recovered	Total TRR [µg a. i. equival./L]	0.256	0.221	0.588	0.505
			acidic TRR [µg a. i. equival./L]	0.218	0.183	0.539	0.477
			¹⁴ CO ₂ -associated radioactivity [% total TRR]	14.87	17.23	8.34	5.64
			Flufenacet [µg /L]	<0.011	<0.014	0.006	<0.005
		Characterisation of acidic TRR ¹⁾	FOE ALC [µg /L]	<0.001	0.006	0.002	0.095
			FOE OXA [µg /L]	0.002	0.007	<0.001	0.005
			FOE SA [µg /L]	0.065	0.025	0.225	0.182
			FOE TGS [µg /L]	0.017	0.009	0.015	0.027

Footnotes to the table:

1) Abbreviations used: FOE ALC – FOE Alcohol, FOE OXA – FOE Oxalate, FOE SA – FOE Sulfonic acid, FOE TGS – FOE Thioglycolate sulfonide.

Table B.8.1.4._CA-10b: The key data and results obtained in the outdoor lysimeter studies (continued).

Parameter				Data for Lysimeter			
				#15	#16	#17	#18
Detailed characterisation of leachates - continued	1 st year leachate with max. TRR	Collection time	Week of experiment	37	35	38	38
			Collection date	28/01/1994	12/01/1994	04/02/1994	04/02/1994
		Volume of leachate [L]		17.2	21.5	21.3	21.3
		Characterisation of TRR – Total Radioactivity Recovered	Total TRR [µg a. i. equivalent/L]	2.350	1.989	5.106	5.455
			acidic TRR [µg a. i. equivalent/L]	2.228	1.915	4.940	5.255
			¹⁴ C ₂ -associated radioactivity [% total TRR]	5.19	3.72	4.26	3.58
		Characterisation of acidic TRR ¹⁾	Flufenacet [µg /L]	<0.007	<0.017	<0.011	<0.001
			FOE ALC [µg /L]	0.001	0.004	0.006	0.044
			FOE OXA [µg /L]	0.007	0.041	0.005	0.036
			FOE SA [µg /L]	1.293	1.090	3.375	3.682
			FOE TGS [µg /L]	0.079	0.036	0.017	0.028
	1 st year late leachate	Collection time	Week of experiment	47	47	47	47
			Collection date	11/04/1994	11/04/1994	11/04/1994	11/04/1994
		Volume of leachate [L]		11.5	15.5	19.4	15.0
		Characterisation of TRR – Total Radioactivity Recovered	Total TRR [µg a. i. equivalent/L]	0.850	0.798	2.545	3.102
			acidic TRR [µg a. i. equivalent/L]	0.767	0.732	1.389	2.916
			¹⁴ C ₂ -associated radioactivity [% total TRR]	9.82	8.27	6.13	6.00
		Characterisation of acidic TRR ¹⁾	Flufenacet [µg /L]	<0.035	0.005	0.002	0.002
			FOE ALC [µg /L]	0.001	<0.001	0.008	0.041
			FOE OXA [µg /L]	0.012	0.031	0.026	0.017
			FOE SA [µg /L]	0.332	0.301	1.302	1.920
			FOE TGS [µg /L]	0.014	0.010	0.005	0.012
	1 st year annual leachate (pooled)	Collection time	Week of experiment	50	50	50	50
			Collection date	29/04/1994	29/04/1994	29/04/1994	29/04/1994
		Volume of leachate [L]		349.8	402.4	399.1	383.1
		Characterisation of TRR – Total Radioactivity Recovered	Total TRR [µg a. i. equivalent/L]	1.062	0.931	2.380	2.699
			acidic TRR [µg a. i. equivalent/L]	0.99	0.87	2.26	2.56
			¹⁴ C ₂ -associated radioactivity [% total TRR]	6.47	6.82	5.31	5.35
		Characterisation of acidic TRR ¹⁾	Flufenacet [µg /L]	0.020	0.033	0.004	0.005
			FOE ALC [µg /L]	<0.002	0.000	0.034	0.016
			FOE OXA [µg /L]	0.015	0.004	0.017	0.006
			FOE SA [µg /L]	0.589	0.489	1.355	1.616
			FOE TGS [µg /L]	0.016	0.014	0.030	0.027
	2 nd year annual leachate (pooled)	Collection time	Week of experiment	103	103	103	103
			Collection date	05/05/1995	05/05/1995	05/05/1995	05/05/1995
		Volume of leachate [L]		317.6	299.9	365.4	368.9
		Characterisation of TRR – Total Radioactivity Recovered	Total TRR [µg a. i. equivalent/L]	0.758	0.516	0.221	0.269
			acidic TRR [µg a. i. equivalent/L]	0.670	0.46	0.19	0.22
			¹⁴ C ₂ -associated radioactivity [% total TRR]	11.10	11.19	17.06	23.02
		Characterisation of acidic TRR ¹⁾	Flufenacet [µg /L]	0.003	0.003	0.002	0.005
			FOE ALC [µg /L]	0.003	0.005	0.001	0.004
			FOE OXA [µg /L]	<0.018	<0.014	0.009	0.006
			FOE SA [µg /L]	0.235	0.149	0.013	0.016
			FOE TGS [µg /L]	0.020	0.015	0.022	0.019

Footnotes to the table:

1) Abbreviations used: FOE ALC – FOE Alcohol, FOE OXA – FOE Oxalate, FOE SA – FOE Sulfonic acid, FOE TGS – FOE Thioglycolate sulfoxide.

Table B.8.1.4._CA-10c: The key data and results obtained in the outdoor lysimeter studies (continued).

Parameter				Data for Lysimeter			
				#15	#16	#17	#18
Detailed characterisation of leachates - continued	3 rd year annual leachate (pooled)	Collection time	Week of experiment	115	115	115	115
			Collection date	26/07/1995	26/07/1995	26/07/1995	26/07/1995
		Volume of leachate [L]		13.0	17.0	17.5	19.1
		Characterisation of TRR – Total Radioactivity Recovered	Total TRR [µg a. i. equival./L]	0.432	0.353	0.239	0.238
			acidic TRR [µg a. i. equival./L]	0.334	0.23	0.15	0.14
			¹⁴ C ₂ -associated radioactivity [% total TRR]	22.80	34.56	35.22	40.88
		Characterisation of acidic TRR: compound/concentration [µg/L]		FOE SA ¹⁾ ≤ 0.25	FOE SA ¹⁾ ≤ 0.17	not performed	not performed
	Total leachate	Collection time	Weeks of experiment	115	115	115	115
			Collection dates: beginning/end	12/05/1993 26/07/1995	12/05/1993 26/07/1995	12/05/1993 26/07/1995	12/05/1993 26/07/1995
		Volume of leachate [L] (total)		680.4	719.3	782.0	771.1
		Characterisation of TRR – Total Radioactivity Recovered; average values	Total TRR [µg a. i. equival./L]	0.906	0.742	1.310	1.492
			acidic TRR [µg a. i. equival./L]	0.83	0.68	1.25	1.38
			¹⁴ C ₂ -associated radioactivity [% total TRR]	8.42	8.39	6.28	6.85

Footnotes to the table:

1) Abbreviations used: FOE SA – FOE Sulfonic acid.

It may be stated that of all the compounds possible to be identified as originating from Flufenacet radiolabelled in fluorophenyl ring (including Flufenacet itself) only FOE Sulfonic acid was demonstrated to be found in leachates in amounts > 0.1 µg/L, what conformed the risk to GW associated to that degradation product demonstrated in GW model exposure assessment (for details please refer to the results of calculations presented under the point B.8.5 in the Vol. 3-CP, B.8 of this Renewal Assessment Report).

Neither Flufenacet nor the second major soil degradation product relevant for that radiolabelling position – FOE Oxalate, were detected in leachates in amounts > 0.1 µg/L, what may indicate that they would not pose a threat to the GW compartment.

In soil and leachates FOE Alcohol was detected – the compound determined in the studies examining the route of degradation of Flufenacet in aerobic soil to be minor/transient and therefore not taken into account in the GW model exposure assessment. It shall be indicated however that the would-be risk it may pose to the GW compartment was covered by the calculations carried out for FOE Oxalate – its immediate degradate.

Also detected in leachates was FOE Thioglycolate sulfoxide (FOE TGS), the compound not taken in the model GW exposure assessment into consideration, being identified as minor soil degradation product. It shall be indicated however, that in the study it was determined in leachates in amounts < 0.1 µg/L, what may indicate that it would not pose a serious threat to the GW compartment.

Finally, it shall be indicated that, due to the fact that in the experiments was used Flufenacet radiolabelled only in the fluorophenyl ring, they gave no information of the laching potential of the degradation products formed from the second moiety present within the molecule of Flufenacet – thiadiazole.

The comparative analysis of the application pattern (crops, application timing and application rates) used in the experiments and the EU-representative application pattern proposed for the current authorisation of Flufenacet in the EU showed that they may be considered as providing supplementary information with regard to the risk posed by Flufenacet and its soil degradation products to the GW compartment, but for the purpose of the decision making should be considered with care.

The PUF – plant uptake factor was determined in three separate experiments for the following major soil degradation products of Flufenacet: FOE Sulfonic acid, FOE Methylsulfone, FOE 5043-Trifluoroethanesulfonic acid – FOE TFESA (for all three in one experiment), and Trifluoroacetic acid – TFA (in two separate experiments). The PUF values for FOE Sulfonic acid, FOE Methylsulfone and FOE TFESA were determined for Wheat as the experimental crop, while for TFA the test crops for which the PUF values were determined were Wheat, Corn (Maize) and Tomato.

Additionally was submitted a study, being in fact a position paper, supporting the value of PUF proposed for TFA.

For all four test compounds the experimental PUF values were determined for Wheat, the crop that may be considered representative for all cereals.

The determined values are:

- for FOE Sulfonic acid the PUF in cereals is **0.46**;
- for FOE Methylsulfone the PUF in cereals is **1.31**;
- for FOE 5043-Trifluoroethanesulfonic acid the PUF in cereals is **1.36**;
- for TFA (Trifluoroacetic acid) the PUF in cereals is **0.59**.

The Applicant proposed to use two of these experimentally derived values – PUF for FOE Sulfonic acid and PUF for TFA, as input values for GW model exposure assessment (please also refer to the point B.8.3. in the document Vol. 3_CP – B.8. of this Renewal Assessment Report).

RMS decided to verify the correctness of that selection in light of the recommendations of the current Guidelines. That was done using the *Generic Guidance for Tier 1 FOCUS Ground Water Assessments, Version 2.2, May 2014*, document, which in paragraph 2.4.4 – *Crop related substance parameters* provides the recommendations with regard to the appropriate selection of the Plant Uptake Factor value. It is stated that the recommended default value for all compounds is 0. However, when a reliable measured K_{OW} value determined for neutral pH is available, the Briggs equation proposed for calculation of TSCF (Transpiration Stream Concentration Factor) may be used and so determined TSCF value used as input parameter for PUF in GW model exposure assessment. The Briggs equation for calculating TSCF presented in the cited above Guidance document looks as follows:

$$TSCF = 0.784 \exp \{(-[\text{Log}(K_{OW}) - 1.78]^2 / 2.44)\}$$

RMS decided to use it in order to calculate the TSCF values for Flufenacet and all its major soil degradation products, for which the GW model exposure assessment shall be performed and for which were available the reliable $\text{Log } P_{OW}$ (= $\text{Log } K_{OW}$) presented in section B.2 (Physicochemical properties) of this Renewal Assessment Report. The results of the calculations, together with the input parameters used in them, are presented below in the table B.8.4._CA-11. As a next step the calculated values were compared with the proposed in the same Guideline maximum recommended TSCF value – 0.8, and, where available, with the experimental value. That was done in order to determine the suitable value representing TSCF/PUF to be used as input parameter in GW model exposure assessment. These value are also presented in the table B.8.1.4._CA-11. The TSCF/PUF values recommended as input for GW/SW modelling are given **in bold**.

Table B.8.1.4._CA-11: The results of the determination of TSCF/PUF value suitable for GW/SW model exposure assessment

Compound	Ionisable substance	Experimental values		TSCF		Measured PUF	TSCF/PUF value selected for modelling
		$\text{Log } P_{OW}$	measured at pH	calculated	Regulatory upper limit		
Flufenacet	No	3.5	7.0	0.744	0.8	n. a. ³⁾	0.744
FOE Oxalate	No	2.2	7.0	0.983	0.8	n. a. ³⁾	0.8
FOE Sulfonic acid	Yes	-2.72	7.0	0.133	0.8	0.46	0.46
FOE Methylsulfone	No	1.7	7.0	0.999	0.8	1.31	0.8
FOE Thiadone	No	0.62	7.0	0.874	0.8	n. a. ³⁾	0.8
FOE TFESA ¹⁾	Yes	-2.95	7.0	0.107	0.8	1.36	0.8
TFA ²⁾	Yes	-2.6	7.0	0.148	0.8	0.59	0.59

Footnotes to the table:

1) FOE TFESA = FOE 5043-Trifluoroethanesulfonic acid;

2) TFA = Trifluoroacetic acid;

3) n. a. = value not available (not determined experimentally).

B.8.2 - Fate and behaviour in water and sediment

In order to adequately evaluate the studies examining the fate and behaviour of Flufenacet in aquatic systems it has become necessary to determine the application rate expressed in volumetric units (mg/L) that may be subsequently used as a reference value. The analysis of the proposed EU-representative application pattern for Flufenacet (please refer to the table B.8.0._CA-1) enabled the identification of the critical use with regard to the soil exposure – 240 g Flufenacet/ha. The calculation of the would be application rate were performed assuming the direct overspray of the theoretical water body having the following dimensions: 1-metre length, 1-metre width and 0.3-metre depth. The resulting application rate expressed in volumetric units (mg/L) is **A = 0.08 mg/L, or 80 µg/L**. This value will be used as a reference in determining the validity of the studies examining fate and behaviour of flufenacet in water.

B.8.2.1. – Route and rate of degradation in aquatic systems (chemical and photochemical degradation)

B.8.2.1.1 – Hydrolytic degradation

For the purpose of the current evaluation the Applicant submitted three study reports presenting the results of the examination of aqueous hydrolysis of Flufenacet. One of them had been evaluated for the previous authorisation of Flufenacet in the EU, while the remaining two are newly submitted studies. Additionally, the literature search resulted in the identification of the study examining the rate of degradation of Flufenacet in aqueous environment in function of pH.

Study 1:

Report: Zeng Z., Wood S., (1992): “Stability of FOE 5043 in Sterile Aqueous Buffer Solution.”; Miles Inc., Agriculture Division, Research and Development Department, P. O. box 4913, Kansas City, MO 64120, USA; study No. F3072401 (Miles Inc.); Report No. 102623 (Miles Inc.); 12 March 1992; study reference number: M-002203-01-1;

Guidelines: The study was performed to comply with the following Guidelines:

- US. EPA Guidelines for Pesticide Registration, 161-1, Hydrolysis Studies.

GLP: Yes;

RMS comments: The study had been evaluated for the previous authorisation of Flufenacet in the EU, by its inclusion into the Annex I of the Directive 91/414/EEC. Its summary can be found under the point B.7.4.1.1., in section B.7 of the Annex B to the Monograph prepared by the RMS – France, for Flufenacet. The study was evaluated for its compliance with OECD Guideline 111 – Hydrolysis as a Function of pH. RMS stated that the study complied with the provisions of the reference Guideline, therefore it can be considered acceptable for the present assessment. It is summarised below.

Summary:

The aim of the study was to investigate the hydrolysis of Flufenacet in aqueous solution in the environmentally relevant pH range of 5-9 and temperature $T = 25^{\circ}\text{C}$.

The test compound used in the experiment was radiolabelled Flufenacet, labelled evenly in phenyl ring, as shown below on figure B.8.2.1.1._CA-1. It had radiochemical purity of 97.48% (determined by HPLC) and specific activity of 60.6 mCi/mmol.

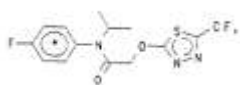


Figure B.8.2.1.1._CA-1: The structural formula of the test compound; radiolabelling position is indicated by an asterisk - (*); (copied from the study report).

The test compound was used to prepare a **Stock solution** having a concentration 7.77 mg/mL.

The test vessels were sterilised 6-mL borosilicate glass vials sealed with Teflon-coated silicone discs and aluminium closure seals. The sealed vials were sterilised prior to the experiment by autoclaving them for 55 min at $T = 120^{\circ}\text{C}$ and pressure 96.53 kPa (14 lbs/in²). Each vial was then weighed and the weight recorded. The amount of so prepared vials was such to prepare for each buffer solution three replicate samples for each time point.

The experiment was performed using three buffer solutions:

- pH 5 buffer (acetate buffer),
- pH 7 buffer (phosphate buffer),
- pH 9 buffer (borate buffer),

each having a concentration of 0.01 M. The detailed information on the composition of each buffer and method of its preparation is given below in the table B.8.2.1.1._CA-1.

Table B.8.2.1.1._CA-1: The composition and properties of the buffer solutions used in the experiment.

Type of buffer solution	Nominal pH	Composition	Method of preparation	Final concentration
<i>Acetate buffer</i>	5	0.01M CH ₃ COOH + 0.01M CH ₃ COONa	a) 0.142 mL of 99.7% CH ₃ COOH was diluted with distilled water to obtain 250 mL 0.01M solution; b) 0.2g of CH ₃ COONa was dissolved in distilled water to obtain 250 mL of 0.01M solution; c) both solutions were mixed, while pH was monitored, until pH = 5 was reached.	0.01M
<i>Phosphate buffer</i>	7	0.01M KH ₂ PO ₄ + 0.01M K ₂ HPO ₄	a) 0.34 g KH ₂ PO ₄ was dissolved in distilled water to obtain 250 mL of 0.01M solution; b) 0.43 g K ₂ HPO ₄ was dissolved in distilled water to obtain 250 mL of 0.01M solution; c) both solutions were mixed, while pH was monitored, until pH = 5 was reached.	0.01M
<i>Borate buffer</i>	9	H ₃ BO ₃ _{aq} + 3M NaOH _{aq}	a) 0.16g H ₃ BO ₃ was dissolved in 100 mL of distilled water; b) pH of the solution was adjusted to 9 with 3M NaOH aqueous solution.	0.01M

The characterised above aqueous buffer solutions were used to prepare the buffer solutions of the test compound used in the experiment. The **test buffer solutions** had the concentration of the test item (Flufenacet) $C = \sim 10$ ppm.

That was done in the following way: three 0.15-mL aliquots of the **Stock solution** were placed in three separate test tubes and the organic solvent removed under the gentle stream of N₂. Next, the residue containing ¹⁴C-Flufenacet was gradually redissolved in 100 mL of the one of characterised above three buffers, to prepare the **test buffer solution** having pH = 5 (**Acetate test buffer solution**), pH = 7 (**Phosphate test buffer solution**) or pH = 9 (**Borate test buffer solution**). The concentration of the dissolved test item in each **test buffer solution** was determined experimentally by LSC.

5-mL aliquots of so prepared **test buffer solutions** were sterilised by filtering them through sterile 0.45-μm nylon filters and injected into the sterilised test vials with sterile needles.

The test vials after introduction of the **test buffer solutions** were weighed in order to determine the exact volume of the solution in each vial (assuming that the density of the **test buffer solutions** was 1.0 g/cm³).

The so prepared samples were then placed in the incubation chamber and incubated in the darkness at the constant temperature $T = 25 \pm 1^{\circ}\text{C}$ for up to 30 days.

At pre-designated time points – 0, 7, 14, 21, 28 and 30 days after the experiment began, triplicate samples of each buffer solution were taken for the analysis.

Some of the test vials were periodically weighed during incubation to determine if there were any loss of solution.

The solution from each sampled vial was analysed for the total radioactivity content. That was done by LSC using three 0.10-mL aliquots. Each sample was also analysed directly by HPLC in order to quantify the levels of the parent compound and the products of hydrolysis. Also the pH of each sample was measured at sampling.

LSC analysis was performed in 15 mL of UltimaGold liquid scintillation cocktail using Packard Tri-Carb LS counter equipped with automatic external standardisation. The minimum sensitivity of LSC analysis was 1.0 E-3

ppm. When expressed as Lowest Acceptable Gross Count Rate (LAGC) it was 70 cpm, while as Lowest Acceptable Net Count Rate (LANC) – 35 cpm, assuming average background (BCGK) of 35 cpm ($LAGC = 2 \times BCGK$ and $LANC = LAGC - BCGK$). The greatest probable error GPE = 8.83%. The average sample counting size was 0.1 mL, sample counting time was 5 min., background counting time 5 min. and the average counting efficiency – 95%.

The quantitative HPLC analysis was performed using Shimadzu-6A HPLC system equipped with UV detector and radioactivity detector. The chromatographic separation was performed in a gradient mode on Econosil C18 chromatographic column. The elution lasted for 35 minutes. The gradient mode used in the analysis is presented below in the table B.8.2.1.1._CA-2.

Table B.8.2.1.1._CA-2: The gradient mode used in the HPLC analysis of samples collected during the study.

Time [minutes]	Solvent system	
	% Solvent A – water + 0.025% CH ₃ COOH	% Solvent B – CH ₃ CN + 0.025% CH ₃ COOH
0	90	10
25	0	100
30	0	100
35	90	10

Additional chromatographic method used in the experiment was TLC. It was carried out on Silica gel 60 F-254, 0.25-mm thick plates developed in 100% CH₃COOC₂H₅. The detection was carried out using TLC-radioactivity scanner and UV detector.

Finally, the GC-MS method was used. The GC system consisted of Hewlett Packard 5890 device, equipped with DB-5ms capillary GC column (15-m long, 0.25-mm i. d, 0.25-μm film thickness). The chromatographic analysis was carried out using the following programme: the initial T = 80°C held for 1 min, then increased to T = 250°C at rate 20°C/min and was hold at T = 250°C for another 20 min. The temperature of injector was T = 250°C. The GC instrument was coupled with Finnigan Incos 50 mass spectrometer, scanning in range 50 – 350 amu at rate 0.4 sec./scan. The source temperature was T = 180°C and the carrier gas was HE administered at rate 25 cm/sec.

Results and their discussion:

The results of the verification of the pH of each **test buffer solution** are presented below in the table B.8.2.1.1._CA-3. On their basis it can be stated that the pH of the buffer solutions was stable throughout the experiment.

Table B.8.2.1.1._CA-3: The results of the verification of the pH of each **test buffer solution** in function of time.

Sampling time point [day]	Measured pH of the buffer solution:		
	pH 5 (Acetate)	pH 7 (Phosphate)	pH 9 (Borate)
0	5.20	7.11	9.01
7	4.92	6.97	8.82
14	5.00	7.06	8.84
21	5.05	7.10	8.81
28	5.01	7.06	8.77
30	5.20	7.14	8.92
Average pH (SD)	5.06 (0.10)	7.07 (0.05)	8.86 (0.08)

The results of the experiment – amount of the radioactivity in the solution at each time point, determined by LSC, and its identity, determined using HPLC, are presented below, separately for each **test buffer solution**, in tables B.8.2.1.1._CA-4 – B.8.2.1.1._CA-6.

These results show that no hydrolytic degradation of Flufenacet was observed at any tested pH and T = 25°C.

It shall be indicated that in case of all three **test buffer solutions** some results of the determination of the total radioactivity in solution were rejected, as being lower and not passing the quotient test. The Applicant attributed those lower amounts of recovered radioactivity to the fact that it could have been bound to the nylon filter during sterilization. RMS decided, in order to distinguish these values, to give them in italics.

Table B.8.2.1.1._CA-4: The results of the experiment in **pH = 5 (Acetate) test buffer solution.**

Sampling time point [day]	Radioactivity recovered [dmp] (results of LSC analysis)					Radioactivity recovered identified as Flufenacet [%AR] (results of HPLC analysis)		
	Replicate 1	Replicate 2	Replicate 3	Average	% of DAT 0 RA	Replicate 1	Replicate 2	Replicate 3
0	316674	354485	353792	354139	100.0	95.0	95.7	95.5
7	346289	345722	351951	347987	98.3	94.0	95.2	95.2
14	353700	351339	355685	353575	99.8	93.9	95.5	95.2
21	348993	342469	338540	343334	96.9	95.5	95.6	95.4
28	357669	353567	353878	355038	100.3	95.4	95.3	95.1
30	349015	349486	353012	350504	99.0	95.0	95.0	94.4

Table B.8.2.1.1._CA-5: The results of the experiment in **pH = 7 (Phosphate) test buffer solution.**

Sampling time point [day]	Radioactivity recovered [dmp] (results of LSC analysis)					Radioactivity recovered identified as Flufenacet [%AR] (results of HPLC analysis)		
	Replicate 1	Replicate 2	Replicate 3	Average	% of DAT 0 RA	Replicate 1	Replicate 2	Replicate 3
0	326198	375428	375929	375679	100.0	95.3	95.4	95.4
7	361652	360805	369169	363875	96.9	95.2	95.5	94.6
14	368124	366984	371505	368871	98.2	95.3	95.4	95.4
21	347580	347134	310242	347357	92.5	95.2	94.5	94.4
28	371972	378954	366336	372221	99.1	94.8	94.4	94.6
30	364997	364878	368555	366143	97.5	93.6	94.4	93.5

Table B.8.2.1.1._CA-6: The results of the experiment in **pH = 9 (Borate) test buffer solution.**

Sampling time point [day]	Radioactivity recovered [dmp] (results of LSC analysis)					Radioactivity recovered identified as Flufenacet [%AR] (results of HPLC analysis)		
	Replicate 1	Replicate 2	Replicate 3	Average	% of DAT 0 RA	Replicate 1	Replicate 2	Replicate 3
0	284237	321739	325162	310379	100.0	94.1	94.6	94.5
7	311875	308930	316212	312339	100.6	93.5	93.4	92.9
14	317704	319742	317290	318245	102.5	93.5	93.5	93.3
21	307000	269167	306608	306804	98.8	92.3	92.6	93.0
28	314580	316899	316666	316048	100.3	91.9	91.7	90.9
30	308242	310027	310855	309708	99.8	91.4	91.1	91.2

The results were kinetically examined using linear regression method. As they do not comply with the current standards RMS decided to repeat that examination using non-linear regression method. The modelling tool used in the kinetic fitting was CAKE ver 3.1. The values used in the analysis are those reported in tables B.8.2.1.1._CA-4 – B.8.2.1.1._CA-6 as *Radioactivity recovered identified as Flufenacet*. The graphical results are presented below on figure B.8.2.1.1._CA-2. The key numerical results of that examination are presented in the table B.8.2.1.1._CA-7

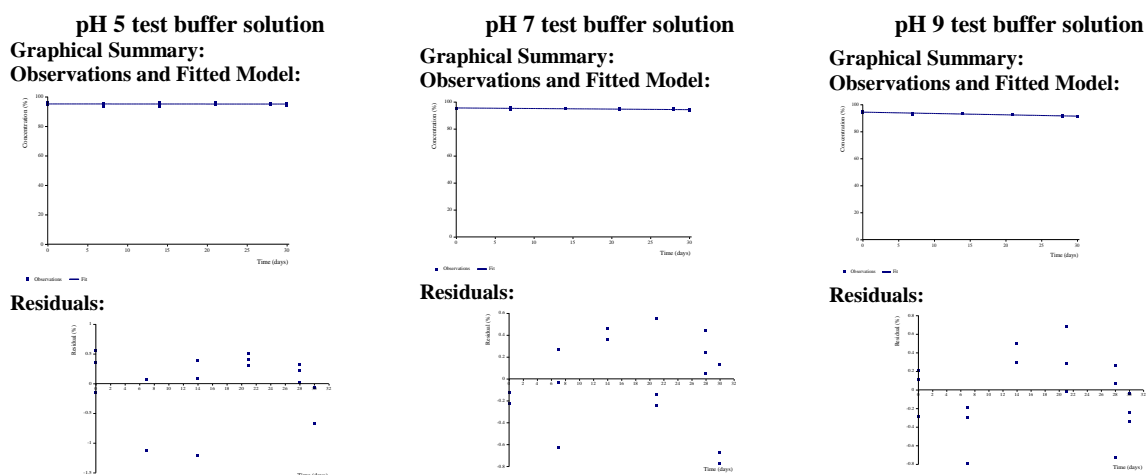


Figure B.8.2.1.1_CA-2: The graphical results of the examination of the rate of abiotic aquatic hydrolysis of Flufenacet.

Table B.8.2.1.1.1_CA-7: The numerical results of the examination of the rate of abiotic aquatic hydrolysis of Flufenacet.

pH 5 test buffer solution										
Kinetic model	Model parameters	Statistical evaluation of the parameter					Statistical evaluation of the fit		Kinetic endpoints (best-fit values)	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R ²	DT ₅₀ [days]	DT ₉₀ [days]
				Lower	Upper					
SFO	M ₀	95.15	0.229	94.66	95.64	n. d. ¹⁾	0.243	0.003	>10000	>10000
	k	2.78 E-5	1.21 E-4	-2.29 E-4	0.00	0.411				
pH 7 test buffer solution										
Kinetic model	Model parameters	Statistical evaluation of the parameter					Statistical evaluation of the fit		Kinetic endpoints (best-fit values)	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R ²	DT ₅₀ [days]	DT ₉₀ [days]
				Lower	Upper					
SFO	M ₀	95.53	0.182	95.14	95.91	n. d. ¹⁾	0.238	0.567	1570	5230
	k	4.41 E-4	9.63 E-5	2.36 E-4	0.001	1.56 E-4				
pH 9 test buffer solution										
Kinetic model	Model parameters	Statistical evaluation of the parameter					Statistical evaluation of the fit		Kinetic endpoints (best-fit values)	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	R ²	DT ₅₀ [days]	DT ₉₀ [days]
				Lower	Upper					
SFO	M ₀	94.39	0.183	94.00	94.78	n. d. ¹⁾	0.255	0.879	655	2180
	k	0.001058	9.83 E-5	8.50 E-4	0.001	4.84 E-9				

Conclusions: The results of the study demonstrated that at $T = 25^{\circ}\text{C}$ Flufenacet was hydrolytically stable in the whole examined pH range pH 5 – pH 9. No products of hydrolytical degradation of that compound were detected.

Study 2:

Report: Shah J. F., Bloomberg A. M., (1999): "Hydrolysis study of Thiadone (A Metabolite of FOE 5043)."; Ricerca LLC, Department of Environmental and Metabolic Fate, 7528 Auburn Road, Painesville, Ohio 44077, USA (performing laboratory) for Bayer Corporation, Agriculture Division, P. O. Box 4913, Kansas City, MO 64120, USA; Ricerca document No. 7410-0058-EF-001, study No. F3082402 (Bayer); Bayer Report No. 108719; 22 February 1999; study reference number: M-009620-01-1;

Guidelines: The study was performed to comply with the following Guidelines:

- US. EPA Guidelines for Pesticide Registration, Subdivision N, Section 161-1.

GLP: Yes;

RMS comments: This is a newly submitted study, examining the aqueous hydrolysis of FOE Thiadone – a major degradation product of Flufenacet in both soil and aquatic environment (water/sediment systems). For the purpose of the current assessment the study was evaluated for its compliance with OECD Guideline 111 – Hydrolysis as a Function of pH. RMS stated that the study complied with the provisions of the reference Guideline, therefore it can be considered acceptable for the present assessment. It is summarised below.

Summary:

The aim of the study was to investigate the hydrolysis of FOE Thiadone – the major soil and aquatic degradation product of Flufenacet, in aqueous solution in the environmentally relevant pH range of 5-9 and temperature $T = 25^{\circ}\text{C}$.

The test compound used in the experiment was radiolabelled FOE Thiadone, labelled in C2 position, as shown below on figure B.8.2.1.1._CA-3. It had radiochemical purity of 97.7% and specific activity of 50.5 mCi/mmol, corresponding to 0.294 mCi/mg or 652680 dpm/ μg .

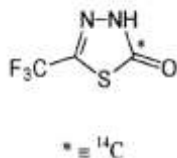


Figure B.8.2.1.1._CA-3: The structural formula of the test compound; radiolabelling position is indicated by an asterisk - (*); (copied from the study report).

Also the non-radiolabelled test compound, having a chemical purity of 99.3%, was used in the experiment. From it a stock solution was prepared by dissolving ~10 mg of the test compound in 10 mL of CH_3CN .

The test vessels were sterile autosampler vials, which were placed in the dark in environmental chambers and kept at $T = 25 \pm 1^{\circ}\text{C}$.

All glassware used in the experiment was sterilised with steam at $\sim 123^{\circ}\text{C}$ for about 20 minutes, after being wrapped in foil. After sterilisation they were kept covered with foil until being used.

The experiment was performed using three buffer solutions:

- pH 5 buffer (acetate buffer),
- pH 7 buffer (phosphate buffer),
- pH 9 buffer (borate buffer),

each having a concentration of 0.05 M. The detailed information on the composition of each buffer and method of its preparation is given below in the table B.8.2.1.1._CA-8.

Table B.8.2.1.1._CA-8: The composition and properties of the buffer solutions used in the experiment.

Type of buffer solution	Nominal pH	Composition	Method of preparation	Final concentration
<i>Acetate buffer</i>	5	0.2 M CH ₃ COOH + 0.2 M CH ₃ COONa	a) 72.5 mL of 0.2M CH ₃ COOH (glacial) were combined with 177,5 mL of 0.2M diluted with CH ₃ COONa; b) The solution was brought to the volume of 1000 mL with HPLC-grade water.	0.05M
<i>Phosphate buffer</i>	7	0.2M KH ₂ PO ₄ + 1.0 M NaOH _{aq}	a) 250 mL of 0.2M KH ₂ PO ₄ were combined with 29 mL of 1.0M NaOH _{aq} ; b) The solution was brought to the volume of 1000 mL with HPLC-grade water.	0.05M
<i>Borate buffer</i>	9	0.2M KCl/H ₃ BO ₃ _{aq} + 1.0 M NaOH _{aq}	a) 250 mL of 0.2M KCl/H ₃ BO ₃ _{aq} solution were combined with 21 mL of 1.0M NaOH _{aq} ; b) The solution was brought to the volume of 1000 mL with HPLC-grade water.	0.05M

The so prepared buffer solutions were sterilised by passing them through a 0.22-µm cellulose acetate membrane filters.

Next the **fortification solution** of FOE Thiadone was prepared by placing 0.75 µL of the stock solution of radiolabelled test compound, having a specific activity of ~2396.7 µg/mL, in 5-mL volumetric flask. The solvent – acetone, was allowed to evaporate and the residue was reconstituted in 3 mL of CH₃CN. The so prepared solution had a specific activity, determined by LSC, of ~59.92 µg/mL. Its purity was conformed by radio-HPLC.

So prepared **fortification solution** was used to treat the samples of each test buffer solution. That was performed in the following way: 0.68 mL of the **fortification solution** was added to the 80 mL of each sterilised buffer using 1-mL gas-tight syringe. The amount of the organic co-solvent – CH₃CN, in so prepared buffer solutions did not exceed 1%. The levels of fortification of so prepared solutions were: ~0.52 ppm for pH 5 buffer, ~0.53 ppm for pH 7 buffer and ~0.53 ppm for pH 9 buffer solutions.

Next, to each sterilised sample vial ~4.7 mL of the given treated buffer solution were introduced using the sterilised pipette. The vials were then capped, adequately labelled and placed in the darkness at T = 25 ± 1 °C to be incubated for up to 30 days.

At pre-designated time points – 0, 3, 7, 14, 21, and 30 days after the experiment began, samples of each buffer solution were taken for the analysis.

The solution from each sampled vial was analysed for the total radioactivity content. That was done by LSC using three 0.10-mL aliquots. Each sample was also analysed directly by HPLC in order to quantify the levels of the parent compound and the products of hydrolysis. Also the pH of each sample was measured at sampling.

LSC analysis was performed in 5 or 10 mL of UltimaGold liquid scintillation cocktail using Beckman LS 6500 LC liquid scintillation counter. Samples were counted for two minutes. The device operated in the constant background subtraction mode.

The quantitative HPLC analysis was performed using Waters HPLC system equipped with Waters 484 Tunable Absorbance detector set to λ = 254 nm, and Radiomatic Flo-One/β A-250 radio-chromatography detector.

The chromatographic separation was performed in a gradient mode on Phenomenex Luna C18 (150 x 4.6 mm, 5 µm) chromatographic column preceded by Zorbax Rx-C18 (12.5 X 4.6 mm) guard column. The elution lasted for 70 minutes. The gradient mode used in the analysis is presented below in the table B.8.2.1.1._CA-9. The flow rate of the mobile phase was 1.0 mL/min.

Table B.8.2.1.1._CA-9: The gradient mode used in the HPLC analysis of samples collected during the study.

Time [minutes]	Solvent system	
	% Solvent A – water + 0.05% CH ₃ COOH	% Solvent B – CH ₃ OH
0	100	0
40	30	70
60	30	70
61	100	0
70	100	0

Additional chromatographic method used in the experiment was LC-MS. The chromatographic analysis was carried out in a gradient mode using Phenomenex Columbus C8 (150 x 2.0 mm, 5 µm) chromatographic column. The mobile phase consisted as 0.05% HCOOH in water as **Solvent A** and CH₃OH as **Solvent B**. The gradient was following: for the first 2 minutes 1:1 then until minute 8th of elution to 3:7 (ratio **Solvent A: Solvent B**). The flow rate of the mobile phase was 0.2 mL/min.

The LC instrument was coupled with Finnigan mass spectrometer, scanning in range 95 – 300 amu at rate 1.5 sec./scan. The source temperature was T = 220°C. The detector worked in (-)ESI ionisation mode.

Results and their discussion:

The results of the verification of the pH of each **test buffer solution** are presented below in the table B.8.2.1.1._CA-10. On their basis it can be stated that the pH of the buffer solutions was stable throughout the experiment.

Table B.8.2.1.1._CA-10: The results of the verification of the pH of each **test buffer solution** in function of time.

Sampling time point [day]	Measured pH of the buffer solution:					
	pH 5 (Acetate)		pH 7 (Phosphate)		pH 9 (Borate)	
	Replicate 1	Replicate 2	Replicate 1	Replicate 2	Replicate 1	Replicate 2
0	5.03	5.03	7.02	7.00	9.07	9.01
3	5.07	5.05	7.03	7.03	9.06	9.04
7	5.05	5.05	7.07	7.05	9.07	9.07
14	5.06	5.05	7.04	7.03	9.05	9.05
21	5.03	5.05	7.05	7.06	9.09	9.09
30	5.06	5.05	7.04	7.06	9.07	9.06

The results of the experiment – amount of the radioactivity in the solution at each time point, determined by LSC, and its identity, determined using HPLC, are presented below, separately for each **test buffer solution**, in tables B.8.2.1.1._CA-11 – B.8.2.1.1._CA-13. These results show that no hydrolytic degradation of FOE Thiadone was observed at any tested pH and T = 25°C. The “Other constituents” fraction is a multi-component fraction, attributed to the presence of impurities in fortification solution. None of its constituents was in amounts enabling its further identification.

Table B.8.2.1.1._CA-11: The results of the experiment in pH = 5 (Acetate) test buffer solution.

Sampling time point [day]	The results of LSC analysis		The results of HPLC analysis					
	Radioactivity recovered as Thiadone equivalents [ppm]	% Recovery	Replicate 1			Replicate 2		
			Radioactivity recovered [% applied]	Identified as Thiadone [%]	Other constituents [%]	Radioactivity recovered [% applied]	Identified as Thiadone [%]	Other constituents [%]
0	0.524	100.0	99.7	96.15	3.85	101.2	95.72	4.28
3	0.523	99.7	99.6	95.60	4.40	100.3	95.67	4.33
7	0.527	100.6	100.6	95.92	4.08	97.6	96.02	3.98
14	0.528	100.7	104.5	95.83	4.17	99.9	95.68	4.32
21	0.516	98.4	101.5	96.12	3.88	101.1	96.15	3.85
30	0.513	97.9	102.6	95.98	4.02	104.5	96.42	3.58

Table B.8.2.1.1._CA-12: The results of the experiment in pH = 7 (Phosphate) test buffer solution.

Sampling time point [day]	The results of LSC analysis		The results of HPLC analysis					
	Radioactivity recovered as Thiadone equivalents [ppm]	% Recovery	Replicate 1			Replicate 2		
			Radioactivity recovered [% applied]	Identified as Thiadone [%]	Other constituents [%]	Radioactivity recovered [% applied]	Identified as Thiadone [%]	Other constituents [%]
0	0.526	100.0	100.7	95.62	4.38	102.9	95.24	4.76
3	0.512	99.1	103.3	97.03	2.97	99.8	97.27	2.73
7	0.522	99.3	100.1	96.17	3.83	98.9	97.31	2.69
14	0.532	101.1	101.7	96.70	3.30	98.5	96.39	3.61
21	0.519	98.7	99.2	96.91	3.09	101.7	97.20	2.80
30	0.514	97.8	110.1	97.75	2.25	100.1	97.10	2.90

Table B.8.2.1.1._CA-13: The results of the experiment in pH = 9 (Borate) test buffer solution.

Sampling time point [day]	The results of LSC analysis		The results of HPLC analysis					
	Radioactivity recovered as Thiadone equivalents [ppm]	% Recovery	Replicate 1			Replicate 2		
			Radioactivity recovered [% applied]	Identified as Thiadone [%]	Other constituents [%]	Radioactivity recovered [% applied]	Identified as Thiadone [%]	Other constituents [%]
0	0.528	100.0	100.8	95.62	4.38	102.8	95.24	4.76
3	0.526	99.6	99.3	97.03	2.97	103.9	97.27	2.73
7	0.520	98.4	100.2	96.17	3.83	102.5	97.31	2.69
14	0.522	98.9	101.4	96.70	3.30	106.3	96.39	3.61
21	0.522	98.9	101.3	96.91	3.09	100.4	97.20	2.80
30	0.526	99.7	104.1	97.75	2.25	100.0	97.10	2.90

The data were not kinetically examined as it was stated that the concentration of FOE Thiadone remained generally the same in all buffer samples throughout the study duration. As a result, it was stated that FOE Thiadone was hydrolytically stable in the environmentally relevant pH range – pH = 5 – 9 and at environmentally relevant temperature T = 25°C.

RMS having examined the results stated that the conclusion drawn by the Applicant was correct and decided not to perform own kinetic analysis of the data as that would not change the final conclusions, but would unnecessary overburden the summary.

Conclusions: The results of the study demonstrated that at T = 25°C FOE Thiadone was hydrolytically stable in the whole examined pH range pH 5 – pH 9. No identifiable products of hydrolytic degradation of that compound were detected and quantified.

Study 3:

Report: Babczinski P., Jantzen T., (2009): “[Thiadiazole-2-¹⁴C]FOE5043-Thiadone (BCS-AA41715): Hydrolytic degradation.”; Bayer Crop Science AG, Alfred-Nobel-Str. 50, D-40789 Monheim am Rhein, Germany; study No. M1111833-8, Report No. MEF-009/308; 2009. 10. 26; study reference number M-358419-01-1;

Guidelines: The study was performed to comply with the following Guidelines:

- OECD Guideline No. 111, Hydrolysis as a Function of pH, 2004;
- Commission Directive 94/37/EC (1994) and 95/36/EC (1995) amending Council Directive 91/414/EEC (Fate and Behaviour in the Environment).

GLP: Yes;

RMS comments: This is a newly submitted study, examining the aqueous hydrolysis of FOE Thiadone – a major degradation product of Flufenacet in both soil and aquatic environment (water/sediment systems). It was evaluated for its compliance with the evoked guideline – OECD Guideline 111, Hydrolysis as a Function of pH. RMS stated that the study complied with the provisions of the reference Guideline, therefore it can be considered acceptable for the present assessment. It is summarised below.

Summary:

The aim of the study was to investigate the hydrolysis of FOE Thiadone – the major soil and aquatic degradation product of Flufenacet, in aqueous solution in the pH range of 4 – 9 and temperature T = 50°C.

The test compound used in the experiment was radiolabelled Flufenacet, labelled evenly in phenyl ring, as shown below on figure B.8.2.1.1._CA-4. It had radiochemical purity of > 99% (determined by radio-HPLC and radio-TLC) and chemical purity of > 99% (determined by HPLC). The compound's specific activity was 4.28 MBq/mg. It was delivered to the test facility as a vacuum-dried solid.

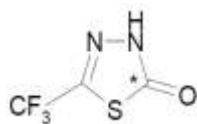


Figure B.8.2.1.1._CA-4: The structural formula of the test compound; radiolabelling position is indicated by an asterisk - (*); (copied from the study report).

The test compound was used to prepare a **Stock solution**, by dissolving the whole delivered sample in 3 mL of CH₃CN. That **stock solution** was used directly as application solution.

The test vessels were sterilised 10-mL glass crimp-top vials, closed with crimp caps with Teflon-faced septa. The vessels and other equipment used in the experiment were sterilised by steam pressure sterilisation.

The experiment was performed using three buffer solutions:

- pH 4 buffer (acetate buffer),
- pH 7 buffer (TRIS buffer),
- pH 9 buffer (borate buffer),

each having a concentration of 0.01 M. The detailed information on the composition of each buffer and method of its preparation is given below in the table B.8.2.1.1._CA-14.

Table B.8.2.1.1._CA-14: The composition and properties of the buffer solutions used in the experiment.

Type of buffer solution	Nominal pH	Composition	Method of preparation	Final concentration
<i>Acetate buffer</i>	4	CH ₃ COOH + CH ₃ COONa	a) 1.36 g of CH ₃ COONa x 3 H ₂ O was dissolved in 900 mL of demineralised ultrapure water; b) the pH of so prepared solution was measured and adjusted to pH = 4.0 using CH ₃ COOH; c) the whole solution was brought to the volume of 1 L with demineralised ultrapure water; d) oxygen was removed from the solution by passing through it N ₂ for 5 minutes; e) the so prepared buffer solution was sterilised by autoclaving it.	0.01M
<i>TRIS buffer</i>	7	(HOCH ₂) ₃ CNH ₂ + 0.1M HCl _{aq}	a) 1.21 g of TRIS – (HOCH ₂) ₃ CNH ₂ , was mixed with 46.6 mL of 0.1M HCl _{aq} and diluted to 800 mL with demineralised ultrapure water; b) the pH of so prepared solution was measured, adjusted to pH = 7.0 using 0.1M HCl _{aq} and its final volume brought to 1L using demineralised ultrapure water; c) oxygen was removed from the solution by passing through it N ₂ for 5 minutes; d) the so prepared buffer solution was sterilised by autoclaving it.	0.01M
<i>Borate buffer</i>	9	H ₃ BO ₃ aq + KCl + 0.5M NaOH _{aq}	a) 0.62g of H ₃ BO ₃ and 0.75 g of KCl were dissolved in ~800 mL of demineralised ultrapure water; b) the pH of so prepared solution was measured, adjusted to pH = 9.0 using 0.5M NaOH _{aq} and its final volume brought to 1L using demineralised ultrapure water; c) oxygen was removed from the solution by passing through it N ₂ for 5 minutes; d) the so prepared buffer solution was sterilised by autoclaving it.	0.01M

The characterised above aqueous buffer solutions were used to prepare the buffer solutions of the test compound used in the experiment. The **test buffer solutions** had the concentration of the test item (FOE Thiadone) $C = 1 \text{ mg/L}$.

That was done in the following way: 0.123-mL aliquots of the **stock solution** were pipetted into sterile Erlenmeyer flasks containing 100 mL of the given sterile and oxygen-free buffer. The solutions were homogenised and their 5-mL samples were pipetted, under sterile conditions, into 10-mL sterilised test vials. The number of prepared test vials was such to obtain, for each **test buffer solution** duplicate samples for each time point, 16 in total for each pH. The test vials were then closed with sterilised Teflon-faced septa, placed in a temperature-controlled water bath and incubated in the darkness at the constant temperature $T = 50 \pm 0.1^\circ\text{C}$ for up to 7 days. The sampling points were set to: 0, 0.1, 0.25, 1, 2, 5 and 7 days after introduction of the **test buffer solution**. The day-0 samples after taking aliquots for analysis were stored in a freezer.

The incubation chamber used in the study is shown below on figure B.8.2.1.1._CA-5.

The samples after removal from the incubation chamber were analysed in line with the general procedure presented on figure B.8.2.1.1._CA-6. The samples were not processed prior to the analysis.

The application rate and homogeneity of the **test buffer solutions** was verified by LSC before and after filling the test vials. All calculations were carried out using as a reference value the specific activity of the sample of the test item delivered to the laboratory performing the experiment – 4.28 MBq/mg.



Figure B.8.2.1.1._CA-5: The incubation chamber used in the experiment (copied from the study report).

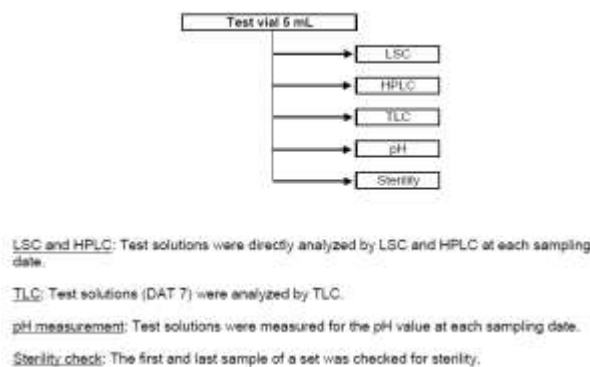


Figure B.8.2.1.1._CA-6: The general procedure for sample analysis used in the study (copied from the study report).

The sterility check in day-0 and day-7 samples was performed in the following way: 100- μL aliquot of the given sample was applied onto a mixed culture medium and incubated for 18 days in the darkness at the constant temperature $T = 30^\circ\text{C}$. After that period the microbial contamination was evaluated visually.

The LSC analysis of the samples was performed for their 0.1-mL aliquots in 2 mL of Quicksafe A + 5% water LS cocktail. The measurements were carried out using LS6000LL/LS6500 (Beckman) counter. The average counting efficiency was 91-92% and background 13-14 cpm.

The HPLC analysis was performed using 1.0-mL aliquots of each sample. It was carried out using Agilent 1100 HPLC system coupled to Ramona Star radioactivity detector and Agilent UV detector set to the wavelength $\lambda = 254 \text{ nm}$. The chromatographic separation was performed in a gradient mode on Purospher STAR RP-18

(250 x 4.6 mm, 5 µm) chromatographic column preceded by an unspecified guard column. The elution lasted for 35 minutes at the flow rate of the mobile phase of 1 mL/min. The gradient mode used in the analysis is presented below in the table B.8.2.1.1._CA-15.

Table B.8.2.1.1._CA-15: The gradient mode used in the HPLC analysis of samples collected during the study.

Time [minutes]	Solvent system	
	% Solvent A – Water + 1% HCOOH	% Solvent B – CH ₃ CN + 1% HCOOH
0	100.0	0.0
2	100.0	0.0
6	80.0	20.0
24	20.0	80.0
25	5.0	95.0
28	5.0	95.0
29	100.0	0.0

The identification of the test item was done by comparison of the retention times. The quantification was performed using the calibration curve, also used to determine the values of LOD and LOQ.

The HPLC-MS(/MS) analysis, used for the verification of the test item, was performed using Agilent HP110 HPLC system coupled with UV detector and Finnigan TSQ 7000 Mass Spectrometer.

The chromatographic separation was performed in a gradient mode on Nucleodur C18 Gravity(250 x 2.0 mm, 5 µm) chromatographic column. The elution lasted for 35 minutes at the flow rate of the mobile phase was set to 0.2 mL/min. The gradient mode used in the analysis is presented below in the table B.8.2.1.1._CA-16.

Table B.8.2.1.1._CA-16: The gradient mode used in the HPLC-MS (/MS) analysis of samples collected during the study.

Time [minutes]	Solvent system	
	% Solvent A – Water + 0.1% HCOOH	% Solvent B – CH ₃ CN + 0.1% HCOOH
0	95	5
1	95	5
25	5	95
35	5	95

Additional chromatographic method used in the experiment was TLC. It was carried out on silica gel plates Merck Si60, F-254, 0.25-mm thick, developed in CH₂Cl₂/CH₃COOC₂H₅/HCOOH 80:20:1 solvent system. The detection was carried out using TLC-radioactivity scanner and UV detector.

Results and their discussion:

The results of the verification of the application rate for each **test buffer solution** are presented below in the table B.8.2.1.1._CA-17.

Table B.8.2.1.1._CA-17: The results of the application rate of each **test buffer solution**.

Test buffer solution	Radioactivity in test buffer solution [Bq/5 mL]	Amount of FOE Thiadone in solution [µg/5 mL]	Concentration of FOE Thiadone in solution [µg/L]
<i>pH 4 (acetate buffer)</i>	21522	5.036	1.007
<i>pH 7 (TRIS buffer)</i>	21193	4.952	0.990
<i>pH 9 (borate buffer)</i>	22258	5.200	1.040

The continuous monitoring of the temperature in the incubation chamber showed that it was constant throughout the study – the temperature of the water bath was T = 50°C and that recorded in the chamber was T = 50.1°C.

The results of the determination of the pH in each buffer solution throughout the experiment were following:

- for pH = 4 (acetate) buffer the mean pH = 4.1 and did not vary;
- for pH = 7 (TRIS) buffer the mean pH = 7.0 with range 6.9 – 7.0;
- for pH = 9 (borate) buffer the mean pH = 9.0 and did not vary.

The results of the sterility check of each test solution showed no contamination with microorganisms, indicating that the sterility was maintained throughout the experiment.

For the HPLC method the determined LOD < 1% AR, corresponding to ~< 10 µg/L.

The results of the experiment – amount of the radioactivity in the solution at each time point, determined by LSC, and its identity, determined using HPLC, are presented below, separately for each **test buffer solution**, in tables B.8.2.1.1._CA-18 – B.8.2.1.1._CA-20.

These results show that no hydrolytic degradation of FOE Thiadone was observed at any tested pH and T = 50°C – the amount of recovered radioactivity identified as a test compound was in all samples > 90% AR and the amount of not identified radioactivity never surpassed 2%AR, most commonly being below 1% AR. For that reason it was decided not to perform the kinetic analysis of the data nor to examine the hydrolysis at lower temperature – T = 25°C or T = 20°C.

Table B.8.2.1.1._CA-18: The results of the experiment in **pH = 4 (Acetate) test buffer solution**.

Sampling time point [day]	Radioactivity recovered [% AR]			Radioactivity identified as FOE Thiadone [% AR]		
	Replicate 1	Replicate 2	Average	Replicate 1	Replicate 2	Average
0	98.9	99.1	99.0	98.4	98.8	98.6
0.1	102.0	100.8	101.4	101.1	100.2	100.7
0.25	101.0	100.4	100.7	100.3	98.8	99.5
1	100.6	100.3	100.4	100.5	100.1	100.3
2	99.7	97.9	98.8	99.6	97.8	98.7
5	94.9	92.9	93.9	94.5	92.4	93.5
7	91.4	94.5	92.9	90.9	94.4	92.6

Table B.8.2.1.1._CA-5: The results of the experiment in **pH = 7 (Phosphate) test buffer solution**.

Sampling time point [day]	Radioactivity recovered [% AR]			Radioactivity identified as FOE Thiadone [% AR]		
	Replicate 1	Replicate 2	Average	Replicate 1	Replicate 2	Average
0	100.0	99.6	99.8	99.3	99.1	99.2
0.1	100.8	100.4	100.6	100.0	100.4	100.2
0.25	101.4	100.2	100.8	100.8	99.5	100.1
1	100.5	100.4	100.4	100.3	99.7	100.0
2	100.8	100.4	100.6	100.4	100.3	100.4
5	98.9	99.5	99.2	97.9	99.0	98.5
7	100.2	99.5	99.8	100.1	99.4	99.7

Table B.8.2.1.1._CA-6: The results of the experiment in **pH = 9 (Borate) test buffer solution**.

Sampling time point [day]	Radioactivity recovered [% AR]			Radioactivity identified as FOE Thiadone [% AR]		
	Replicate 1	Replicate 2	Average	Replicate 1	Replicate 2	Average
0	100.1	99.8	100.0	99.9	99.0	99.5
0.1	100.9	100.8	100.9	100.7	100.4	100.5
0.25	100.9	100.4	100.6	100.1	100.0	100.1
1	102.1	101.2	101.6	101.8	101.1	101.5
2	101.3	99.8	100.6	100.5	98.9	99.7
5	100.5	100.5	100.5	100.5	99.7	100.1
7	99.8	100.3	100.0	99.8	99.8	99.8

The data were not kinetically examined as it was stated that the concentration of FOE Thiadone remained the generally same in all buffer samples throughout the study duration. As a result, it was stated that FOE Thiadone was hydrolytically stable in the pH range 4 – 9 and at temperature – T = 50°C.

RMS having examined the results stated that the conclusion drawn by the Applicant was correct and decided not to perform own kinetic analysis of the data as that would not change the final conclusions, but would unnecessary overburden the summary.

Conclusions: The results of the study demonstrated that at T = 50°C FOE Thiadone was hydrolytically stable in the whole examined range of pH = 4 – 9. No identifiable products of hydrolytical degradation of that compound were detected and quantified.

Additionally RMS, performing the repeated literature search, identified one paper relevant for the evaluation of Flufenacet in the area of its hydrolytical degradation in aqueous environment. The study is summarised below as **Study 4**.

Study 4:

Report: Sunita Rani, Beena Kumari, TS Kathpal, (2006): “Effect of pH on the Dissipation Behaviour of Flufenacet (FOE-5043) in Water.”; Department of Entomology, CCS Haryana Agricultural University, Hisar (India); published study - published in: “Pesticide Research Journal”, 2006, 18 (2), 201 – 204;

Guidelines: : None declared as this is an open-source study, therefore not submitted for the regulatory purposes.

GLP: no, not applicable – peer-reviewed scientific paper

RMS comments: The paper presents the results of the examination of the effect of pH on the rate of dissipation of Flufenacet from water column. The experiment was performed for two different concentrations of Flufenacet – 0.5 µg/mL (0.5 mg/L) and 1.0 µg/mL (1.0 mg/L) at three different pH values – pH = 5.2, pH = 7.2 and pH = 8.2. The tested pH range corresponded to that observed in the environment. In the study report it was not specified what kind of water was used – natural, tap, distilled or specially prepared water, nor whether the test water was sterilised or not. The paper however bears several references to the microbial activity of water, therefore it may be assumed that the test medium – water used in the experiment, was not sterilised.

It shall be indicated that the study does not seem to follow the analytical protocol outlined in the OECD 111 Guideline. However, it provides a good insight into the problem of whether the pH of water may have any influence on the dissipation/degradation of Flufenacet from water column and what may be the extent of that effect. For that reason RMS decided to include it into the assessment. However, due to the noted drawbacks:

- water used in the study was not characterised,
- the exact sampling dates, in days after treatment, were not provided,
- the concentrations of Flufenacet are provided only for water column and there is no information on the amount of the test compound remaining in the test system (adhering to the test vessels, precipitated at the bottom of the test vessels, forming an emulsion film on its surface), so there is no proper mass balance performed,
- the temperature during incubation period, lasting for 28 weeks, was not constant, but, being room temperature, it varied in a substantial range of (as reported in the summarised paper) T = 1.0 – 39.5°C,

RMS is of the opinion that the results it provides are only indicative. Therefore they may be regarded only as supplementary and should not be used as a source of regulatory endpoints.

Summary:

The publication contained a summary in English. However, because of the copyright restrictions, RMS decided not to present it here and the readers are kindly asked to consult the relevant document. Instead, below is presented the extended summary prepared by the RMS.

Extended summary prepared by RMS:

The aim of the study was to investigate the dissipation of Flufenacet in water at different pH levels. The test compound was non-radiolabelled analytical grade (99% purity) Flufenacet obtained from M/s Bayer India Ltd. It

was used to prepare the stock solution, having the concentration of 0.1 mg/mL, in hexane. The application solutions were prepared by diluting it.

The dissipation was examined in water samples having three different pH levels – 5.2, 7.2 or 8.2. The water samples having pH = 5.2 were obtained using the phosphate buffer ($\text{KH}_2\text{PO}_4 + 10\% \text{H}_3\text{PO}_4$ in water) and those having pH = 8.2 using the ammonium buffer ($\text{NH}_4\text{Cl} + \text{NH}_4\text{OH}$ in water). It was not specified how the water samples having pH = 7.2 were obtained, but it may be assumed that that was probably the original pH of water used in the experiment and as such it was probably not adjusted.

The water samples having a different pH, were prepared in triplicate for each fortification level, which was either 0.5 mg Flufenacet/L or 1.0 mg Flufenacet/L. The volume of each replicate sample was 6 litres.

The treated water samples were stored in Winchester bottles from July 2001 to February 2002 at room temperature ($T = 1.0 - 39.5^\circ\text{C}$). The untreated control samples were set along the treated ones. At pre-designated time points – 0 (1 hour), 1, 2, 5, 8, 11, 14, 16 and 28 weeks after treatment samples were drawn from each replicate and analysed for the content of Flufenacet.

The water samples taken at each sampling point were processed as follows: representative 200-mL samples were placed into 1-L funnel to which 5-10 g NaCl was added, and extracted three times with n-hexane, using 50 mL-, 30 mL- and 30 mL-portions of the organic solvent. The organic extracts were combined, passed through the anhydrous Na_2SO_4 and concentrated to dryness under vacuum. The residues were reconstituted in 1 mL of n-hexane and analysed by GC-ECD.

The chromatographic analysis was carried out using SPB-5 capillary column, 30-metres long, 0.32 mm i.d. 0.25 μm film thickness. The GC oven temperature was set to $T = 210^\circ\text{C}$. The identification was performed by means of the retention time – $R_t = 3.76$ min.

The LOD determined for the analytical procedure was 0.005 $\mu\text{g/mL}$ and the procedural recoveries of the test item were 88.98% at pH = 7.0 and 88.97% at pH = 8.2 (for the fortification levels of 0.25 $\mu\text{g/mL}$ and 0.50 $\mu\text{g/mL}$).

The numerical results of the experiments – the concentration of Flufenacet in water in function of time, at different pH and fortification levels, are presented below in the table B.8.2.1.1._CA-7. On their basis the authors performed the kinetic analysis of the process of dissipation of Flufenacet from water using the linear regression method. The key results of that analysis are presented in the next table – B.8.2.1.1._CA-8.

Table B.8.2.1.1._CA-7: The concentrations of Flufenacet in water at different pH and fortification levels in function of time.

Time point [weeks]	Amount of Flufenacet in water having pH = 5.2 and the fortification level:				Amount of Flufenacet in water having pH = 7.2 and the fortification level:				Amount of Flufenacet in water having pH = 8.2 and the fortification level:			
	0.5 $\mu\text{g/mL}$		1.0 $\mu\text{g/mL}$		0.5 $\mu\text{g/mL}$		1.0 $\mu\text{g/mL}$		0.5 $\mu\text{g/mL}$		1.0 $\mu\text{g/mL}$	
	in $\mu\text{g/mL}$ (SD)	in % dissipated	in $\mu\text{g/mL}$ (SD)	in % dissipated	in $\mu\text{g/mL}$ (SD)	in % dissipated	in $\mu\text{g/mL}$ (SD)	in % dissipated	in $\mu\text{g/mL}$ (SD)	in % dissipated	in $\mu\text{g/mL}$ (SD)	in % dissipated
0	0.492 (0.002)	----	0.984 (0.010)	----	0.488 (0.005)	----	0.977 (0.003)	----	0.490 (0.002)	----	0.965 (0.004)	----
1	0.480 (0.009)	2.4	0.950 (0.024)	3.5	0.473 (0.032)	3.1	0.946 (0.004)	3.2	0.479 (0.013)	2.2	0.941 (0.057)	2.5
2	0.443 (0.013)	9.9	0.830 (0.004)	15.7	0.437 (0.007)	10.5	0.838 (0.008)	14.2	0.410 (0.026)	16.3	0.819 (0.017)	15.2
5	0.363 (0.004)	26.2	0.733 (0.022)	25.5	0.365 (0.007)	25.2	0.755 (0.026)	22.7	0.309 (0.008)	36.9	0.637 (0.046)	34.0
8	0.302 (0.012)	38.6	0.615 (0.008)	37.5	0.313 (0.010)	35.9	0.579 (0.020)	40.7	0.256 (0.011)	47.8	0.532 (0.022)	44.9
11	0.157 (0.003)	68.1	0.274 (0.010)	72.2	0.209 (0.035)	57.2	0.349 (0.002)	64.3	0.113 (0.013)	76.9	0.233 (0.005)	75.9
14	0.040 (0.007)	91.9	0.093 (0.004)	90.5	0.047 (0.004)	90.4	0.101 (0.010)	89.7	0.022 (0.003)	95.5	0.060 (0.007)	93.8
16	9.020 (0.002)	95.9	0.072 (0.020)	91.2	0.023 (0.004)	95.3	0.065 (0.004)	93.3	0.015 (0.001)	96.9	0.052 (0.004)	94.6
20	0.014 (0.004)	97.2	0.042 (0.005)	95.7	0.015 (0.001)	96.9	0.045 (0.002)	95.4	0.012 (0.001)	97.6	0.040 (0.002)	95.9

Table B.8.2.1.1._CA-8: The results of the kinetic analysis of the data presented in the table B.8.2.1.1._CA-7.

Parameters of the test system		Results of the kinetic analysis			
pH	Fortification level [µg Flufenacet/mL]	Regression equation	Dissipation rate		Correlation coefficient
			Rate constant	DT ₅₀ [days]	
5.2	0.5	$y = 2.76 - 0.0651 x$	0.0214	32.4	0.94
	1.0	$y = 3.03 - 0.0568 x$	0.0187	37.0	0.95
7.2	0.5	$y = 2.77 - 0.0627 x$	0.0206	33.6	0.94
	1.0	$y = 3.03 - 0.0559 x$	0.0184	37.7	0.94
8.0	0.5	$y = 2.71 - 0.0694 x$	0.0228	30.4	0.92
	1.0	$y = 3.00 - 0.0600 x$	0.0197	35.1	0.93

Characterising the performed kinetic analysis the authors of the publication stated that the decline curves were three-phase 1st order curves, with slow initial and terminal phases and fast middle phase. On the figures presenting the graphical results of the kinetic analysis of the data they had sigmoidal shape, similar to that taken by the titration curves.

It was also stated that the shape of the decline curves and the concentrations at each time point for the given fortification level were similar for all three tested pH values. Therefore it was stated that the process of dissipation of Flufenacet from water phase was independent of its pH.

RMS comments:

The study, because of its design, provides results that can be considered solely as indicative and supplementary with regard to the examination of hydrolytic degradation of Flufenacet in aquatic systems. For that reason it cannot be used to derive the EU regulatory endpoints. They confirm however the statement that abiotic hydrolysis will not play any significant role in transformation of Flufenacet in water.

Summary – Hydrolysis of Flufenacet

The abiotic hydrolysis of Flufenacet was examined at three different pH – pH = 5, pH = 7 and pH = 9 (environmentally relevant pH range) and T = 25°C. The results of that examination, presented in one study report, demonstrated that Flufenacet was hydrolytically stable within the whole examined pH range. The determined in that experiment half-lives at T = 25°C were: DT₅₀ > 1000 days for pH 5-7 and DT₅₀ = 655 days for pH = 9.

Additionally the results presented in the open source paper identified as a relevant for the evaluation of Flufenacet showed that the pH of the aqueous solution, and hence the hydrolysis, had only minimal influence on the rate of dissipation/degradation of Flufenacet from water (biologically viable). The results of that study were considered however only as indicative and were not used to derive the regulatory endpoints.

Also stable to abiotic hydrolysis in the aquatic environment, for the same environmentally relevant conditions, was demonstrated to be the major soil and aquatic major degradation product of Flufenacet – FOE Thiadone. The determined half-lives were DT₅₀ > 1000 days for the whole tested range pH = 5-9 and T = 25°C.

The results of the examination of the hydrolytic degradation of Flufenacet in water, in form recommended for reporting the regulatory endpoints in the EU, are presented below.

Hydrolytic degradation (Regulation (EU) N° 283/2013, Annex Part A, point 7.2.1.1

Hydrolytic degradation of the active substance and metabolites > 10 % *results for Flufenacet – active substance*

pH 5: *stable (DT₅₀ > 10000 days) at 25 °C (1st order - SFO, $\chi^2=0.234$)*
no degradation products detected

pH 7: *stable (DT₅₀ = 1570 days) at 25 °C (1st order - SFO, $\chi^2=0.238$)*
no degradation products detected

pH 9: *stable (DT₅₀ = 655 days) at 25 °C (1st order - SFO, $\chi^2=0.255$)*
no degradation products detected

Hydrolytic degradation of the active substance and metabolites > 10 % *results for FOE Thiadone – major soil and aquatic degradation product of Flufenacet*

pH 5: *stable at 25 °C*
no degradation products detected

pH 7: *stable at 25 °C*
no degradation products detected

pH 9: *stable at 25 °C*
no degradation products detected

B.8.2.1.2 – Photochemical degradation

To address the issue of photochemical degradation of Flufenacet and its major degradation products in aquatic environment the Applicant submitted four study reports. Two of them, both for Flufenacet, were also submitted for the previous authorisation of Flufenacet in the EU. One of them is summarised under the data point for direct aqueous photolysis and under that for indirect aqueous photolysis, as it covers both aspects of phototransformation in the aquatic environment. The second study is related only to the direct photochemical transformation in water.

The Applicant also submitted two new studies, not previously evaluated in the EU. Their aim was to examine the direct and indirect photodegradation of FOE Thiadone – the major aquatic degradation product of Flufenacet identified in water/sediment studies. Each of them will be summarised under the relevant data point of this Renewal Assessment Report.

It shall be indicated that in the previous Assessment Report it was stated that “As no relevant metabolites were formed in the photolysis study on the active ingredient, no further studies are necessary”.

However, FOE Thiadone, although not a photodegrade of Flufenacet, was shown to be formed from the parent compound in the aquatic environment, in other processes, in substantial amounts (> 80%). Due to its physicochemical properties – aqueous solubility $S \geq 95.5$ g/L at $T = 20^{\circ}\text{C}$ and whole environmentally relevant pH range – pH = 5-9, as well as its moderate adsorption potential – in soil the Freundlich adsorption constant was in range $K_f = 0.115 - 0.703$ mL/g, that compound is expected to be present mainly in water phase (the results of water/sediment study seem to confirm that). Therefore the examination of its potential direct aqueous photodegradation, and possibly also indirect, is required.

B.8.2.1.2.1. – Direct Photochemical degradation

The following two studies present the results of the examination of the direct photolysis of Flufenacet in water.

Study 1:

Report: Kasper A. M., Shadrick B. A., (1995): “Aqueous Photolysis of [Phenyl- ^{14}C] FOE 5043.”; Bayer Corporation (formerly Miles Inc.), Agriculture Division, P. O. Box 4913, Kansas City, Missouri 64120-0013, USA; study No. F3082401 (Bayer); unpublished Miles Report No. MR 106246; 30 May 1995; study reference number: M-002206-01-1;

Guidelines: The study was performed to comply with the following Guidelines:

- US. EPA Guidelines for Pesticide Registration, Subdivision N, Section 161-2, Aqueous Photolysis Studies.

GLP: Yes, for the part off the study aimed on the examination of direct aqueous photolysis

RMS comments: The study had been evaluated for the previous authorisation of Flufenacet in the EU. Its summary can be found under the point B.7.4.2.1., in section B.7 of the Annex B to the Monograph prepared by the RMS – France, for Flufenacet. It presents the results of the examination of both direct photolysis of Flufenacet in water (a GLP study) and the indirect aqueous photolysis of that compound (a non-GLP study). For the purpose of the current assessment the study was evaluated for its compliance with the following guidelines:

- OECD Guideline 316: Phototransformation of Chemicals in Water – Direct Photolysis, Adopted 3 October 2008;
- US EPA Guideline OPPTS 835.2210 – Direct Photolysis Rate in Water by Sunlight; January 1998;
- US EPA Guideline OPPTS 835.2240 – Photodegradation in Water; October 2008;
- US. EPA Guidelines for Pesticide Registration, Subdivision N, Section 161-2, Aqueous Photolysis Studies (indicated as reference Guideline in the study report);
- OECD Guidelines for the Testing of Chemicals, Proposal for a New Guideline – Phototransformation of Chemicals in Water – Direct and Indirect Photolysis, Draft Document August 2000 (additional reference document);

RMS stated that the study was compliant with the provisions of the Guidelines listed above, therefore it was found acceptable. It is summarised, in its part related to the examination of direct aqueous photolysis, below. The summary for the part of the experiment aimed on the examination of indirect aqueous photolysis of Flufenacet will be provided under the data point B.8.2.1.2.2.

Summary:

The aim of the study was to examine the direct photodegradation of Flufenacet in aqueous solution through:

- determining the half-life of that compound when exposed to artificial sunlight in sterile aqueous buffer;
- identifying the transformation pattern and in particular the degradation products formed in amounts greater than 10% AR.

The experiment was performed in sterilised buffer solution having pH = 5, as at that pH Flufenacet was demonstrated to display the highest hydrolytic stability. The glassware used in it was sterilised by autoclaving for 20 minutes at T = 121°C and p = 14 psi.

The buffer used in the experiment was 0.01 M acetate buffer, prepared by mixing 0.01M CH₃COONa_{aq} with 0.01M CH₃COOH_{aq} solutions until reaching pH = 5. It was used to prepare the test solution.

The test compound was [Phenyl-U-¹⁴C] Flufenacet, having a specific radioactivity of 66.5 mCi/mmol. Its structural formula is presented below on figure B.8.2.1.2.1._CA-1. It was delivered in form of benzene solution, having a concentration 4.55 mg Flufenacet/mL.

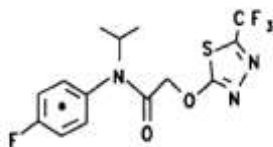


Figure B.8.2.1.2.1._CA-1: The structural formula of the test compound; radiolabelling position indicated with an asterisk (copied from the study report).

To prepare the test solution 0.44 mL of the benzene solution of [Phenyl-U-¹⁴C] Flufenacet was transferred to 45-mL graduated centrifuge tube and evaporated to dryness. The residue was dissolved in 20 mL of CH₃CN and quantitatively transferred to a sterilised 2-L volumetric flask, where it was brought to the volume with the appropriate amount of acetate buffer. So prepared test solution had the concentration 1 mg Flufenacet/L and the content of organic co-solvent of 1%. Its radiochemical purity, determined by HPLC, was 99.2%, and when determined by TLC – 99.9%.

At the beginning of the experiment 60-mL portions of the test solution characterised above were filtered through a Millex GV 0.22 µm sterile filters into the sterilised, foil-wrapped quartz vessels used as test vessels.

The sterility of filtered test solution was checked using Petrifilm Aerobic Count Plates. To do that 1 mL of filtered test solution was plated on the film and placed in incubator set at T = 21°C. The plates were checked for colony growth after 24 and 48 hours.

The vessels filled with test solution were sealed with the volatile trapping columns to form the incubation vessels shown below on figure B.8.2.1.2.1._CA-2. The joints were wrapped with parafilm to grant the air-tightness.

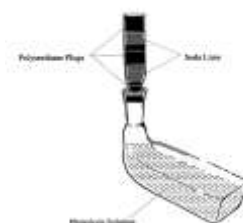


Figure B.8.2.1.2.1._CA-2: Test vessel used in the experiment (copied from the study's report).

The so prepared test vessels designated to be irradiated were placed, after removal of the foil wrapping them, in the irradiation chamber to be irradiated for up to 246 hours (10.25 days). The irradiation chamber was Suntest CPS unit, equipped with Heraeus xenon-arc lamp as light source. It is presented below on figure

B.8.2.1.2.1._CA-3. The lamp was equipped with a UV-filter to cut-off all radiation below $\lambda = 290$ nm. The Suntest CPS unit was a part of the photolysis system shown on the figure B.8.2.1.2.1._CA-4.

The dark-control samples were prepared alongside the irradiated samples. The test vessels were prepared in the same way as described above for irradiation samples, but without removing the foil wrapping them after they were sealed with the volatile trapping columns, and they were placed in the water bath and incubated for the same time and at the same temperature as irradiated samples. The number of prepared test vessels was such to grant duplicate irradiated samples and a single dark control sample per each sampling points. The number of sampling points was 7. The sampling protocol (sampling dates and number of samples collected at each time point) is provided below in the table B.8.2.1.2.1._CA-1.

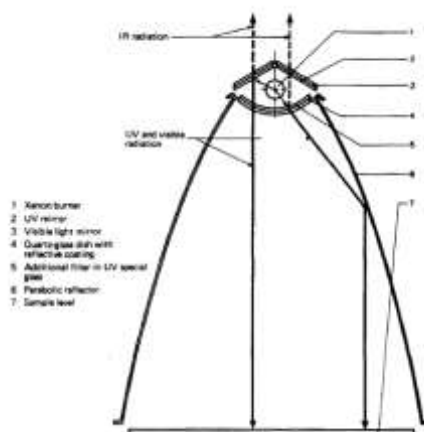


Figure B.8.2.1.2.1._CA-3: The Suntest CPS unit used in the experiment (copied from the study report).

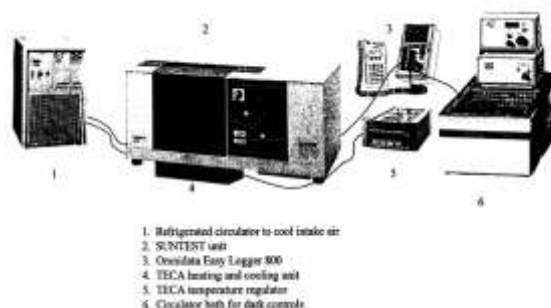


Figure B.8.2.1.2.1._CA-4: The photolysis system used in the experiment (copied from the study report).

The vessels were kept in the irradiation/incubation chambers for up to 246 h, or 10.25 Suntest days (24-hours periods), the irradiated samples under constant exposure to the light emitted by xenon-arc lamp. That exposure period was determined to match a 30-days exposure to sunlight at worst case conditions in Phoenix, Arizona. That estimate was based on the following assumptions:

- total irradiance <800 nm measured in a weather station in Phoenix, AZ (site: New River), on 23rd June 1988 was **681.7 W/m²** (68%),
- total radiant exposure measured at the same site on the same day was **29.5 MJ/m²**.

The calculated from these values daily “global irradiation” at noon on the 23rd June 1988 in Phoenix, AZ, was **20 MJ/m²**.

Using that value it was determined that simulating such irradiation conditions with Suntest unit operating at 680 W/m² would result in **8.2-h** exposure corresponding to one solar day under the worst case conditions assumed above. Using that value the time of irradiation corresponding to the required in Guidelines 30-days exposure to natural sunlight was determined.

The experiment was performed under the constant temperature of 25⁰C by placing all test vessels – irradiated and dark controls (wrapped with foil to cut the light off), in the water bath set to the constant temperature $T = 25 \pm 1^0\text{C}$.

Table B.8.2.1.2.1._CA-1: The sampling protocol used in the study.

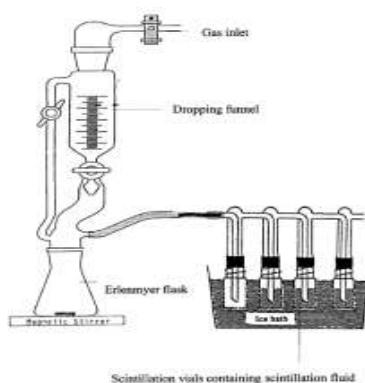
Sampling interval	Sampling time for:			Samples collected – type and number
	Suntest unit (real sampling dates)		Natural sunlight (calculated) [days]	
	[hours]	[days]		
1	0	0	0	Irradiated samples – 2 vessels; dark control – 1 vessel;
2	41	1.71	5	Irradiated samples – 2 vessels; dark control – 1 vessel;
3	86	3.58	10.5	Irradiated samples – 2 vessels; dark control – 1 vessel;
4	123	5.13	15	Irradiated samples – 2 vessels; dark control – 1 vessel;
5	164	6.83	20	Irradiated samples – 2 vessels; dark control – 1 vessel;
6	206	8.58	25.1	Irradiated samples – 2 vessels; dark control – 1 vessel;
7	246	10.25	30	Irradiated samples – 2 vessels; dark control – 1 vessel;

After sample removal, at specified sampling intervals, from the incubation/irradiation chamber, irradiated samples were wrapped with aluminium foil, tower traps for volatile compounds removed and processed for the content of radioactivity.

From each collected test vessel three 0.2-mL aliquots of the test solution were sampled to be analysed for radioactivity content by LSC. Then the pH of the solution was determined and the sterility of the solution in irradiated samples checked using the solution taken from one of the replicates. The sterility was checked using a Pertifilm Aerobic Count Plate method, the same as used to check the sterility of filtered test solution introduced to the test vessels. Next, 1-mL aliquots of each sample were analysed by HPLC. That was done immediately after collecting the test vessels at the given sampling point. Finally 14-mL aliquots of each sample were concentrated to 1 mL on rotary evaporator and analysed by TLC.

The collected traps for volatile compounds were analysed in a following way:

- Polyurethane plugs were removed, rinsed with CH₃CN and both rinse and the plug were analysed for the content of radioactivity using LSC;
- ¹⁴CO₂ captured in soda lime was liberated using the apparatus presented on figure B.8.2.1.2.1._CA-5. This was done by placing the whole 4-g portion of soda lime from each trapping column in 250-mL Erlenmeyer flask containing 10 mL of H₂O, to which 15 mL of concentrated HCl was added. The system was vented with N₂ and released ¹⁴CO₂ captured in a set of three scintillation vials, each containing 15 mL of scintillation cocktail – Carbo-Sorb E and Permafluor E⁺ 2:5 (v/v). The content of vials was analysed quantitatively by LSC.

**Figure B.8.2.1.2.1._CA-5:** The apparatus used to liberate ¹⁴CO₂ from soda lime traps (copied from the study report).

All samples were analysed for the content of radioactivity using LSC method. The LSC (Liquid Scintillation Counting) analysis was performed using a Packard Tri-Carb Model 4640 counter, equipped with automatic external standardisation.

Liquid samples were analysed in triplicate, with 15 of Ultima Gold solution added to 0.1-mL aliquots of the analysed sample. The minimum sensitivity of LSC analysis for those samples was 3.9 E-4 ppm. It corresponded to 60 cpm when expressed as Lowest Acceptable Gross Count Rate (LAGC) and 30 cpm for Lowest Acceptable Net Count Rate (LANC), assuming Average Background (BCGK) of 30 cpm ($LAGC = 2 \cdot BCGK$ and $LANC = LAGC - BCGK$). The greatest probable error $GPE = 9.54\%$.

All samples were also analysed using the following techniques:

- HPLC – identification and quantitation method for parent compound and its degradation products;
- TLC – identification and quantitation method for parent compound and its degradation products;

The HPLC analysis was performed using a Shimadzu SCL-6A HPLC chromatograph coupled to Ramona 5-LS radioactivity monitor and Shimadzu SPD-6A UV detector set to $\lambda = 280$ nm. The system was equipped with PRP-1, 5 μ m, 305 \cdot 7 mm chromatographic column (Hamilton Co., Reno) and PRP-1 cartridge as a guard column. The chromatographic separation was performed in a gradient mode, using the mobile phase consisting of:

- water + 0.4% CH_3COOH as **Solvent A**, and
- CH_3CN + 0.4% CH_3COOH as **Solvent B**.

Gradient elution lasted 90 minutes. Its parameters are shown below in the table B.8.2.1.2.1._CA-2. The flow rate was set to 2 mL/min.

Table B.8.2.1.2.1._CA-2: The HPLC gradient mode used in the study.

Time [min]	Solvent ratio	
	<i>Solvent A – Water + 0.4% CH_3COOH</i>	<i>Solvent B – Acetonitrile + 0.4% CH_3COOH</i>
0	100	0
15	70	30
65	40	60
70	0	100
80	0	100
90	100	0

The LOD for chromatographic method, in reference to the performance of the used radioactivity detector, was determined to be 3000 dpm, what corresponded to 0.7% AR. The value was determined experimentally on the basis of the comparison of radioactivity injected and integrated area under the chromatographic peak. The linearity of the analysis, expressed as r^2 , was: $r^2 = 1.00$. Sample recoveries from the column were on average 93.2% with range 88.6 – 97.2% AR.

The identification of the chromatographic peaks was performed by means of the comparison of their retention times R_t with those of the standards. The retention times of the known reference standards are presented below in the table B.8.2.1.2.1._CA-3.

Table B.8.2.1.2.1._CA-3: HPLC identification of Flufenacet and its degradation products in the study.

Compound	HPLC identification – retention time (R_t) [min]:
<i>Flufenacet (FOE 5043)</i>	70.4
<i>FOE Alcohol</i>	33.7
<i>FOE Oxalate</i>	19.4
<i>FOE Sulfonic acid</i>	19.8
<i>FOE Methylsulfoxide</i>	25.3
<i>FOE Methylsulfone</i>	38.5
<i>FOE 5043 N-isomer</i>	74.4

The TLC analysis of the extracts was performed as RP-TLC (reversed phase TLC). It was carried out on Whatman $KC_{18}F$ TLC plates, having a dimensions 20x20 cm and 200- μ m thick, with a fluorescent indicator. The solvent system used to develop the TLC plates was $CH_3CN:CH_3OH:0.5N NaCl_{aq}$ 2:2:1 (v/v) solution. The identification of each individual constituent of the analysed extract was performed by means of the comparison of R_f values with those of the known standards. In case of Flufenacet the average $R_f = 0.47$.

The quantitative analysis was performed using RITA 68000 Radio-TLC analyser. The LOD of the method was experimentally determined to be 300 dpm, what enabled to detect the radioactivity residues at the level of at least 1 % AR. The linearity of the analysis, expressed as r^2 was: $r^2 = 0.9998$.

The UV-Vis absorption spectra of Flufenacet were determined at different pH – pH = 5, pH = 7 and pH = 9, using Shimadzu UV 260 spectrometer with a slit of 0.8 nm. The absorption spectrum was scanned within the wavelength range of $\lambda = 190 - 400$ nm.

Results and their discussion:

The absorption spectrum of Flufenacet, recorded at various pH for the wavelength range of $\lambda = 190 - 400$ nm, is presented below on figure B.8.2.1.2.1._CA-6. It shows that the maximum absorption for the test compound occurred at $\lambda \approx 220$ nm and the effective absorption range may be estimated to occur within the range of $\lambda = 200 - 250$ nm. Within the environmentally relevant range of $\lambda = 290 - 400$ nm the absorption of radiation was residual, what may indicate that the direct photolysis of Flufenacet in aqueous solutions would be negligible.

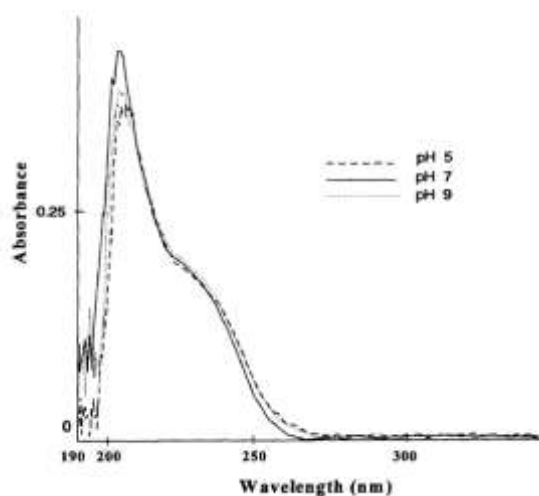


Figure B.8.2.1.2.1._CA-6: The UV-Vis absorption spectrum of Flufenacet recorded for $\lambda = 190 - 400$ nm (copied from the study report).

The examination of the sterility of irradiated samples showed that they were sterile throughout the duration of the experiment.

The irradiated samples in the Suntest unit and dark control samples in the water bath were kept in the constant temperature $T = 25 \pm 1^\circ\text{C}$. In case of the dark control samples that parameter was kept in a range $25.0 - 25.1^\circ\text{C}$, while for irradiated samples the range of incubation temperature was slightly broader: $23.3 - 25.6^\circ\text{C}$, but generally the temperature was $\geq 25.0^\circ\text{C}$.

The pH of the buffer solution in irradiated and dark control samples was on the generally constant level of 5.00. The detailed results of its determination are presented below in the table B.8.2.1.2.1._CA-4.

Table B.8.2.1.2.1._CA-4: The results of the determination of pH in irradiated and dark control samples.

Sampling point	Sampling time – hours of irradiation/incubation	pH measured in		
		Irradiated samples		Dark control samples
		Replicate 1	Replicate 2	
1	0	----	----	5.02 (Rep 1)/5.02 (Rep 2)
2	41	5.03	5.01	5.02
3	86	5.03	5.01	4.99
4	123	5.07	5.04	5.04
5	164	5.01	5.05	5.06
6	206	5.10	5.11	5.20
7	246	5.26	5.23	5.50

The characteristics of the light source – xenon lamp, is presented below in graphical form on figures B.8.2.1.2.1._CA-7 – spectral irradiance graph, and B.8.2.1.2.1._CA-8 – comparison of spectral distribution of xenon lamp used in the experiment and that of the natural sunlight.

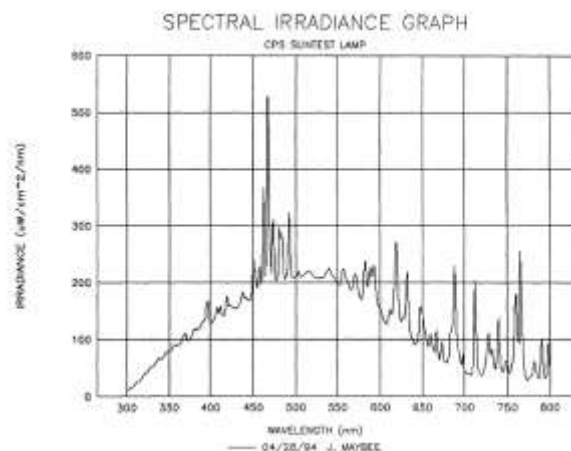


Figure B.8.2.1.2.1._CA-7: Spectral characteristic of the light source – xenon lamp, used in the study (copied from the study report).

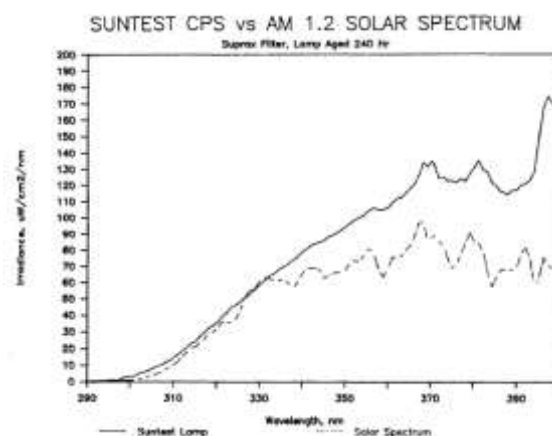


Figure B.8.2.1.2.1._CA-8: The comparison of the spectra of xenon lamp used in the study and of the natural sunlight (copied from the study report).

The quantitative analysis of solutions and traps for volatile compounds, showed that the recovery of applied radioactivity throughout the study was within the recommended range:

- for irradiated samples it ranged from 98.7% AR to 101.2% AR;
- for dark control samples it was in range of 95.0 – 101.1% AR.

The recovered radioactivity was generally found in the solution, with <0.1% AR detected in traps for volatile compounds at any sampling points.

The HPLC analysis showed that the recovered radioactivity consisted mainly of the test compound – Flufenacet, in amounts > 98%. Additionally two degradation products were identified: FOE Methylsulfone and FOE Alcohol. None of them was detected in amounts > 1.0% AR.

The TLC analysis of the content of the test vessels showed that the solutions contained only Flufenacet in amounts > 98%.

Practically no decrease of the concentration of Flufenacet was observed in either irradiated samples or in the dark control samples.

The detailed results are presented below in the table B.8.2.1.2.1._CA-5. The results of the HPLC and TLC analysis – the content of Flufenacet and other identified and quantified components of the sample are given as they were presented in the study report. The Applicant stated that since virtually all radioactivity was recovered in the solution, it was decided to report the concentrations as they were determined in integrated HPLC or TLC

chromatograms, not correcting them for the %AR determined in LSC analysis. In RMS's opinion that approach is acceptable.

Table B.8.2.1.2.1._CA-5: The detailed results of the experiment.

Results obtained for irradiated samples:								
Parameter		Value determined for the sampling point:						
Sampling point	Suntest days	0	1.71	3.58	5.13	6.83	8.58	10.75
	Natural sunlight days	0	5	10.5	15	20	25.1	30
Results of LSC analysis – [%AR] in:	Solution	95.0	100.7	100.6	100.0	100.4	101.2	98.7
	Volatile traps	----	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
	Total recovered:	95.0	100.7	100.6	100.0	100.4	101.2	98.7
Results of HPLC analysis - % in sample identified as:	Flufenacet	99.1	98.4	98.8	98.7	98.6	98.5	98.7
	FOE Methylsulfone	0.5	0.9	0.8	0.9	0.9	1.0	0.9
	FOE Alcohol	0.4	0.7	0.4	0.4	0.5	0.5	0.4
Results of TLC analysis - % in sample identified as Flufenacet:		98.7	98.0	99.0	99.0	98.5	99.0	99.1
Results obtained for dark control samples:								
Parameter		Value determined for the sampling point:						
Sampling point	Suntest days	0	1.71	3.58	5.13	6.83	8.58	10.75
	Natural sunlight days	0	5	10.5	15	20	25.1	30
Results of LSC analysis – [%AR] in:	Solution	95.0	100.7	100.5	100.4	101.1	100.2	99.6
	Volatile traps	----	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
	Total recovered:	95.0	100.7	100.5	100.4	101.1	100.2	99.6
Results of HPLC analysis - % in sample identified as:	Flufenacet	99.1	99.0	99.1	99.0	98.8	98.5	99.0
	FOE Methylsulfone	0.5	0.5	0.6	0.4	0.5	0.7	0.7
	FOE Alcohol	0.4	0.5	0.3	0.6	0.7	0.4	0.3
Results of TLC analysis - % in sample identified as Flufenacet:		98.7	99.3	99.4	99.1	99.2	99.2	99.2

The results presented above indicate that there was practically no degradation of Flufenacet during the experimental period in either irradiated samples or in the dark control. Also the results obtained in irradiated control samples and in the dark control samples were almost identical indicating that the negligible transaformation of the test compound observed in irradiated samples could not be attributed to the influence of light.

The data obtained for Flufenacet were further kinetically examined. The analysis was performed using first order kinetics and linear-regression model. As it does not comply with the current standards set by FOCUS Kinetics Guidance [FOCUS, 2006], it was repeated by the RMS. It was performed using CAKE 3.1 kinetic tool developed by Tessella. The input data used in the repeated kinetic analysis are presented below in the table B.8.2.1.2.1._CA-6. The analysis was performed using solely the SFO model. RMS decided, to maintain the consistency of the results, to use the Suntest days as time points for both irradiated samples and the dark control samples, as in case of dark control samples the use of recalculated time points – Natural sunlight days would bias the results. Additional fitting was performed for the irradiated samples using the Natural Sunlight days. The concentrations of Flufenacet used in the kinetic examination were those determined in HPLC analysis.

Table B.8.2.1.2.1._CA-6: The data for Flufenacet used in the kinetic examination performed by RMS.

Irradiated sample			Dark control sample	
Time point [days]		Concentration of Flufenacet [%]	Time point [days]	Concentration of Flufenacet [% AR]
Suntest days (real time point)	Natural Sunlight Days (converted time point)		Suntest days (real time point)	
0.00	0.0	99.1	0.00	99.1
1.71	5.0	98.4	1.71	99.0
3.68	10.5	98.9	3.68	99.1
5.13	15.0	98.7	5.13	99.0
6.83	20.0	98.6	6.83	98.8
8.58	25.1	98.5	8.58	98.9
10.25	30.0	98.7	10.25	99.0

The results of the repeated kinetic analysis of the data obtained for Flufenacet are presented below in the graphical form on figure B.8.2.1.2.1._CA-9 and in numerical form in table B.8.2.1.2.1._CA-7.

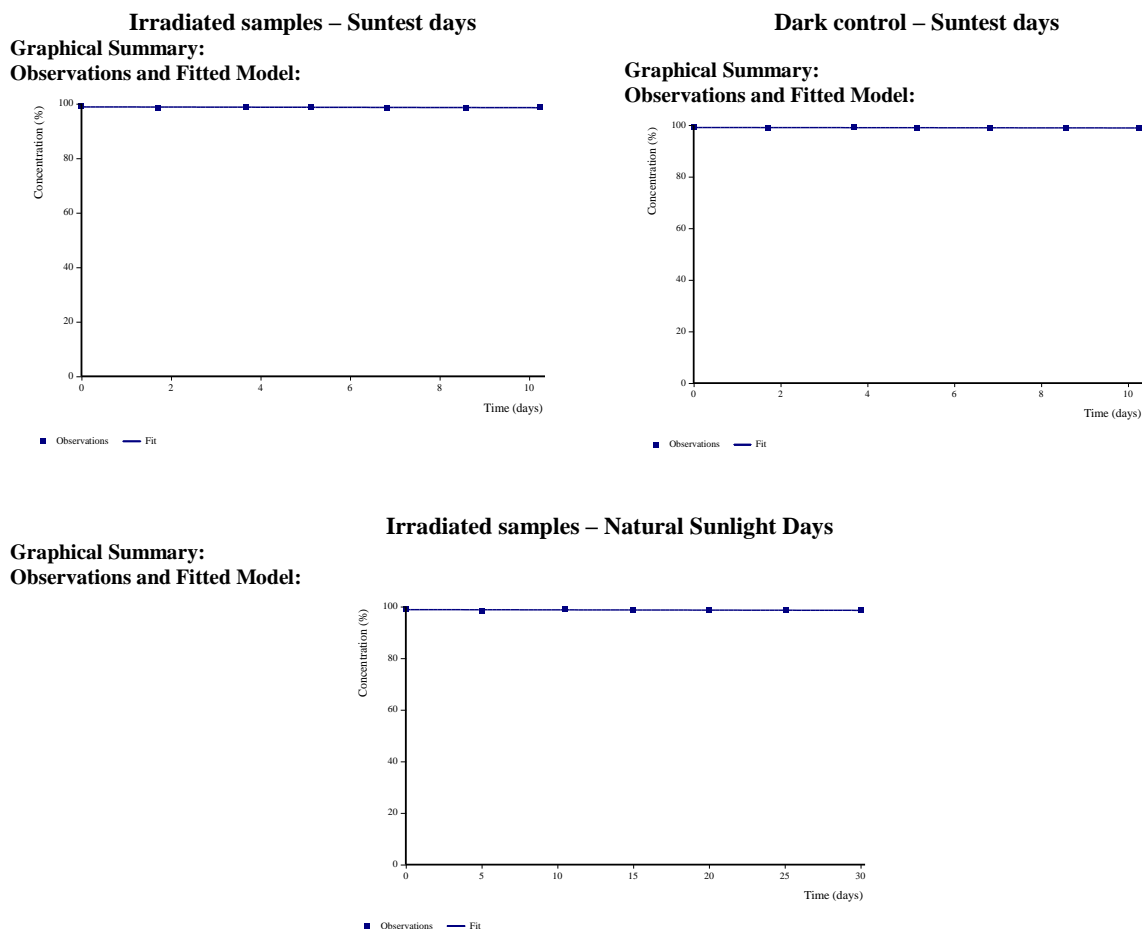


Figure B.8.2.1.2.1._CA-9: The graphical results of the examination of the direct aqueous photolysis of Flufenacet.

Table B.8.2.1.2.1._CA-7: The numerical results of the examination of the direct aqueous photolysis of Flufenacet.

Type of samples	Kinetic model	Model parameters	Statistical evaluation of the parameter					Statistical evaluation of the fit	
			Value	Error	Confidence intervals		Prob. > t	χ^2 % error	r
					Lower	Upper			
Irradiated-Suntest days	SFO	M_0	98.84	0.162	98.42	99.26	----	0.162	0.172
		k	0.000272	0.000267	-4.14 E-4	0.0001	0.177		
Dark control-Suntest days	SFO	M_0	99.07	0.066	98.9	99.24	----	0.065	0.322
		k	0.000167	0.000108	-1.11 E-4	0.00	0.092		
Irradiated-Natural Sunlight days	SFO	M_0	98.84	0.162	98.42	99.26	----	0.161	0.174
		k	0.0000934	0.0000909	-1.40 E-4	0.00	0.176		

The obtained fits, because virtually no degradation was observed, are of limited reliability. However, the tool returned the DT_{50} values, that may be considered indicative. They are following:

- for irradiated sample using Suntest days $DT_{50} = 2550$ days;
- for irradiated sample using Natural Sunlight days $DT_{50} = 7430$ days;
- for the dark control sample $DT_{50} = 4160$ days

These results clearly indicate that Flufenacet in water is photolytically stable and that direct photolysis as a mechanism of degradation of Flufenacet in surface water bodies will be of the negligible relevance.

Conclusions:

On the basis of the obtained results it may be stated that Flufenacet is not prone to direct photolysis in water. The relevance of that process for the overall degradation of Flufenacet in aquatic environment is therefore negligible.

Study 2:

Report: Hellpointner E., (1993): “Determination of the Quantum Yield and Assessment of the Environmental Half-life of the Direct Photodegradation of FOE 5043 in Water.”; Bayer AG, Crop Protection, Development, Institute for Metabolism Research, 51368 Leverkusen, Germany Study No. M 112 0566-1, Report No. PF-3919 (HPO-103); 27 September 1993; study reference number M-002206-01-1;

Guidelines: The study was performed to comply with the following Guidelines:

- Phototransformation of Chemicals in Water, Part A: Direct Phototransformation, UBA, Berlin, FRG, 1990;
- ECETOC (polychromatic light); (RMS’s comment: the full reference to that document is: *ECETOC, Technical Report No. 12. The Phototransformation of Chemicals in Water: Results of a Ring-Test. Brussels June 1984*;

GLP: Yes;

RMS comments: The study had been evaluated for the previous authorisation of Flufenacet in the EU. Its summary can be found under the point B.7.4.2.1., in section B.7 of the Annex B to the Monograph prepared by the RMS – France, for Flufenacet. It presents the results of the determination of quantum yield of direct photolysis of Flufenacet in water. For the purpose of the current assessment the study was evaluated for its compliance with the following guidelines:

- OECD Guideline 316: Phototransformation of Chemicals in Water – Direct Photolysis, Adopted 3 October 2008;
- US EPA Guideline OPPTS 835.2210 – Direct Photolysis Rate in Water by Sunlight; January 1998;
- US EPA Guideline OPPTS 835.2240 – Photodegradation in Water; October 2008;
- *ECETOC, Technical Report No. 12. The Phototransformation of Chemicals in Water: Results of a Ring-Test. Brussels June 1984* (indicated as technical reference Guideline in the study report);
- OECD Guidelines for the Testing of Chemicals, Proposal for a New Guideline – Phototransformation of Chemicals in Water – Direct and Indirect Photolysis, Draft Document August 2000 (additional reference document);

RMS stated that the study was compliant with the provisions of the Guidelines listed above, therefore it was found acceptable and as such it is summarised below. At the same time it can be stated that the study may be considered as facultative, because, in light of the recommendations provided by the Commission Regulation (EC) 283/2013, the determination of the quantum yield shall be carried out in case the direct photolysis of the given compound is demonstrated to be significant. The results of the study summarised above as **Study 1** show that Flufenacet is photolytically stable in the aquatic environment.

Summary:

The aim of the study was to determine the quantum yield of the direct photodegradation of Flufenacet in water and to estimate “environmental half-lives” of Flufenacet for that transformation process. The experiment was performed in line with the methodology presented in the document: *ECETOC, Technical Report No. 12. The Phototransformation of Chemicals in Water: Results of a Ring-Test. Brussels June 1984*

The test compound used in the experiment was non-radiolabelled Flufenacet, having a chemical purity of 99.5%. Its structural formula is presented below on figure B.8.2.1.2.1._CA-10.

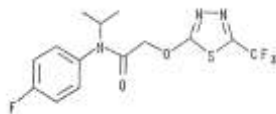


Figure B.8.2.1.2.1._CA-10: The structural formula of the test compound – Flufenacet (copied from the study report).

It was used to prepare the **Stock solution** by dissolving 50.9 mg of it in 10 mL of C₂H₅OH in 10-mL volumetric flask. The concentration of so prepared **Stock solution** was 5.09 mg/mL. That solution was subsequently used to prepare the test solutions used in the study.

The study consisted of the experimental part and the numerical analysis of the results using two numerical models.

The experimental part consisted of two steps:

- recording of UV-absorption spectrum of Flufenacet,
- the degradation experiment,

The test vessels used in the experiment were quartz cuvettes with teflon plugs, having optical path length $d = 1\text{ cm}$ and height $h = 4.4\text{ cm}$.

The recording of UV-absorption spectrum was carried out using UV-Vis spectrometer DMS 90 working in wavelength range $\lambda = 190 - 400\text{ nm}$. The absorption spectrum was collected using test solutions prepared in a following way: 0.2-mL, 0.5-mL and 1.0-mL aliquots of the **Stock solution** were diluted to 100 mL with the appropriate amount of CH₃CN/H₂O 1:9 solution. The obtained solutions had concentrations 10.18 mg/L, 25.45 mg/L and 50.9 mg/L. For calculations of quantum yield was used the UV spectrum determined for the solution having the concentration of 25.45 mg Flufenacet/L.

The degradation experiment was performed using a merry-go-round irradiation apparatus equipped with Hg lamp TO 150 and Duran 50 filter tube to cut-off the UV-radiation having wavelengths $\lambda < 295\text{ nm}$. It is presented below on figure B.8.2.1.2.1._CA-11.

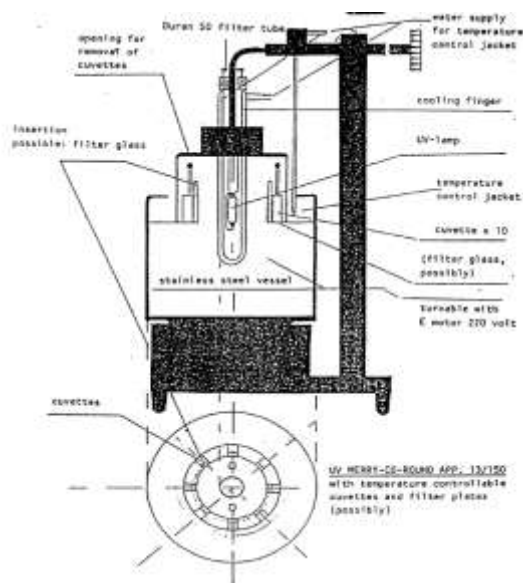


Figure B.8.2.1.2.1._CA-11: The merry-go-round irradiation apparatus used in the study (copied from the study report).

The experiment was carried out using the test solutions prepared from the **Stock solution** of Flufenacet by diluting its 0.1-mL aliquots to 100 mL with the appropriate amount of CH₃CN/H₂O 1:9 solution. The nominal concentration of so prepared test solutions was 5 mg Flufenacet/L and the measured concentrations were: 5.68 mg Flufenacet/L for the test solution used in the **Experiment 1** and 5.56 for the test solution used in the **Experiment 2**.

Other solutions used in the experiment were:

- **Actinometer solution (A)** prepared by dissolving 1.255g of uranyl nitrate (UO₂(NO₃)₂ · 6 H₂O) and 1.576g of oxalic acid ((COOH)₂ · 2 H₂O) in 250 mL water to obtain a solution containing 0.01 M UO₂²⁺ and 0.05M (COOH)₂;
- **Catalyzer solution for the titration (K)** prepared by dissolving 8.5 g manganese sulfate (MnSO₄ · H₂O) in 250 mL 1M sulphuric acid (1M H₂SO_{4 aq});
- **Titration solution (T)** – 0.05 N KMnO_{4 aq};

The irradiation apparatus was started approx. 30 minutes before the beginning of the exposure of the samples. That was done to guarantee the constant intensity of radiation emitted by the light source. The whole experiment was performed at constant temperature T = 25°C.

After that period two test vessels containing each 3 mL of the **Actinometer solution (A)** were placed in the apparatus and irradiated for 10 minutes. Then ten test vessels, each containing 3 mL of the test solution, were placed in the apparatus on a merry-go-round and irradiated for up to 7.5 hours. At pre-defined time points single samples were removed from the irradiation chamber to be analysed.

These sampling points, expressed in [hours of irradiation] were following:

- for **Experiment 1**: 0.00 hours, 0.65 hours, 1.46 hours, 2.26 hours, 3.08 hours, 4.71 hours, 5.40 hours, 6.15 hours, 6.78 hours, 7.31 hours;
- for **Experiment 2**: 0.00 hours, 0.75 hours, 1.48 hours, 2.25 hours, 3.00 hours, 3.75 hours, 4.50 hours, 5.25 hours, 6.00 hours, 6.76 hours, 7.46 hours;

At the end of the irradiation period another two vessels with 3 mL of the **Actinometer solution (A)** were placed on vacated positions in the irradiation apparatus and exposed to irradiation for 10 minutes.

The actinometers were used to determine the intensity of light acting on the testing solution. For that purpose the content of each actinometer (**Actinometer solution**) after irradiation was transferred to Erlenmeyer flask and brought to 50 mL with water. Next, 5 mL of the **Catalyzer solution for the titration (K)** was added to each flask and titrated with **Titration solution (T)** until the solution became permanently pink after addition of one droplet of the solution **T**. In the same way was titrated the unexposed **Actinometer solution**. The results were used to calculate the intensity of radiation absorbed by actinometers in range $\lambda = 295 - 490$ nm. That was done using QUANT programme calculating the light intensity and quantum yield.

The irradiated test solutions were analysed for the content of Flufenacet using RP-HPLC method. The HPLC analysis was carried out on HP1090 work station coupled with DAD detector set to $\lambda = 200$ nm, equipped with Select B RP 18 chromatographic column, 250mm · 4 mm, 5 μ m. The column was kept at constant temperature T = 40°C. The chromatographic elution lasted for 12 minutes and was carried out in isocratic mode using the mixture of two solvents: **A** and **B** in ratio 45:55. **Solvent A** was water/acetonitrile/phosphoric acid in ratio 95:5:0.2 (v:v:v) and **Solvent B** – 100% acetonitrile. The identification of the test compound was performed by means of the comparison of retention time with that of the standard. The quantitative analysis was also carried out using the external standard.

The calculation of quantum yield was carried out using the following sets of equations presented below on figure B.8.2.1.2.1._CA-12.

$$c_2 = \frac{E_1 + 1000}{V_1 \cdot F_1} ; c_3 = \frac{c_1}{M \cdot 1000} ; \epsilon_{10\%} = \frac{c_2 \cdot M \cdot V_3 \cdot 0.1}{1000}$$

Input of the user

E_1 : Amount weighed for degradation experiment
 V_1 : Volume in which the weighed amount is dissolved
 F_1 : Dilution factor concerning experiment 1
 M : Molecular weight of the test substance
 V_3 : Irradiated volume [ml]
Constants: $M_L = 5,022 \cdot 10^{23}$; $\tau = 0,05$;

Calculated values

c_1 : Concentration of the test substance [mg/l]
 c_2 : Concentration of the test substance [mole/l]
 $\epsilon_{10\%}$: 10% of applied molar extinction of the test substance

$$V_4 = V_3 - V_5 ; I_{ak} = \frac{V_4 \cdot E + E_0}{1000 \cdot 0,55 + 60 \cdot \tau} ; I_0 = \frac{E_0 \cdot I_1}{E_2}$$

Input of the user

τ : Time of exposure [min]
 V_4 : Consumption for the zero sample [ml]
 V_5 : Consumption for the irradiated solution [ml]

Calculated values

I_{ak} : Intensity of the radiation being absorbed by the actinometer [photons/e/exposed volume]
 I_0 : Intensity of the radiation entering in the degradation experiment
 V_4 : Volume difference in the case of the titration of the actinometer solution

Established values given by the data file (Quant.Quant.SAT):
 I_1 : Intensity of the radiation emitted by the lamp
 I_2 : Intensity of the radiation absorbed by the actinometer

$$c_3 = \frac{E_2 + 1000}{V_2 \cdot F_2} ; \epsilon_4 = \frac{c_3}{M \cdot 1000}$$

Input of the user

E_2 : Amount weighed for the UV-spectrum
 V_2 : Volume, in which the weighed amount was dissolved
 F_2 : Dilution factor (UV-spectrum)

Calculated values

c_3 : Concentration of the test substance [mg/l]
 c_4 : Concentration of the test substance [mole/l]

$$\epsilon = \frac{E}{c_4 \cdot d}$$

Input of the user

E : Extinction values for the individual wavelength
Constants: $d = 1$
 d : optical path length of the measuring cuvette

The molar extinction coefficients ϵ are then averaged over various ranges. These ranges are also included as established values in the data file of configurations Quant.Quant.SAT.

The averaging is done as follows:

Wavelength range [nm]	Number of values
295 - 300 nm	5 values
301 - 400 nm	10 values each
401 - 490 nm	10 values each

These averaged molar extinction coefficients are used for the following calculations:

$$OO = \epsilon \cdot c_2 ; \alpha = 1 - \frac{1}{10^{\frac{OO}{10}}} ; I_a = I_0 \cdot \alpha ; \epsilon = \frac{c_2 \cdot 10\%}{t_{10\%} \cdot 60 \cdot 0,95 \cdot 22}$$

Input of the user

$t_{10\%}$: Time for the degradation of 10% of the test substance [min]

Calculated values

OO: Optical density
 α : Degree of absorption
 I_a : Radiation being absorbed by the test substance in the degradation experiment
 ϵ : Quantum yield

Figure B.8.2.1.2.1._CA-12: The equations used in calculation of quantum yield (copied from the study report).

The calculated quantum yield was used to calculate the environmental half-lives for Flufenacet using GC-SOLAR and Frank-and Klöpffer computer models.

Results and their discussion:

The absorption spectrum of Flufenacet, recorded at various pH for the wavelength range of $\lambda = 190 - 400$ nm, is presented below on figure B.8.2.1.2.1._CA-13. It shows that the effective absorption range may be estimated to occur within the range of $\lambda = 190 - 250$ nm. Within the environmentally relevant range of $\lambda = 290 - 400$ nm the absorption of radiation was residual, what may indicate that the direct photolysis of Flufenacet in aqueous solutions would be negligible. The results – values of absorbance (in the study report called *Extinction* – E) and molar absorption coefficient ϵ (in the study report named *molar extinction coefficient*) for wavelength range $\lambda = 290 - 336$ nm, are presented in the table B.8.2.1.2.1._CA-8.

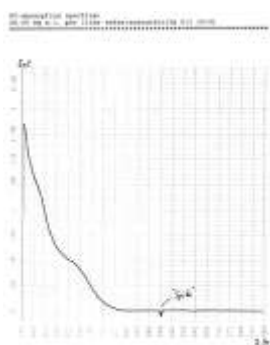


Figure B.8.2.1.2.1._CA-13: The absorption spectrum recorded for the solution of Flufenacet having concentration 25.45 mg/L (copied from the study report).

Table B.8.2.1.2.1._CA-8: The results of the determination of absorbance and molar absorption coefficient of Flufenacet in solution having concentration $C = 25.45 \text{ mg/L}$.

Wavelength [nm]	Results		Wavelength [nm]	Results		Wavelength [nm]	Results	
	Absorbance E	molar absorption coefficient ϵ		Absorbance E	molar absorption coefficient ϵ		Absorbance E	molar absorption coefficient ϵ
290	0.002	28	305	0.001	14	320	0.002	28
291	0.002	28	306	0.001	14	321	0.002	28
292	0.002	28	307	0.001	14	322	0.002	28
293	0.002	28	308	0.001	14	323	0.001	148
294	0.002	28	309	0.001	14	324	0.002	28
295	0.002	28	310	0.001	14	325	0.002	28
296	0.002	28	311	0.001	14	326	0.002	28
297	0.002	28	312	0.001	14	327	0.001	14
298	0.002	28	313	0.002	28	328	0.002	28
299	0.002	28	314	0.002	28	329	0.002	28
300	0.002	28	315	0.002	28	330	0.002	28
301	0.001	14	316	0.002	28	331	0.001	14
302	0.001	14	317	0.002	28	332	0.001	14
303	0.001	14	318	0.002	28	333	0.002	28
304	0.001	14	319	0.002	28	334-336	0.001	14

The results of the determination of the concentration of Flufenacet in irradiated solution in function of time are presented below in the table B.8.2.1.2.1._CA-9. These values were logarithmically transformed to determine the parameters of the degradation kinetics of Flufenacet in the process of direct aqueous photolysis. The graphical results of that determination are presented on figure B.8.2.1.2.1._CA-14 and the numerical results in the table B.8.2.1.2.1._CA-10. The rate constant determined that way was used to calculate the DT_{10} – value necessary to calculate the quantum yield ϕ .

Table B.8.2.1.2.1._CA-8: The results of the determination of concentration of Flufenacet in irradiated test solutions in function of time.

Experiment 1		Experiment 2	
Irradiation time [hours]	Concentration of Flufenacet [mg/L]	Irradiation time [hours]	Concentration of Flufenacet [mg/L]
0.00	5.68	0.00	5.56
0.65	5.64	0.75	5.54
1.46	5.67	1.48	5.50
2.26	5.64	2.25	5.51
3.08	5.64	3.00	5.51
4.71	5.63	3.75	5.52
5.40	5.59	4.50	5.49
6.15	5.45	5.25	5.43
6.78	5.57	6.00	5.43
7.31	5.53	6.76	5.49
		7.46	5.51



Table B.8.2.1.2.1._CA-14: The graphical results of the determination the rate of degradation of Flufenacet in the process of direct aqueous photolysis (copied from the study report).

Table B.8.2.1.2.1._CA-9: The key numerical results of the determination the rate of degradation of Flufenacet in the process of direct aqueous photolysis (as presented in the study report).

Parameter	Values for	
	Experiment 1	Experiment 2
Number of data points	10	11
Calculated rate constant k [hours ⁻¹]	0.0038	0.0018
DT ₅₀ [hours]	179.12	373.61
DT ₁₀ [minutes]	1663.59	3511.80
Correlation coefficient R	-0.8032	-0.6350
Determination coefficient R^2	0.6449	0.4031

The calculated quantum yield values were:

- for the **Experiment 1** $\phi = 1.307 \text{ E-3}$;
- for the **Experiment 2** $\phi = 0.622 \text{ E-3}$;
- the average $\phi = 0.00096$.

The detailed results of the determination of quantum yield in each experiment – the reports generated by the computer programme QUANT, are presented below on figure B.8.2.1.2.1._CA-15.

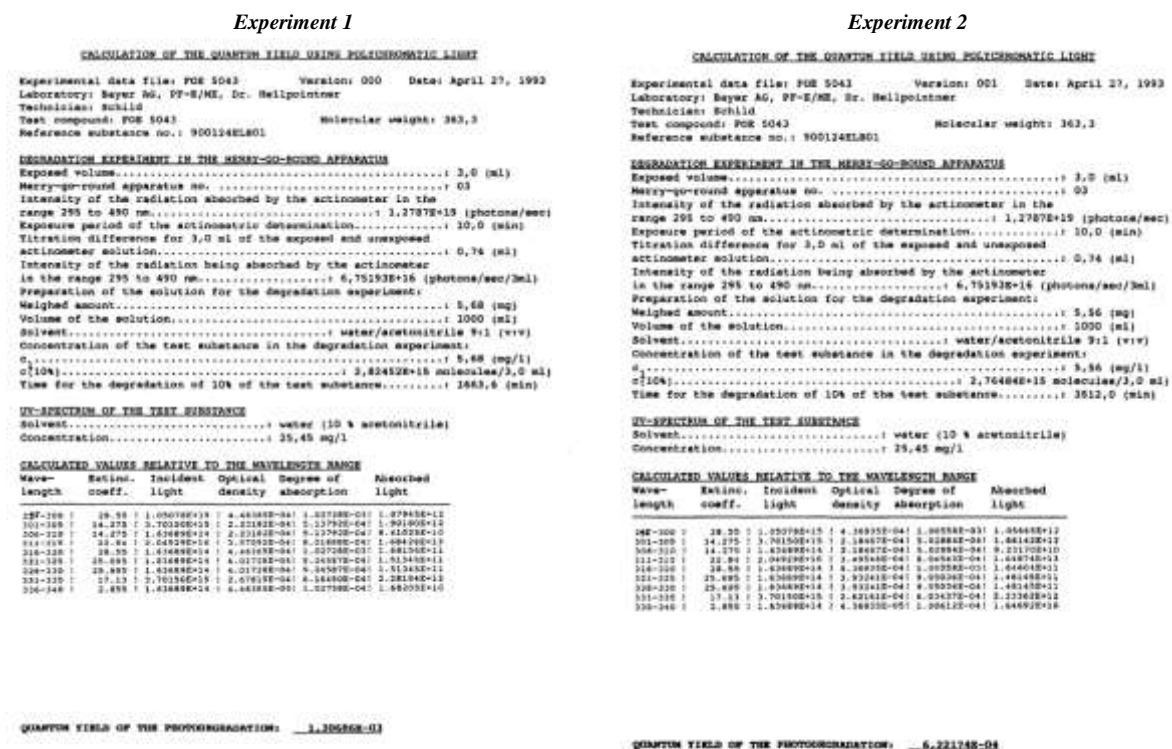


Figure B.8.2.1.2.1._CA-15: The results of the determination of quantum yield for Flufenacet – the reports generated by programme QUANT (copied from the study report).

The results of the determination of environmental half-lives for Flufenacet undergoing direct photodegradation in water, calculated using GC-SOLAR modeling tool and Frank-and-Klöpffer method, are presented below on figure B.8.2.1.2.1._CA-16. In case of the results obtained using Frank-and-Klöpffer method the calculations were performed for the latitude 50°N – the conditions representative for Germany.

GC-SOLAR method					Frank-and-Klöpffer method			
Environmental half-life [days] of FOE 5043					FOE 5043			
Season	30th	40th	50th	60th degree of latitude	Month	Photolysis ₁ constant [s ⁻¹]	Environmental half-life [days] minimum	mean
Spring	144	163	198	257	March	0,144 10E-7	290	> 1 a
Summer	126	131	142	160	April	0,268 10E-7	170	> 1 a
Fall	212	292	> 1 a	> 1 a	May	0,363 10E-7	140	> 1 a
Winter	308	> 1 a	> 1 a	> 1 a	June	0,413 10E-7	130	> 1 a
					July	0,367 10E-7	150	> 1 a
					August	0,346 10E-7	150	> 1 a
					September	0,190 10E-7	250	> 1 a
					October	0,225 10E-8	> 1 a	> 1 a

Figure B.8.2.1.2.1_CA-16: The results of the degermination of the environmental half-lives for the process of the direct photolysis of Flufenacet in aquatic environment (copied from the study report).

Conclusions:

The results of the study show that Flufenacet displayed very low level of absorption of UV-Vis radiation in the environmentally relevant wavelength range - $\lambda = 290 - 400$ nm.

The calculated quantum yield for the direct aqueous photolysis of Flufenacet was very low - $\phi = 0.00096$, what resulted in very low environmental half-lives – the $DT_{50} = 130$ days - > 365 days..

On the basis of those results it was stated that the direct aqueous photolysis will not be a relevant degradation process for Flufenacet in natural water bodies.

These results are in line with the results of the previously summarised *Study 1*.

Study 3:

Report: Lentz N. R., Bloomberg A. M., (1999): “Aqueous Photolysis of Thiadone (A Metabolite of FOE 5043).”; Ricerca Inc., Department of Environmental and Metabolic Fate, 7528 Auburn Road, Painesville, Ohio 44077, USA (performing laboratory) for Bayer Corporation, Agriculture Division, P. O. Box 4913, Kansas City, MO 64120, USA; Ricerca document No. 7410-98-0056-EF-001, study No. F3082402 (Bayer); Bayer Report No. 108720; 19 August 1999; study reference number: M-017985-01-1;

Guidelines: The study was performed to comply with the following Guidelines:

- US. EPA Guidelines for Pesticide Registration, Subdivision N, Section 161-2, Aqueous Photolysis Study.

GLP: Yes;

RMS comments: This is a newly submitted study, the aim of which was to further examine the photolytic degradation of Flufenacet in soil through the determination of the would-be photodegradation of one of its major degradation products – FOE Thiadone. For the purpose of the current assessment the study was evaluated for its compliance with the following guidelines:

- OECD Guideline 316: Phototransformation of Chemicals in Water – Direct Photolysis, Adopted 3 October 2008;
- US EPA Guideline OPPTS 835.2210 – Direct Photolysis Rate in Water by Sunlight; January 1998;
- US EPA Guideline OPPTS 835.2240 – Photodegradation in Water; October 2008;
- US. EPA Guidelines for Pesticide Registration, Subdivision N, Section 161-2, Aqueous Photolysis Studies (indicated as reference Guideline in the study report);
- OECD Guidelines for the Testing of Chemicals, Proposal for a New Guideline – Phototransformation of Chemicals in Water – Direct and Indirect Photolysis, Draft Document August 2000 (additional reference document);

RMS stated that the study was compliant with the provisions of the Guidelines listed above, therefore it was found acceptable and is summarised below.

Summary:

The aim of the study was to examine direct aqueous photodegradation of FOE Thiadone – the metabolite of Flufenacet, through:

- determining the half-life of that compound when exposed to artificial sunlight in sterile aqueous buffer;
- identifying the transformation pattern, and in particular the degradation products formed in amounts greater than 10% AR.

The experiment was performed in sterile pH = 7 aqueous buffer – 0.05M phosphate buffer, prepared by mixing 250 mL of 0.2M KH_2PO_4 aq with 29 mL of 1M NaOH aq and bringing the solution to the volume of 1L with HPLC-grade water. So prepared buffer solution was sterilised by steam autoclaving at $T = 123^\circ\text{C}$.

The experiment was performed in 59-mL (2 oz.) flint glass sample jars with either quartz glass lids (irradiated samples) or opaque screw caps (dark control samples).

The test vessels, like all remaining glassware used in the study, were sterilised by steam autoclaving at $T = 123^\circ\text{C}$.

The test compound was $[2\text{-}^{14}\text{C}]$ -Thiadone, having a specific activity of 50 mCi/mmol, corresponding to 652680 dpm/ μg . It was provided in form of a solution in acetone (**Stock solution**), having a volume of 9 mL and containing 6 mCi (0.12 mmol) of the test compound. **Stock solution** was shipped and stored frozen until being used. The structural formula of the test compound, with radiolabelling position indicated by an asterisk, is presented below on figure B.8.2.1.2.1._CA-17.

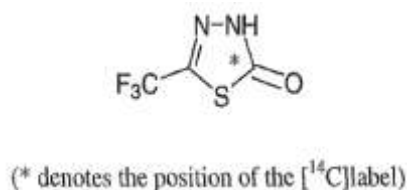


Figure B.8.2.1.2.1._CA-17: The structural formula of $[2\text{-}^{14}\text{C}]$ -Thiadone used in the experiment (copied from the study report).

Stock solution was used to prepare the **Application solution** used in the experiment. To do that ~210 μL of the **Stock solution**, containing 0.486 mg of FOE Thiadone, were transferred to 5-mL volumetric flask, evaporated to dryness under the stream of N_2 , and the residue redissolved in small portion of CH_3CN . The solution was once again evaporated to dryness and then brought to volume with CH_3CN . Prior to application the so prepared solution was analysed by LSC (quantitation of $[^{14}\text{C}]$ -FOE Thiadone), as well as by HPLC with LSC detection, to determine its radiopurity. The measured concentration of the **Application solution** was 4.86 $\mu\text{g}/50 \mu\text{L}$ (3,171,787 dpm/50 μL) and radiochemical purity 95.3%.

The experiment was carried out using 18 dark-control sample jars (sterilised), including two for additional analysis and four for sterility check, and 18 irradiated sample jars (sterilised), including eight extra jars for additional analyses. The test vessels are characterised above, in the third paragraph of the summary. The dark-control sample jars and irradiated sample jars were assigned sequential numbers.

Next, to each of the test vessels used as the dark-control and irradiated samples, 10 mL of sterilised buffer were added. Then 50 μL of the characterised above **Application solution** were added to each vessel. That volume was selected to obtain the fortification level of 0.49 mg FOE Thiadone/L, declared to be the half of the application rate of Flufenacet used to examine its aqueous photolysis. It was determined assuming that 100% of Flufenacet is converted into FOE Thiadone and using the molar weights for Flufenacet $M = 363 \text{ g/mol}$ and for FOE Thiadone $M' = 170 \text{ g/mol}$.

Duplicate dark-control samples were taken immediately after fortification for sterility check and determination of the concentration of the test compound.

The remaining test vessels were sealed with opaque screw caps fitted with Teflon liners, wrapped with foil and stored in the darkness at $T = 25 \pm 2^\circ\text{C}$ until being analysed.

All samples designated to be irradiated were sealed immediately after treatment with quartz lids and placed in the water bath set to $T = 25 \pm 2^\circ\text{C}$ in irradiation chamber.

The irradiation was performed in 12 hours light/12 hours darkness regime using light having a range $\lambda = 250 - 750 \text{ nm}$ and intensity comparable to that of natural sunlight measured at Painesville, Ohio, USA, in June. The light source used in the experiment was a 5000-W Xenon lamp, emitting light in range of $\lambda > 290 \text{ nm}$ – a range of natural sunlight reaching the soil surface. Lower wavelengths were eliminated using appropriate filters. The design of the irradiation device used in the experiment is shown below on figure B.8.2.1.2.1._CA-18.

The samples were irradiated or incubated in the darkness (the dark-control samples) for up to 30 days, corresponding for the irradiated samples to 30 Natural Sunlight Days.

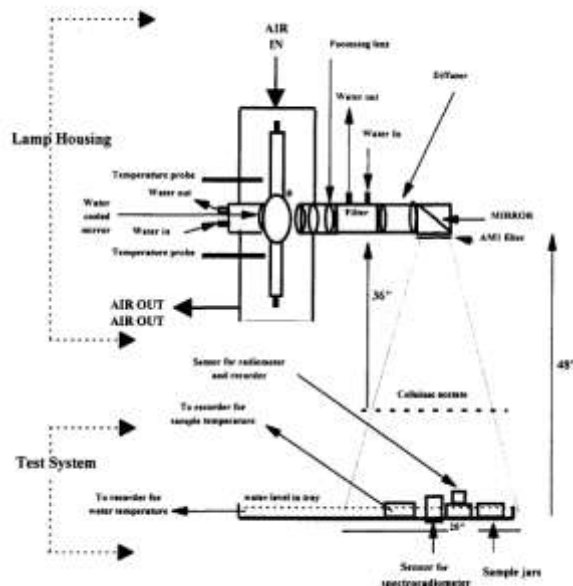


Figure B.8.2.1.2.1._CA-18: The schematic presentation of the photolysis system used in the experiment (copied from the study report).

At the following sampling dates: DAT 0, DAT 3, DAT 7, DAT 14, DAT 21 and DAT 30 (DAT stands for Days After Treatment), duplicate dark-control and irradiated samples were taken for the analysis. In case DAT 0 samples only the dark-control samples were analysed, as they were considered to be representative for both dark-control and irradiated parts of the experiment.

All samples were analysed, immediately after sampling, for their pH, and for the content of FOE Thiadone and other compounds using LSC and HPLC. For that reason it was not necessary to examine the sample stability.

Samples were processed in the following way:

- **for the dark-control samples** the contents of the vessels sampled on the given time point were transferred to the graduated cylinders and the volumes recorded; next two 0.25-mL aliquots were taken for LSC analysis; finally the 0.25-mL aliquots were diluted with 0.25 mL of 0.5% CH_3COOH in HPLC-grade H_2O , mixed with 0.01 mL of the standard solution and analysed by HPLC; the entire HPLC-effluents were collected and their 2-mL aliquots analysed by LSC;
- **for the dark-control samples** the whole procedure was slightly modified and looked as follows: the contents of the vessels sampled on the given time point were transferred to the graduated cylinders, then the vessels rinsed with small amounts of MeOH, rinses combined with the samples and the total volumes recorded; next two 0.25-mL aliquots were taken for LSC analysis; finally the 0.25-mL aliquots were diluted with 0.25 mL of 0.5% CH_3COOH in HPLC-grade H_2O , mixed with 0.01 mL of the standard solution and analysed by HPLC; the entire HPLC-effluents were collected and their 2-mL aliquots analysed by LSC;

All samples were analysed for the content of radioactivity using LSC method. The LSC (Liquid Scintillation Counting) analysis was performed using either Tractor Mark V Model 5303 LS counter or Beckman LS 6500 counter.

Liquid samples were analysed in duplicate with 5 mL of Ultima Gold liquid scintillation cocktail. The counting of each analysed sample lasted for 2 minutes. The detection limit was calculated to be 87 dpm with 95% confidence level. The average background level was set to 38 dpm.

Sample extracts were analysed using the following techniques:

- HPLC – major identification and quantitation method for parent compound and its degradation products;
- LC-MS – conformatory identification method for parent compound and its degradation products.

The HPLC analysis was performed using a Waters™ HPLC system equipped with autosampler, Tunable Absorbance Detector and fraction collector, coupled to one of the following LSC detectors:

- Radiomatic A-500 Radio-chromatography Detector;
- IN/US β-RAM Radio-HPLC Detector.

The system was equipped with Phenomenex Luna™, 5 µm C18, 150 · 4.6 mm chromatographic column and Zorbax® Rx-C18 10 · 4.6 mm guard column. The chromatographic separation was performed in a gradient mode, using the mobile phase consisting of:

- water + 0.5% CH₃COOH as **Solvent A**, and
- CH₃OH as **Solvent B**.

Gradient elution lasted 70 minutes. Its parameters are shown below in the table B.8.2.1.2.1._CA-10. The flow rate was set to 1.0 mL/min.

Table B.8.2.1.2.1._CA-10: The HPLC gradient mode used in the study.

Time [min]	Solvent ratio	
	<i>Solvent A – Water + 0.5% CH₃COOH</i>	<i>Solvent B – Methanol</i>
0	100	0
40	30	70
60	30	70
61	100	0
70	100	0

The minimum detection limit for HPLC method was 1000 dpm and its linearity, expressed as r^2 , was: $r^2 = 0.9$. That corresponded to 1.25% AR when the injected volume of analysed sample was 0.25 mL. The average recovery of the chromatographed samples was 100.8% AR (with range 96.5 – 105.6% AR).

The identification of the chromatographic peaks was performed by means of the comparison of their retention times R_t with those of the standards.

The LC-MS analysis was performed using Finnigan SSQ710 LC/MS device equipped with a Phenomenex Columbus 5µm C8 100 · 2 mm LC column. The chromatographic analysis was carried out in a gradient mode. Its parameters were following:

- **Mobile phase A:** 0.05% HCOOH in Water,
- **Mobile phase B:** CH₃OH,
- **Gradient mode:** A/B1:1 hold 2 min. to A/B 3:7 at 8 min.

The flow rate was set to 0.2 mL/min.

The reported parameters of MS detector were following:

- Ionization mode: (-)ESI;
- Mass range: 95 – 300 amu;
- Scan rate: 1.5 sec/scan;
- Source temperature: 220°C;
- ESI spray voltage: 4.5 kV.

The UV-Vis absorption spectrum of FOE Thiadone was determined using GBC 918 UV-Vis spectrometer with a slit of 2 nm. The absorption spectrum was scanned within the wavelength range of $\lambda = 200 – 800$ nm at a scanning rate 720 nm/min.

Results and their discussion:

The experiment was performed in sterile phosphate buffer having pH = 7. The results of the determination of the pH of test solutions collected at each time point showed that that parameter was stable throughout the study duration. It shall be indicated that the pH in irradiated samples for DAT 0 time point was not recorded, as they

were not collected. Instead, it was assumed that the results recorded at that sampling point for the dark-control samples should be representative also for them.

The sterility checks showed that the samples maintained their sterility throughout the whole irradiation/incubation period. The monitoring of the temperature during the experiment showed that both irradiated and dark-control samples were kept at constant temperature $T = 25 \pm 2^{\circ}\text{C}$.

The characteristic of the light source – xenon lamp, is presented in a graphical form on figure B.8.2.1.2.1._CA-19 (comparison of spectral distribution of xenon lamp used in the experiment and natural sunlight).

Table B.8.2.1.2.1._CA-11: The results of the determination of pH of the test slutions.

Sampling time point (corresponding for irradiated samples to [Natural Sunlight Days])	pH measured in:			
	Irradiated samples		Dark-control samples	
	Replicate 1	Replicate 2	Replicate 1	Replicate 2
<i>DAT 0</i>	----	----	7.04	7.05
<i>DAT 3</i>	7.06	7.03	7.06	7.06
<i>DAT 7</i>	6.98	7.00	7.07	7.11
<i>DAT14</i>	7.03	7.02	7.09	7.00
<i>DAT 21</i>	7.05	7.04	7.03	7.07
<i>DAT 30</i>	7.07	7.02	7.07	7.07

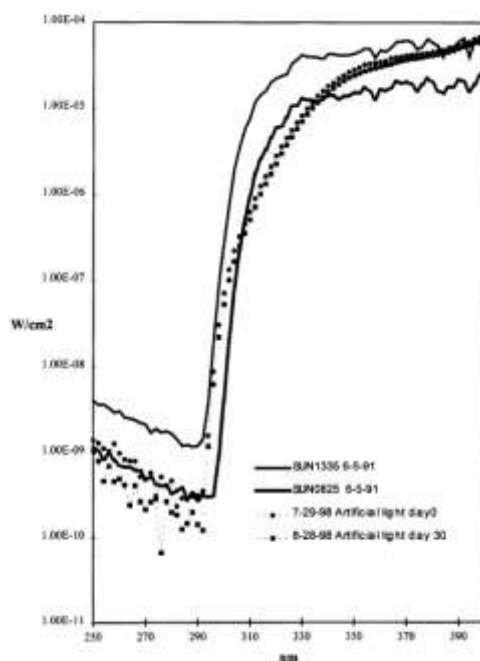


Figure B.8.2.1.2.1._CA-19: The comparison of the spectra of xenon lamp used in the study and of natural sunlight (copied from the study report).

The absorption spectrum of FOE Thiadone recorded for the wavelength range of $\lambda = 200 - 800$ nm is presented below on figure B.8.2.1.2.1._CA-20. It shows that the effective absorption occurred within the wavelength range of $\lambda = 200 - 270$ nm. Within the environmentally relevant range of $\lambda = 290 - 800$ nm it was residual.

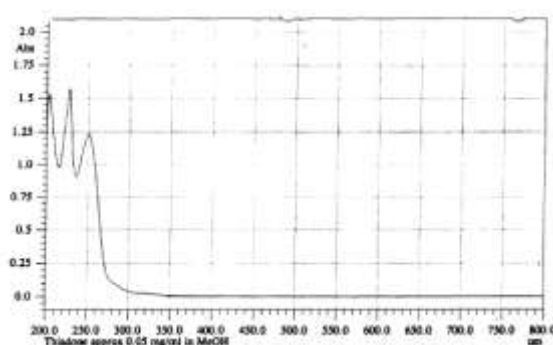


Figure B.8.2.1.2.1._CA-20: The UV-Vis absorption spectrum of FOE Thiadone recorded for $\lambda = 200 - 800$ nm (copied from the study report).

The preliminary study showed no loss of radioactivity from samples, therefore no trapping system for volatile compounds was used in the definitive part of the study. The recovery of radioactivity, determined by LSC, was in range 95.0% AR – 104.7% AR, with the average value of 100.2% AR. The detailed results are presented below in the table B.8.2.1.2.1._CA-12. The values given for irradiated and the dark-control samples at each sampling point are the averages of the two replicates.

Table B.8.2.1.2.1._CA-12: The results of the determination of the recovery of radioactivity in the test samples, as determined by LSC.

Sampling time point (corresponding for irradiated samples to [Natural Sunlight Days])	Radioactivity recovered in the samples, expressed as [% AR]:	
	Irradiated samples	Dark-control samples
<i>DAT 0</i>	----	104.7
<i>DAT 3</i>	104.3	101.5
<i>DAT 7</i>	101.3	98.2
<i>DAT14</i>	100.5	101.9
<i>DAT 21</i>	96.4	100.7
<i>DAT 30</i>	95.0	97.2

The HPLC profiling of recovered radioactivity showed that it consisted almost totally of FOE Thiadone, with small amounts, individually not surpassing 2%, of three other fractions, of which two are fortification impurities. The detailed results are presented in the table B.8.2.1.2.1._CA-13.

Table B.8.2.1.2.1._CA-13: The detailed results of the HPLC-profiling of radioactivity recovered in the test samples at each sampling point.

Sampling time point (corresponding in irradiated samples to [Natural Sunlight Days])	Amounts [% in chromatogram] detected in irradiated samples of				Amounts [% in chromatogram] detected in the dark-control sample of			
	Fortification impurity 1	FOE Thiadone	Fortification impurity 2	Other	Fortification impurity 1	FOE Thiadone	Fortification impurity 2	Other
<i>DAT 0</i>	----	----	----	----	1.2	97.1	1.8	0.0
<i>DAT 3</i>	0.9	98.6	0.3	0.3	1.1	98.9	not detected	0.0
<i>DAT 7</i>	0.4	99.3	not detected	0.3	1.0	99.1	not detected	0.0
<i>DAT14</i>	not detected	99.8	not detected	0.2	1.1	99.0	not detected	0.0
<i>DAT 21</i>	not detected	100.0	not detected	0.0	1.1	98.9	not detected	0.0
<i>DAT 30</i>	not detected	100.0	not detected	0.0	not detected	100.0	not detected	0.0

The results demonstrated virtually no degradation of FOE Thiadone in either irradiated samples or in the dark control ones. On that basis it was stated that FOE Thiadone was not prone to the direct photolysis. The kinetic analysis of the obtained results was therefore not carried out.

Conclusions:

On the basis of the obtained result it may be stated that FOE Thiadone is not prone to direct photolysis in the aquatic environment.

Summary – Direct aqueous photolysis of Flufenacet

The direct aqueous photolysis of Flufenacet was examined in a sterile buffer solution having pH = 5 and T = 21°C. The samples were exposed to UV-Vis radiation generated by the artificial light source. The irradiation conditions were similar to those recorded during 30-days exposure to natural summer sunlight in Phoenix, Arizona, USA. The results demonstrated that Flufenacet was not prone to the direct aqueous photolysis – practically no photodegradation of Flufenacet, in comparison to what was observed in the dark control samples, was stated. The determined half-lives were: for irradiated sample DT₅₀ = 7430 days when expressed in Natural Sunlight days, and for the dark control samples DT₅₀ = 4160 days.

In a separate experiment the quantum yield of the process of direct photodegradation of Flufenacet in water was determined. The quantum yield value determined in that experiment was $\phi = 0.00096$ [mol/Einstein]. The calculated using that value environmental photolytical half-lives for Flufenacet, determined using GC-Solar method in water were:

- for the latitude 30°N in range DT₅₀ = 126 – 308 days;
- for the latitude 40°N in range DT₅₀ = 131 – >365 days;
- for the latitude 50°N in range DT₅₀ = 142 – >365 days;
- for the latitude 60°N in range DT₅₀ = 160 – >365 days;

Additionally, in a separate study, was examined the direct aqueous photolysis of the major soil and aquatic degradation product of Flufenacet – FOE Thiadone. The experiment was performed in a sterile buffer solution having pH = 7 and T = 25°C. The samples were exposed to UV-Vis radiation generated by the artificial light source. The irradiation conditions were similar to those recorded during 30-days exposure to natural summer sunlight in Phoenix, Arizona, USA. The results demonstrated that FOE Thiadone was not prone to the direct aqueous photolysis – practically no photodegradation of that compound was observed in either irradiated samples or in dark control ones, and it was not possible to determine the reliable DT₅₀ values.

The results of the examination of the direct aqueous photolysis of Flufenacet and FOE Thiadone in water, in form recommended for reporting the regulatory endpoints in the EU, are presented below.

Aqueous photochemical degradation (Regulation (EU) N° 283/2013, Annex Part A, points 7.2.1.2 / 7.2.1.3)

Photolytic degradation of active substance and metabolites above 10 % - [results for Flufenacet, direct photolysis](#)

Quantum yield of direct phototransformation in water at $\lambda > 290$ nm- [results for Flufenacet](#)

Photolytic degradation of active substance and metabolites above 10 % - [results for FOE Thiadone, direct photolysis](#)

DT ₅₀ : <i>2550 days (compound considered to be photolytically stable in sterile aqueous buffer solution)</i>
Estimated DT ₅₀ at 33°26'N (Phoenix, AZ, USA) 7430 days (June)
$9.6 \cdot 10^{-4}$ mol · Einstein ⁻¹
DT ₅₀ : <i>not determined – the compound is photolytically stable in sterile aqueous buffer solution</i>

B.8.2.1.2.2. – Indirect Photochemical degradation

To address this data requirement the Applicant submitted two study reports, one for Flufenacet as a test substance and another for FOE Thiadone as a test substance.

The examination of the indirect photodegradation of Flufenacet in the aquatic environment was a part of a broader study examining the photodegradation of Flufenacet in water. It is summarised below as **Study 1**.

The indirect aqueous photolysis of FOE Thiadone – the major soil and aquatic degradation product of Flufenacet, was examined in a separate study presented below as **Study 2**.

Study 1:

Report: Kasper A. M., Shadrick B. A., (1995): “Aqueous Photolysis of [Phenyl-U-¹⁴C] FOE 5043.”; Bayer Corporation (formerly Miles Inc.), Agriculture Division, P. O. Box 4913, Kansas City, Missouri 64120-0013, USA; study No. F3082401 (Bayer); unpublished Miles Report No. MR 106246; 30 May 1995; study reference number: M-002206-01-1;

Guidelines: The study was performed to comply with the following Guidelines:

- US. EPA Guidelines for Pesticide Registration, Subdivision N, Section 161-2, Aqueous Photolysis Studies.

GLP: Yes, for the part off the study aimed on the examination of direct aqueous photolysis; for the examination of indirect aqueous photolysis of Flufenacet it was declared to be a non-GLP study

RMS comments: The study had been evaluated for the previous authorisation of Flufenacet in the EU. Its summary can be found under the point B.7.4.2.1., in section B.7 of the Annex B to the Monograph prepared by the RMS – France, for Flufenacet. It presents the results of the examination of both direct photolysis of Flufenacet in water (a GLP study) and the indirect aqueous photolysis of that compound (a non-GLP study). For the purpose of the current assessment the study was evaluated for its compliance with the following guidelines:

- OECD Guideline 316: Phototransformation of Chemicals in Water – Direct Photolysis, Adopted 3 October 2008;
- US EPA Guideline OPPTS 835.2210 – Direct Photolysis Rate in Water by Sunlight; January 1998;
- US EPA Guideline OPPTS 835.2240 – Photodegradation in Water; October 2008;
- US. EPA Guidelines for Pesticide Registration, Subdivision N, Section 161-2, Aqueous Photolysis Studies (indicated as reference Guideline in the study report);
- OECD Guidelines for the Testing of Chemicals, Proposal for a New Guideline – Phototransformation of Chemicals in Water – Direct and Indirect Photolysis, Draft Document August 2000 (additional reference document);

RMS stated that in general the study was compliant with the provisions of the Guidelines listed above, therefore it was found acceptable. However, in its part related to the examination of the indirect aqueous photolysis, because at the time of examination that part was considered to be only supplementary, it was only briefly summarised in Appendix 12 to the study report. Additionally the part of the experiment that examined indirect aqueous photolysis was declared to be a non-GLP study. RMS examined the provided summary. The characteristic is provided only in the areas where the study protocol differed from the GLP-part of the study – the experiment on the direct photolysis, characterisation of reaction medium and irradiation-and sampling protocol, as well as the presentation of obtained results, however it bears several indications enabling to make a conclusion that it was carried out in the same way as the experiment on the direct aqueous photolysis of Flufenacet. For that reason RMS decided to consider the study valid also in its part related to the indirect aqueous photodegradation of Flufenacet, although it may be considered to have a merit only as supplementary/indicative study. For that reason RMS decided not to include its results into the List of EndPoints. It is summarised, in its part strictly related to indirect photolysis, below.

Summary:

The aim of the experiment was to examine the indirect aqueous photolysis of Flufenacet. The examination was carried out in:

- natural pond water sampled at two different locations (**Experiment 1** and **Experiment 2**),
- aqueous solution containing humic material 15 ppm (**Experiment 3**),
- aqueous solution containing 50 ppm of KNO₃ (**Experiment 4**)

That part of the study focused only on the determination of the rate of the process, as the examination of the direct aqueous photolysis of Flufenacet showed, that the compound did not degrade under the influence of light.

The test compound used in ther experiment was [Phenyl-U-¹⁴C] Flufenacet, having a specific radioactivity of 66.5 mCi/mmol. Its structural formula is presented below on figure B.8.2.1.2.2._CA-1. It was delivered in form of benzene solution, having a concentration 4.55 mg Flufenacet/mL.

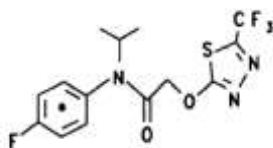


Figure B.8.2.1.2.2._CA-1: The structural formula of the test compound; radiolabelling position indicated with an asterisk (copied from the study report).

It was used to prepare three different test solutions:

- **Test Solution 1**, used in the experiments with natural pond water; to prepare it 0.243 mL of the benzene solution of [Phenyl-U-¹⁴C] Flufenacet was transferred to 45-mL graduated centrifuge tube and evaporated to dryness; the residue was redissolved in 10.8 mL of CH₃CN (1% of co-solvent);
- **Test solution 2**, used in the experiment with aqueous solution of humic material; to prepare it 0.173 mL of the benzene solution of [Phenyl-U-¹⁴C] Flufenacet was transferred to 45-mL graduated centrifuge tube and evaporated to dryness; the residue was redissolved in 8.0 mL of CH₃CN (1% of co-solvent);
- **Test solution 3**, used in the experiment with aqueous solution of KNO₃; to prepare it 0.206 mL of the benzene solution of [Phenyl-U-¹⁴C] Flufenacet was transferred to 45-mL graduated centrifuge tube and evaporated to dryness; the residue was redissolved in 9.5 mL of CH₃CN (1% of co-solvent);

Experiment 1 was performed using natural pond water sampled from the pond located in Howe, Indiana, USA. It had the following characteristic:

- pH = 6.5;
- Alkalinity: 65 [mg/CaCO₃/L];
- Total Suspended Solids: 160 mg/L;
- Hardness: 66 [mg CaCO₃/L];
- Conductivity: 220 [μmho/cm];
- NO₃⁻: not determined;
- NO₂⁻: 0.015 [mg/L];
- NH₄⁺: not determined;
- Total Organic Carbon: 20.7 [mg/L].

To the foil-wrapped (with aluminium foil) test vessels, presented in the summary of the same study (as **Study I**) under the point B.8.2.1.2.1. on figure B.8.2.1.2.1._CA-2, were introduced 60-mL portions of the pond water characterised above, filtered through Curity® cheese cloth. Next, to each test vessel 0.6-mL portions of the **Test solution 1** were introduced. The number of so prepared test vessels was such to be sufficient for six single irradiation samples and six single dark-control samples including DAT-0 sample. The DAT 0 sample was analysed immediately after treatment by LSC and HPLC for the content of [¹⁴C]-Flufenacet and radiochemical purity. The determined concentration of the test compound was 0.95 ppm with radiochemical purity of 99.5%.

The remaining test vessels, irradiated samples and the dark-control samples, were placed in the Suntest irradiation unit and kept there for up to 10.83 days (corresponding to 31.7 Natural Sunlight Days; for the

definition please refer to the summary of the *Study 1* presented under the point B.8.2.1.2.1.). In case of irradiated samples the foil wrapping vessels was removed, while the dark-control samples were kept wrapped with it.

At pre-designated time points irradiated samples and the dark-control samples were taken for the analysis.

The sampling points for the **dark-control samples** were set at the following time points, expressed as Natural Sunlight Days: 0, 0.5, 1.1, 2.4, 11.3 and 31.7. When recalculated by the RMS to the Suntest days, representing the real incubation time the sampling time-points, expressed as DAT (Days After Treatment), were following: 0, 0.17 (4.1 hours), 0.38 (9.02 hours), 0.82 (19.68 hours), 3.86 (92.66 hours) and 10.83 (259.94 hours). The calculations were based on the statement provided by the Applicant, that 1 Natural Sunlight Day is equivalent to 8.2 hours in the Suntest unit. The DAT 0 sample in the dark control can be also considered the DAT-0 irradiated sample.

The sampling points for the **irradiated samples** were set at the following time points, expressed as Natural Sunlight Days: 0.5, 1.1, 2.4, 11.3, 20.1 and 31.7. When recalculated by the RMS to the Suntest days, representing the real incubation time the sampling time-points, expressed as DAT (Days After Treatment), were following: 0.17 (4.1 hours), 0.38 (9.02 hours), 0.82 (19.68 hours), 3.86 (92.66 hours), 6.87 (164.82 hours) and 10.83 (259.94 hours). The calculations were based on the statement provided by the Applicant, that 1 Natural Sunlight Day is equivalent to 8.2 hours in the Suntest unit.

At sampling intervals listed above single irradiated and dark control samples were removed from the Suntest unit. Vessels containing irradiated samples were immediately wrapped with aluminium foil to cut-off the light.

0.2-mL aliquots were analysed by LSC to quantify the [^{14}C] residues. Next 1-mL aliquots were analysed by HPLC to identify the compounds present in sample and quantify them. The example chromatograms for the irradiated and dark-control samples collected on DAT 10.83 (Suntest days) are presented below on figure B.8.2.1.2.2._CA-2.

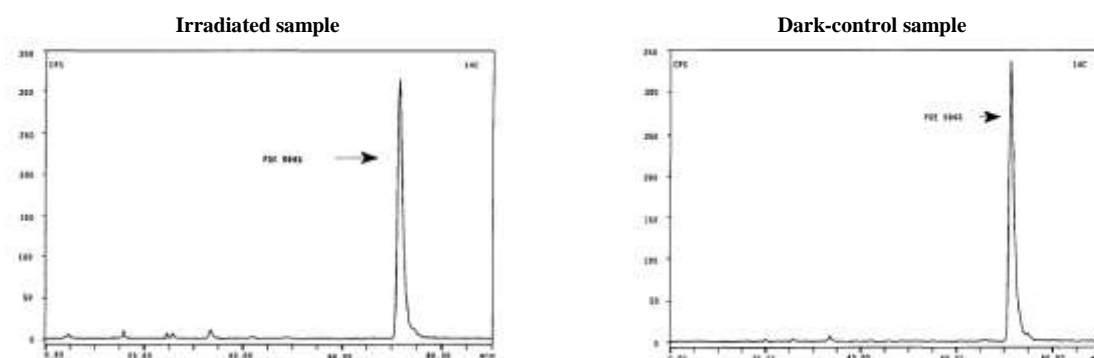


Figure B.8.2.1.2.2._CA-2: The DAT 10.83 (Suntest days; corresponding to 31.7 Natural Sunlight Days timepoint) HPLC chromatograms for irradiated and Dark-control samples (copied from the study report).

In all analysed samples Flufenacet was demonstrated to be the dominant compound. The numerical results of the analysis – the amounts of Flufenacet in each sample determined by HPLC are presented below in the table B.8.2.1.2.2._CA-1. The time-points expressed in Suntest days and Suntest hours were recalculated by the RMS on the basis of the time-points expressed in Natural Sunlight Days provided in the study report.

Table B.8.2.1.2.2._CA-1: The concentration of Flufenacet in the irradiated and dark-control samples in function of time.

Time point			Content of Flufenacet [%] in:	
Natural Sunlight Days	Sunttest Days	Sunttest hours	Irradiated sampels	Dark-control samples
0	0	0	99.5	99.5
0.5	0.17	4.1	98.5	98.8
1.1	0.38	9.02	98.5	99.4
2.4	0.82	19.68	98.2	98.8
11.3	3.86	92.66	97.0	98.7
20.1	6.87	164.82	92.2	not determined
31.7	10.83	259.94	92.9	96.5

The Applicant performed the kinetic analysis of the data presented in the table above. The kinetic fitting was carried out using linear regression for logarithmically-transformed concentrations of Flufenacet. RMS decided to repeat the analysis using the non-linear regression method, as recommended by FOCUS.

The analysis was performed for irradiated samples using time points expressed as Suntest Days and as Natural Sunlight Days. In case of the dark-control samples the kinetic fitting was carried out using solely Suntest Days, as these are the real sampling points and the dark-control samples do not require any conversion of the sampling points to make them representative for natural irradiation conditions.

The fitting was carried out using CAKE 3.1 modelling tool with IRLS as optimisation method. Only SFO kinetic model was tested, as very low level of degradation was observed.

The results are presented below, in graphical form on figure B.8.2.1.2.2._CA-3 and in the numerical form in the table B.8.2.1.2.2._CA-2.

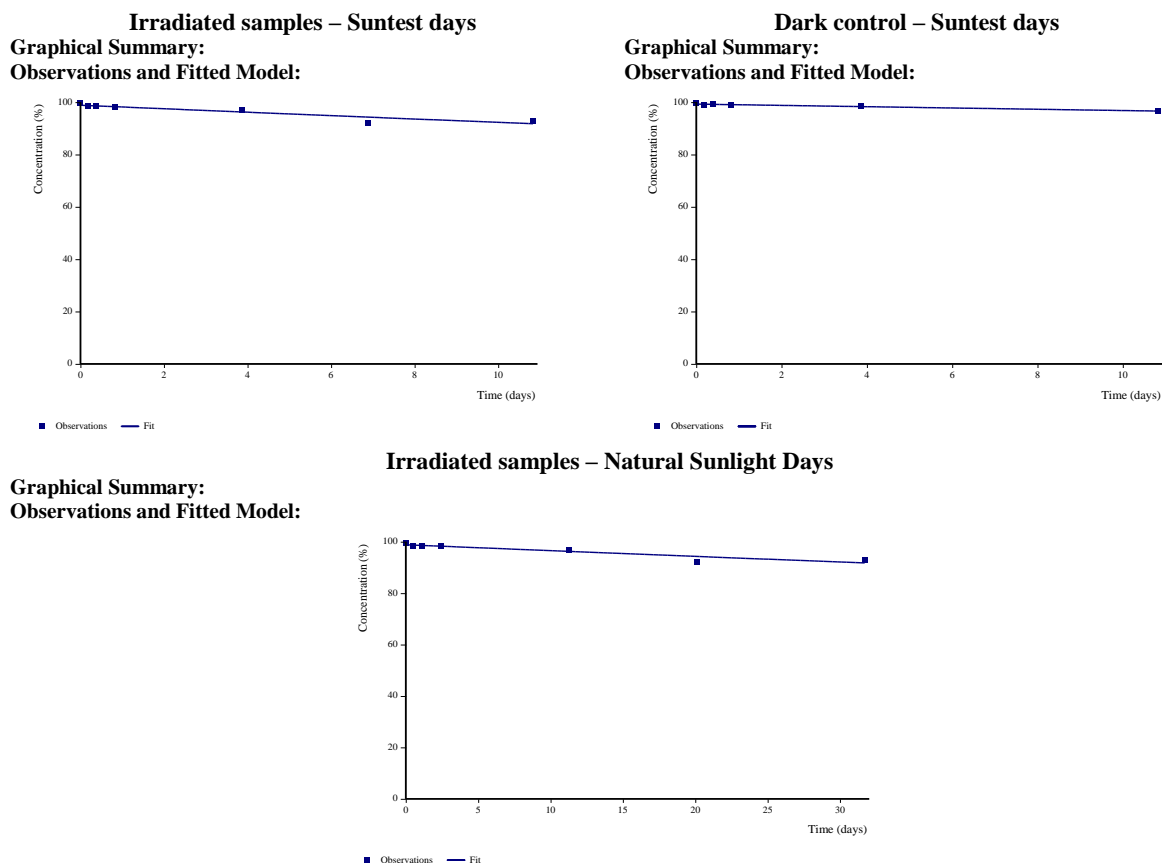


Figure B.8.2.1.2.2._CA-3: The graphical results of the examination of the indirect aqueous photolysis of Flufenacet in Howe pond water.

Table B.8.2.1.2.2._CA-2: The numerical results of the examination of the indirect aqueous photolysis of Flufenacet in Howe pond water.

Type of samples	Kinetic model	Model parameters	Statistical evaluation of the parameter					Statistical evaluation of the fit	
			Value	Error	Confidence intervals		Prob. > t	χ^2 % error	r
					Lower	Upper			
Irradiated-Suntest days	SFO	M_0	98.84	0.577	97.36	100.3	----	0.805	0.869
		k	0.006836	0.001198	0.003756	0.001	0.001156		
Dark control-Suntest days	SFO	M_0	99.28	0.179	98.78	99.77	----	0.237	0.913
		k	0.002506	3.90 E-4	0.0014234	0.004	0.001507		
Irradiated-Natural Sunlight days	SFO	M_0	98.84	0.577	97.36	100.3	----	0.806	0.869
		k	0.002335	4.1 E-4	0.0012824	0.003	0.001159		

The obtained fits are reliable. They also returned the DT_{50} values, which are following:

- for irradiated sample using Suntest days $DT_{50} = 101$ days;
- for irradiated sample using Natural Sunlight days $DT_{50} = 297$ days;
- for the dark control sample using Suntest days $DT_{50} = 277$ days

Comparison of the results obtained for irradiated samples and the dark-control samples using the Suntest days showed that Flufenacet degraded much faster in irradiated samples. That in turn indicates that indirect photolysis played an important role in degradation of that compound. For that reason the net degradation rate constant for photolysis was calculated using the following equation: $k_{\text{photol}} = k_{\text{irrad}} - k_{\text{dark}}$. The resulting $k_{\text{photol}} = 0.00433 \text{ [days}^{-1}\text{]}$. That value was subsequently used to calculate the DT_{50} for the net indirect aqueous photolysis of Flufenacet in Howe pond water. The calculated $DT_{50} = 160.08$ days for Suntest days. RMS additionally recalculated that value to Natural Sunlight Days, using assumption that 1 Natural Sunlight Day is equal to 8.2 Suntest hours. The resulting $DT_{50} = 468.53$ days when expressed in Natral Sunlight Days.

Experiment 2 was performed using natural pond water sampled from the pond located in Stilwell, Kansas, USA. It had the following characteristic:

- pH = 7.8;
- Alkalinity: 159 [mg/CaCO₃/L];
- Total Suspended Solids: 9 mg/L;
- Hardness: 186 [mg CaCO₃/L];
- Conductivity: 400 [μmho/cm];
- NO₃⁻: 0.8 [mg/L];
- NO₂⁻: 0.54 [mg/L];
- NH₄⁺: not determined;
- Total Organic Carbon: 1.55 [mg/L].

To the foil-wrapped (with aluminium foil) test vessels, presented in the summary of the same study (as *Study I*) under the point B.8.2.1.2.1. on figure B.8.2.1.2.1._CA-2, were introduced 60-mL portions of the pond water characterised above, filtered through Curity® cheese cloth. Next to each test vessel 0.6-mL portions of the **Test solution 1** were introduced. The number of so prepared test vessels was such to be sufficient for four single irradiation samples and five single dark-control samples including DAT-0 sample. The DAT 0 sample was analysed immediately after treatment by LSC and HPLC for the content of [¹⁴C]-Flufenacet and radiochemical purity. The determined concentration of the test compound was 0.95 ppm with radiochemical purity of 98.9%.

The remaining test vessels, irradiated samples and the dark-control samples, were placed in the Suntest irradiation unit and kept there for up to 10.25 days (corresponding to 30.0 Natural Sunlight Days; for the definition please refer to the summary of the *Study I* presented under the point B.8.2.1.2.1.). In case of irradiated samples the foil wrapping vessels was removed, while the dark-control samples were kept wrapped with it.

At pre-designated time points irradiated samples and the dark-control samples were taken for the analysis.

The sampling points for the **dark-control samples** were set at the following time points, expressed as Natural Sunlight Days: 0, 8.0, 13.9, 19.8 and 30.0. When recalculated by the RMS to the Suntest days, representing the real incubation time the sampling time-points, expressed as DAT (Days After Treatment), were following: 0, 2.73 (65.6 hours), 4.75 (113.98 hours), 6.77 (162.36 hours) and 10.25 (246 hours). The calculations were based on the statement provided by the Applicant, that 1 Natural Sunlight Day is equivalent to 8.2 hours in the Suntest unit. The DAT 0 sample in the dark control can be also considered the DAT-0 irradiated sample.

The sampling points for the **irradiated samples** were set at the following time points, expressed as Natural Sunlight Days: 8.0, 13.9, 19.8 and 30.0. When recalculated by the RMS to the Suntest days, representing the real incubation time the sampling time-points, expressed as DAT (Days After Treatment), were following: 2.73 (65.6 hours), 4.75 (113.98 hours), 6.77 (162.36 hours) and 10.25 (246 hours). The calculations were based on the statement provided by the Applicant, that 1 Natural Sunlight Day is equivalent to 8.2 hours in the Suntest unit.

At sampling intervals listed above single irradiated and dark control samples were removed from the Suntest unit. Vessels containing irradiated samples were immediately wrapped with aluminium foil to cut-off the light.

0.2-mL aliquots were analysed by LSC to quantify the [¹⁴C] residues. Next 1-mL aliquots were analysed by HPLC to identify the compounds present in sample and quantify them. The example chromatograms for the irradiated and dark-control samples collected on DAT 10.25 (Sunttest days) are presented below on figure B.8.2.1.2.2._CA-4.

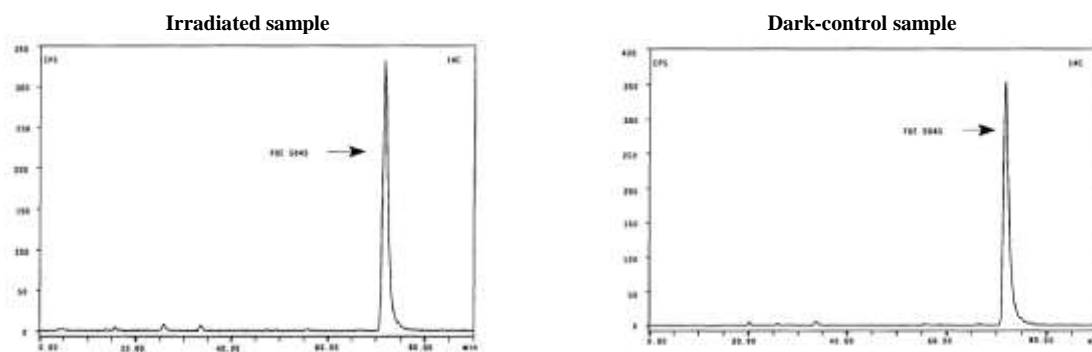


Figure B.8.2.1.2.2._CA-4: The DAT 10.25 (Suntest days; corresponding to 31.7 Natural Sunlight Days timepoint) HPLC chromatograms for irradiated and Dark-control samples (copied from the study report).

In all analysed samples Flufenacet was demonstrated to be the dominant compound. The numerical results of the analysis – the amounts of Flufenacet in each sample determined by HPLC are presented below in the table B.8.2.1.2.2._CA-3. The time-points expressed in Suntest days and Suntest hours were recalculated by the RMS on the basis of the time-points expressed in Natural Sunlight Days provided in the study report.

Table B.8.2.1.2.2._CA-3: The concentration of Flufenacet in the irradiated and dark-control samples in function of time.

Time point			Content of Flufenacet [%] in:	
<i>Natural Sunlight Days</i>	<i>Suntest Days</i>	<i>Suntest hours</i>	<i>Irradiated samples</i>	<i>Dark-control samples</i>
0	0	0	98.9	98.9
8.0	2.73	65.6	97.7	98.2
13.9	4.75	113.98	97.8	95.7
19.8	6.77	162.36	96.2	96.2
30.0	10.25	246	96.6	98.5

The Applicant performed the kinetic analysis of the data presented in the table above. The kinetic fitting was carried out using linear regression for logarithmically-transformed concentrations of Flufenacet. RMS decided to repeat the analysis using the non-linear regression method, as recommended by FOCUS.

The analysis was performed for irradiated samples using time points expressed as Suntest Days and as Natural Sunlight Days. In case of the dark-control samples the kinetic fitting was carried out using solely Suntest Days, as these are the real sampling points and the dark-control samples do not require any conversion of the sampling points to make them representative for natural irradiation conditions.

The fitting was carried out using CAKE 3.1 modelling tool with IRLS as optimisation method. Only SFO kinetic model was tested, as very low level of degradation was observed.

The results are presented below, in graphical form on figure B.8.2.1.2.2._CA-5 and in the numerical form in the table B.8.2.1.2.2._CA-4.

Table B.8.2.1.2.1._CA-4: The numerical results of the examination of the indirect aqueous photolysis of Flufenacet in Stilwell pond water.

Type of samples	Kinetic model	Model parameters	Statistical evaluation of the parameter					Statistical evaluation of the fit	
			Value	Error	Confidence intervals		Prob. > t	χ^2 % error	r
					Lower	Upper			
Irradiated-Suntest days	SFO	M_0	98.62	0.462	97.15	100.1	----	0.379	0.767
		k	0.002467	7.86 E-4	-3.34 E-5	0.05	0.02583		
Dark control-Suntest days	SFO	M_0	97.92	1.256	93.93	101.9	----	1.03	0.054
		k	8.84 E-4	0.002139	-0.005922	0.008	0.3535		
Irradiated-Natural Sunlight days	SFO	M_0	98.62	0.463	97.15	100.1	----	0.380	0.766
		k	8.43 E-4	2.69 E-4	-1.21 E-5	0.002	0.02588		

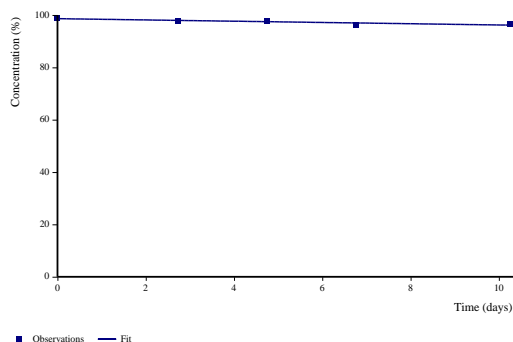
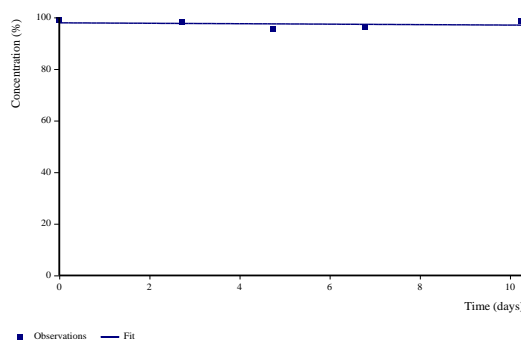
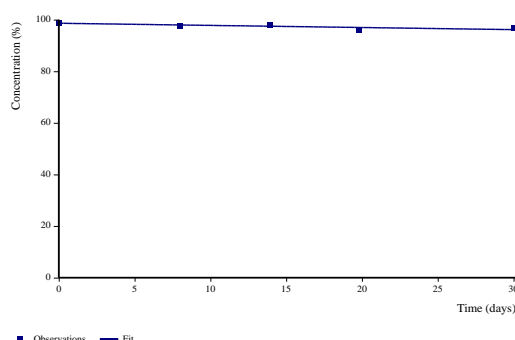
Irradiated samples – Suntest days**Graphical Summary:****Observations and Fitted Model:****Dark control – Suntest days****Graphical Summary:****Observations and Fitted Model:****Irradiated samples – Natural Sunlight Days****Graphical Summary:****Observations and Fitted Model:**

Figure B.8.2.1.2.2_CA-5: The graphical results of the examination of the indirect aqueous photolysis of Flufenacet in Stilwell pond water.

The fits obtained for irradiated samples can be considered reliable. The fit for the dark control bears a significant level of uncertainty, what can be attributed to virtually no degradation of the test compound observed in these samples. Therefore these results should be considered as indicative only. The determined kinetic endpoints were following:

- for irradiated sample using Suntest days $DT_{50} = 281$ days;
- for irradiated sample using Natural Sunlight days $DT_{50} = 822$ days;
- for the dark control sample using Suntest days $DT_{50} = 784$ days

Comparison of the results obtained for irradiated samples and the dark-control samples using the Suntest days showed that Flufenacet degraded much faster in irradiated samples. That in turn indicates that indirect photolysis played an important role in degradation of that compound. As practically no degradation of Flufenacet was observed in the dark control, in comparison to the irradiated samples, it may be assumed that the net degradation rate constant for photolysis $k_{\text{photol}} = k_{\text{irrad}}$. Therefore resulting $k_{\text{photol}} = 0.002467 \text{ [days}^{-1}\text{]}$. The DT_{50} for the net indirect aqueous photolysis of Flufenacet in Stilwell pond water is therefore following: **$DT_{50} = 160.08$ days** for Suntest days. As it was not necessary to correct the value provided by the modelling tool, also that expressed in Natural Sunlight Days may be left the same as returned by the kinetic model – **$DT_{50} = 822$ days** when expressed in Natral Sunlight Days.

Experiment 3 was performed using ultrapure water containing 15 ppm of Humic material.

The solution of humic material used in the experiment was prepared by dissolving 11.25 mg of humic acid in 2.5 mL of water.

To the foil-wrapped (with aluminium foil) test vessels, presented in the summary of the same study (as **Study 1**) under the point B.8.2.1.2.1. on figure B.8.2.1.2.1_CA-2, were introduced 60-mL portions of ultrapure water, to which 0.20 mL of the solution of humic material, characterised above, was added. Next, to each test vessel 0.6-mL portions of the **Test solution 2** were introduced and the test vessels sonicated for 5 minutes. The

number of so prepared test vessels was such to be sufficient for five single irradiation samples and three single dark-control samples including DAT-0 sample. The DAT 0 sample was analysed immediately after treatment by LSC and HPLC for the content of [^{14}C]-Flufenacet and radiochemical purity. The determined concentration of the test compound was 0.99 ppm with radiochemical purity of 98.6%. The concentration of the humic material was 15 ppm.

The remaining test vessels, irradiated samples and the dark-control samples, were placed in the Suntest irradiation unit and kept there for up to 10.01 days (corresponding to 29.3 Natural Sunlight Days; for the definition please refer to the summary of the *Study 1* presented under the point B.8.2.1.2.1.). In case of irradiated samples the foil wrapping vessels was removed, while the dark-control samples were kept wrapped with it.

At pre-designated time points irradiated samples and the dark-control samples were taken for the analysis.

The sampling points for the **dark-control samples** were set at the following time points, expressed as Natural Sunlight Days: 0, 23.4, and 29.3. When recalculated by the RMS to the Suntest days, representing the real incubation time the sampling time-points, expressed as DAT (Days After Treatment), were following: 0, 8.00 (191.88 hours) and 10.01 (240.26 hours). The calculations were based on the statement provided by the Applicant, that 1 Natural Sunlight Day is equivalent to 8.2 hours in the Suntest unit. The DAT 0 sample in the dark control can be also considered the DAT-0 irradiated sample.

The sampling points for the **irradiated samples** were set at the following time points, expressed as Natural Sunlight Days: 2.9, 11.7, 23.4 and 29.3. When recalculated by the RMS to the Suntest days, representing the real incubation time the sampling time-points, expressed as DAT (Days After Treatment), were following: 0.99 (23.78 hours), 2.02 (48.38 hours), 5.02 (120.54 hours), 8.00 (191.88 hours) and 10.01 (240.26 hours). The calculations were based on the statement provided by the Applicant, that 1 Natural Sunlight Day is equivalent to 8.2 hours in the Suntest unit.

At sampling intervals listed above single irradiated and dark control samples were removed from the Suntest unit. Vessels containing irradiated samples were immediately wrapped with aluminium foil to cut-off the light.

0.2-mL aliquots were analysed by LSC to quantify the [^{14}C] residues. Next 1-mL aliquots were analysed by HPLC to identify the compounds present in sample and quantify them. The example chromatograms for the irradiated and dark-control samples collected on DAT 10.01 (Suntest days) are presented below on figure B.8.2.1.2.2._CA-6.

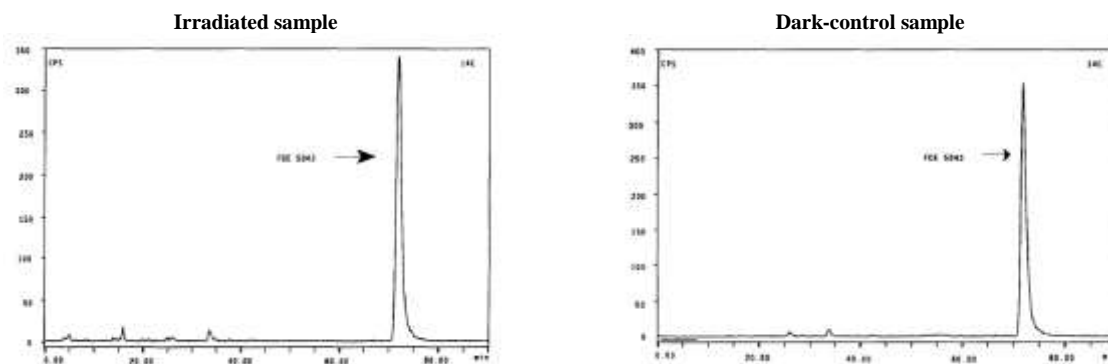


Figure B.8.2.1.2.2._CA-6: The DAT 10.01 (Suntest days; corresponding to 29.3 Natural Sunlight Days timepoint) HPLC chromatograms for irradiated and Dark-control samples (copied from the study report).

In all analysed samples Flufenacet was demonstrated to be the dominant compound. The numerical results of the analysis – the amounts of Flufenacet in each sample determined by HPLC, are presented below in the table B.8.2.1.2.2._CA-5. The time-points expressed in Suntest days and Suntest hours were recalculated by the RMS on the basis of the time-points expressed in Natural Sunlight Days provided in the study report.

Table B.8.2.1.2.2._CA-5: The concentration of Flufenacet in the irradiated and dark-control samples in function of time.

Time point			Content of Flufenacet [%] in:	
<i>Natural Sunlight Days</i>	<i>Suntest Days</i>	<i>Suntest hours</i>	<i>Irradiated sampels</i>	<i>Dark-control samples</i>
0	0	0	98.6	98.6
2.9	0.99	23.78	98.0	not determined
5.9	2.02	48.38	97.5	not determined
14.7	5.02	120.54	94.2	not determined
23.4	8.00	191.88	93.9	97.8
29.3	10.01	240.26	93.0	96.1

The Applicant performed the kinetic analysis of the data presented in the table above. The kinetic fitting was carried out using linear regression for logarithmically-transformed concentrations of Flufenacet. RMS decided to repeat the analysis using the non-linear regression method, as recommended by FOCUS.

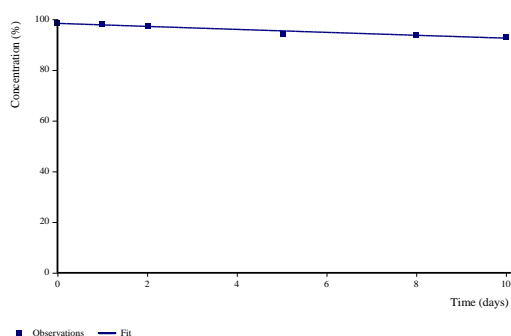
The analysis was performed for irradiated samples using time points expressed as Suntest Days and as Natural Sunlight Days. In case of the dark-control samples the kinetic fitting was carried out using solely Suntest Days, as these are the real sampling points and the dark-control samples do not require any conversion of the sampling points to make them representative for natural irradiation conditions.

The fitting was carried out using CAKE 3.1 modelling tool with IRLS as optimisation method. Only SFO kinetic model was tested, as very low level of degradation was observed.

The results are presented below, in graphical form on figure B.8.2.1.2.2._CA-7 and in the numerical form in the table B.8.2.1.2.2._CA-6.

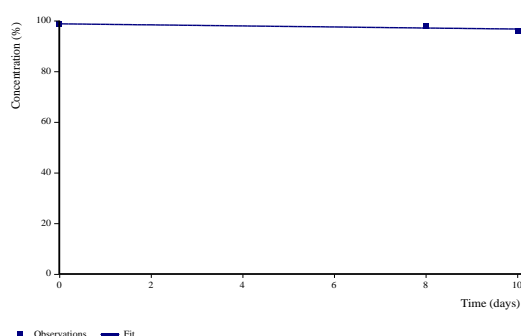
Irradiated samples – Suntest days

Graphical Summary:
Observations and Fitted Model:



Dark control – Suntest days

Graphical Summary:
Observations and Fitted Model:



Irradiated samples – Natural Sunlight Days

Graphical Summary:
Observations and Fitted Model:

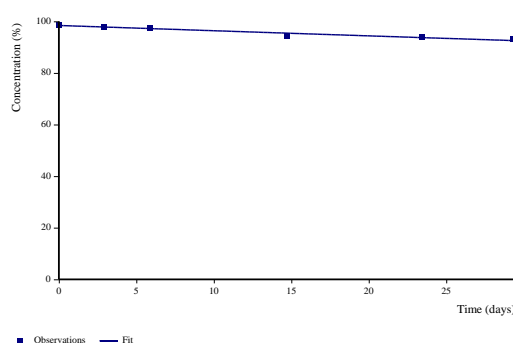
**Figure B.8.2.1.2.2._CA-7:** The graphical results of the examination of the indirect aqueous photolysis of Flufenacet in pure water with Humic material.

Table B.8.2.1.2.2._CA-6: The numerical results of the examination of the indirect aqueous photolysis of Flufenacet in pure water with Humic material.

Type of samples	Kinetic model	Model parameters	Statistical evaluation of the parameter					Statistical evaluation of the fit	
			Value	Error	Confidence intervals		Prob. > t	χ^2 % error	r
					Lower	Upper			
Irradiated-Suntest days	SFO	M ₀	98.42	0.439	97.20	99.64	----	0.468	0.936
		k	0.006109	8.04 E-4	0.003876	0.008	8.06 E-4		
Dark control-Suntest days	SFO	M ₀	98.74	0.917	87.10	110.40	----	0.485	0.736
		k	0.002114	0.001263	-0.01394	0.018	0.1714		
Irradiated-Natural Sunlight days	SFO	M ₀	98.42	0.439	97.20	99.64	----	0.467	0.936
		k	0.002088	2.75 E-4	0.00136	0.003	8.02 E-4		

The fits obtained for irradiated samples can be considered reliable. The fit for the dark control bears a significant level of uncertainty, what can be attributed to small amount of experimental points (three) combined with very low level of degradation of the test compound observed in these samples. Therefore these results should be considered as indicative only. The determined kinetic endpoints were following:

- for irradiated sample using Suntest days DT₅₀ = 114 days;
- for irradiated sample using Natural Sunlight days DT₅₀ = 332 days;
- for the dark control sample using Suntest days DT₅₀ = 328 days

Due to the fact that the results of the fitting obtained for the dark-control samples bears significant level of uncertainty with regard to the rate degradation constant *k*, it was not possible to calculate the net degradation rate constant for photolysis *k*_{photol}. The results however indicate that the degradation of Flufenacet in solution containing humic material can be at least partly attributed to the indirect photolysis. It is therefore proposed to consider the values obtained for irradiated samples, presented above as good estimates of the rate of indirect photolysis of Flufenacet in water containing humic substances.

Experiment 4 was performed using ultrapure water containing 50 ppm of KNO₃.

The solution of KNO₃ used in the experiment was prepared by dissolving 45.0 mg of KNO₃ in 1.5 mL of water.

To the foil-wrapped (with aluminium foil) test vessels, presented in the summary of the same study (as **Study 1**) under the point B.8.2.1.2.1. on figure B.8.2.1.2.1._CA-2, were introduced 60-mL portions of ultrapure water, to which 0.10 mL of the solution of KNO₃, characterised above, was added. Next to each test vessel 0.6-mL portions of the **Test solution 3** were introduced and the test vessels sonicated for 5 minutes. The number of so prepared test vessels was such to be sufficient for four single irradiation samples and three single dark-control samples including DAT-0 sample. The DAT 0 sample was analysed immediately after treatment by LSC and HPLC for the content of [¹⁴C]-Flufenacet and radiochemical purity. The determined concentration of the test compound was 0.99 ppm with radiochemical purity of 99.4%. The concentration of KNO₃ was 50 ppm.

The remaining test vessels, irradiated samples and the dark-control samples, were placed in the Suntest irradiation unit and kept there for up to 10.01 days (corresponding to 29.3 Natural Sunlight Days; for the definition please refer to the summary of the **Study 1** presented under the point B.8.2.1.2.1.). In case of irradiated samples the foil wrapping vessels was removed, while the dark-control samples were kept wrapped with it.

At pre-designated time points irradiated samples and the dark-control samples were taken for the analysis.

The sampling points for the **dark-control samples** were set at the following time points, expressed as Natural Sunlight Days: 0, 23.4, and 29.3. When recalculated by the RMS to the Suntest days, representing the real incubation time the sampling time-points, expressed as DAT (Days After Treatment), were following: 0, 8.00 (191.88 hours) and 10.01 (240.26 hours). The calculations were based on the statement provided by the Applicant, that 1 Natural Sunlight Day is equivalent to 8.2 hours in the Suntest unit. The DAT 0 sample in the dark control can be also considered the DAT-0 irradiated sample.

The sampling points for the **irradiated samples** were set at the following time points, expressed as Natural Sunlight Days: 2.9, 11.7, 23.4 and 29.3. When recalculated by the RMS to the Suntest days, representing the real incubation time the sampling time-points, expressed as DAT (Days After Treatment), were following: 0.99 (23.78 hours), 4.00 (95.94 hours), 8.00 (191.88 hours) and 10.01 (240.26 hours). The calculations were based on the statement provided by the Applicant, that 1 Natural Sunlight Day is equivalent to 8.2 hours in the Suntest unit.

At sampling intervals listed above single irradiated and dark control samples were removed from the Suntest unit. Vessels containing irradiated samples were immediately wrapped with aluminium foil to cut-off the light.

0.2-mL aliquots were analysed by LSC to quantify the [^{14}C] residues. Next 1-mL aliquots were analysed by HPLC to identify the compounds present in sample and quantify them. The example chromatograms for the irradiated and dark-control samples collected on DAT 10.01 (Suntest days) are presented below on figure B.8.2.1.2.2._CA-8.

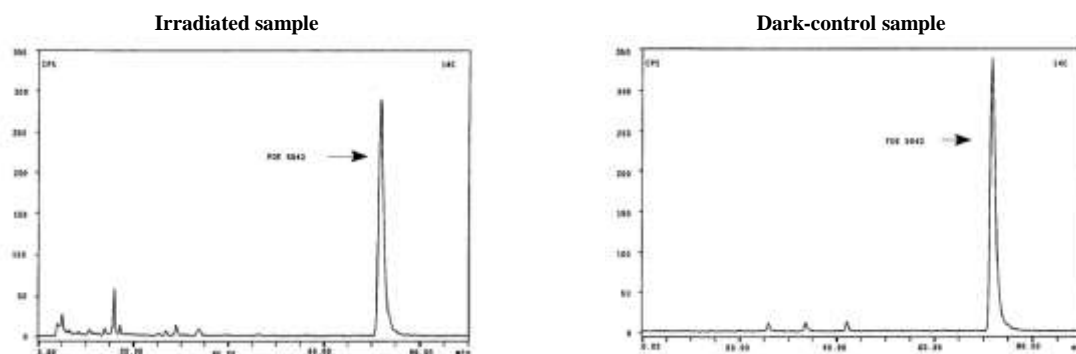


Figure B.8.2.1.2.2._CA-8: The DAT 10.01 (Suntest days; corresponding to 29.3 Natural Sunlight Days timepoint) HPLC chromatograms for irradiated and Dark-control samples (copied from the study report).

In all analysed samples Flufenacet was demonstrated to be the dominant compound. The numerical results of the analysis – the amounts of Flufenacet in each sample determined by HPLC, are presented below in the table B.8.2.1.2.2._CA-7. The time-points, expressed in Sunttest days and Sunttest hours, were recalculated by the RMS on the basis of the time-points expressed in Natural Sunlight Days provided in the study report.

Table B.8.2.1.2.2._CA-7: The concentration of Flufenacet in the irradiated and dark-control samples in function of time.

Time point			Content of Flufenacet [%] in:	
Natural Sunlight Days	Sunttest Days	Sunttest hours	Irradiated samples	Dark-control samples
0	0	0	99.4	99.4
2.9	0.99	23.78	97.7	not determined
11.7	4.00	95.94	96.0	not determined
23.4	8.00	191.88	81.3	95.8
29.3	10.01	240.26	77.5	95.2

The Applicant performed the kinetic analysis of the data presented in the table above. The kinetic fitting was carried out using linear regression for logarithmically-transformed concentrations of Flufenacet. RMS decided to repeat the analysis using the non-linear regression method, as recommended by FOCUS.

The analysis was performed for irradiated samples using time points expressed as Sunttest Days and as Natural Sunlight Days. In case of the dark-control samples the kinetic fitting was carried out using solely Sunttest Days, as these are the real sampling points and the dark-control samples do not require any conversion of the sampling points to make them representative for natural irradiation conditions.

The fitting was carried out using CAKE 3.1 modelling tool with IRLS as optimisation method. Only SFO kinetic model was tested, as very low level of degradation was observed.

The results are presented below, in graphical form on figure B.8.2.1.2.2._CA-9 and in the numerical form in the table B.8.2.1.2.2._CA-8.

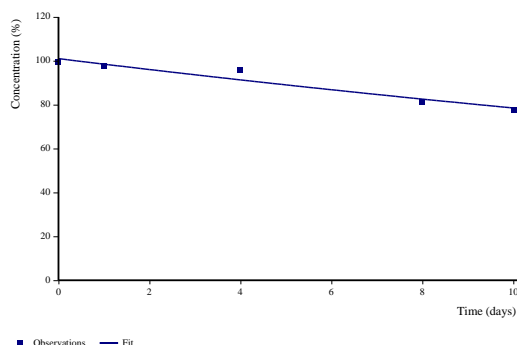
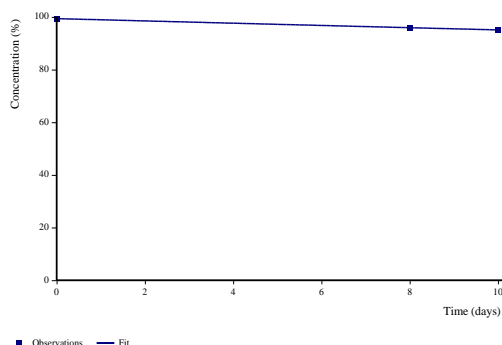
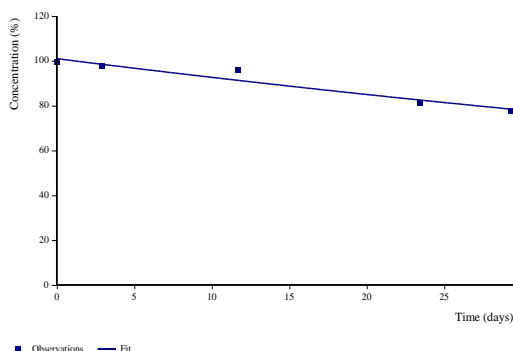
Irradiated samples – Suntest days**Graphical Summary:****Observations and Fitted Model:****Dark control – Suntest days****Graphical Summary:****Observations and Fitted Model:****Irradiated samples – Natural Sunlight Days****Graphical Summary:****Observations and Fitted Model:**

Figure B.8.2.1.2.2._CA-9: The graphical results of the examination of the indirect aqueous photolysis of Flufenacet in pure water with KNO_3 .

Table B.8.2.1.2.2._CA-8: The numerical results of the examination of the indirect aqueous photolysis of Flufenacet in pure water with KNO_3 .

Type of samples	Kinetic model	Model parameters	Statistical evaluation of the parameter					Statistical evaluation of the fit	
			Value	Error	Confidence intervals		Prob. > t	χ^2 % error	r
					Lower	Upper			
Irradiated-Suntest days	SFO	M_0	101.0	2.168	94.11	107.9	----	2.08	0.933
		k	0.02519	0.003984	0.01251	0.038	0.004		
Dark control-Suntest days	SFO	M_0	99.37	0.174	97.16	101.6	----	0.093	0.997
		k	0.004401	2.41 E-4	0.001346	0.007	0.01737		
Irradiated-Natural Sunlight days	SFO	M_0	101.1	2.167	94.11	107.9	----	2.08	0.933
		k	0.008607	0.001361	0.004277	0.013	0.003993		

The obtained fits are reliable. They also returned the DT_{50} values, which are following:

- for irradiated sample using Suntest days $\text{DT}_{50} = 27.5$ days;
- for irradiated sample using Natural Sunlight days $\text{DT}_{50} = 158$ days;
- for the dark control sample using Suntest days $\text{DT}_{50} = 80.5$ days

Comparison of the results obtained for irradiated samples and the dark-control samples using the Suntest days showed that Flufenacet degraded much faster in irradiated samples. That in turn indicates that indirect photolysis played an important role in degradation of that compound. For that reason the net degradation rate constant for photolysis was calculated using the following equation: $k_{\text{photol}} = k_{\text{irrad}} - k_{\text{dark}}$. The resulting $k_{\text{photol}} = 0.020789$ [days^{-1}]. That value was subsequently used to calculate the DT_{50} for the net indirect aqueous

photolysis of Flufenacet in natural water containing salts (marine water, saline water). The calculated $DT_{50} = 33.34$ days for Suntest days. RMS additionally recalculated that value to Natural Sunlight Days, using assumption that 1 Natural Sunlight Day is equal to 8.2 Suntest hours. The resulting $DT_{50} = 97.59$ days when expressed in Natural Sunlight Days.

Conclusions:

The results of the study showed that Flufenacet in natural water will be prone to indirect photolysis and that process will be much faster than the direct aqueous photolysis of Flufenacet. It was also demonstrated that in presence of natural photosensitizer – humic substances, and inorganic salts generating hydroxyl radicals when exposed to solar radiation, the process of indirect aqueous photodegradation of Flufenacet may contribute to overall rate of degradation of that compound in surface water bodies.

The following study was carried out with aim to examine the indirect aqueous photolysis of FOE Thiadone – the major degradation product of Flufenacet in soil and aquatic environment.

Study 2:

Report: Stupp H.-P., Unold M., (2011): “[Thiadiazole-2-¹⁴C] BCS-AA41715 (FOE 5043-thiadone). Phototransformation in Natural Water.”; Bayer CropScience AG, Development, Environmental Safety, Metabolism /ADME and Environmental Fate, BCS-D-EnSDa-MeA/Efate, Alfred-Nobel-Str. 50, D-40789 Monheim am Rhein, Germany, study No. M 1121843-0, Report No. MEF-09/506; 21. 03. 2011; study reference number M-404931-01-1;

Guidelines: The study was performed to comply with the following Guidelines:

- EU Commission Directive 94/37/EC amending Council Directive 91/414/EEC, July 29, 1994;
- EU Commission Directive 95/36/EC amending Council Directive 91/414/EEC, July 14, 1995;
- US. Pesticide Assessment Guidelines, Subdivision N, Environmental Fate, EPA 161-2: Aqueous Photolysis Studies, 1982;
- Japanese JMAFF New Test Guidelines, 2000;
- Canada PMRA DACO Number 8.2.3.3.2.

GLP: Yes;

RMS comments: This is a newly submitted study, performed with aim to examine the indirect aqueous photolysis (photodegradation in natural water) of FOE Thiadone. For the purpose of the current assessment the study was evaluated for its compliance with the following guidelines:

- OECD Guideline 316: Phototransformation of Chemicals in Water – Direct Photolysis, Adopted 3 October 2008;
- US EPA Guideline OPPTS 835.2210 – Direct Photolysis Rate in Water by Sunlight; January 1998;
- US EPA Guideline OPPTS 835.2240 – Photodegradation in Water; October 2008;
- US. EPA Guidelines for Pesticide Registration, Subdivision N, Section 161-2, Aqueous Photolysis Studies (indicated as reference Guideline in the study report);
- OECD Guidelines for the Testing of Chemicals, Proposal for a New Guideline – Phototransformation of Chemicals in Water – Direct and Indirect Photolysis, Draft Document August 2000 (additional reference document),
-

RMS stated that the study was compliant with the provisions of the Guidelines listed above, therefore it was found acceptable. It is summarised below.

Summary:

The aims of the study were:

- a) to determine the rate of photodegradation of FOE Thiadone in natural water exposed to UV-Vis light;
- b) to identify and quantify of major degradation products of that process.

The experiment was performed in two variants – as **Main Test 1** or **Main Test 2**, both characterised further down this summary.

The test compound used in the experiment was [^{14}C]- FOE Thiadone radiolabelled in position C2 of the thiadiazole ring, as shown below on figure B.8.2.1.2.2._CA-10. It had a specific radioactivity of 4.28 MBq/mg, radiochemical purity (determined by radio-HPLC) of >99% and chemical purity (determined by HPLC with UV detection) of >99%. To the test facility it was delivered in form of vacuum-dried solid. In the test facility the 2.59 mg of the test compound was dissolved in 3 mL of CH_3CN to obtain the solution having concentration of ~1 mg/mL, which was stored in the freezer in the dark until being used. That solution was further called **Stock solution (I12431)**. Its purity, determined chromatographically, was 100%.



Figure B.8.2.1.2.2._CA-10: The structural formula of the test compound – [^{14}C] FOE Thiadone, used in the study. The radiolabelling position is marked with an asterisk (*)
(copied from the study report).

The experiment was carried out using natural water sampled from the Rhine River in the vicinity of the test facility, at 717th-718th km of the river course. It was collected on the 31st March 2009 at a distance of ~1 m from the river bank, from the depth of 10-30 cm using 5-L plastic flask. After delivery to the test facility it was stored for 1 day at room temperature before being used. To justify the selection of the test medium – Rhine River water, it was stated that the river was well known to represent typical natural water in agricultural areas and that the amount of organic material was in range that did not influence the irradiation in the environmentally relevant wavelength range ($\lambda \geq 290$ nm) due to the absorption of light.

The characteristic of the test medium – river water, is presented in the table B.8.2.1.2.2._CA-9 and its UV-Vis absorption spectrum on figure B.8.2.1.2.2._CA-11. From that spectrum it can be clearly seen that the maximum absorption in test medium – natural river water, was observed for $\lambda < 290$ nm, while for $\lambda = 290$ nm it was only 0.056 and decreased for longer wavelengths.

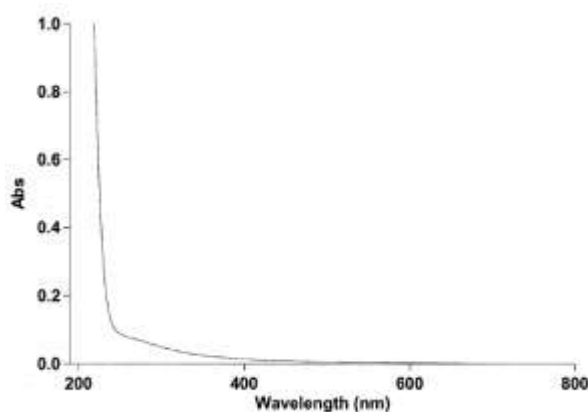


Figure B.8.2.1.2.2._CA-11: The UV-Vis absorption spectrum of the test medium – natural water, used in the experiment (copied from the study report).

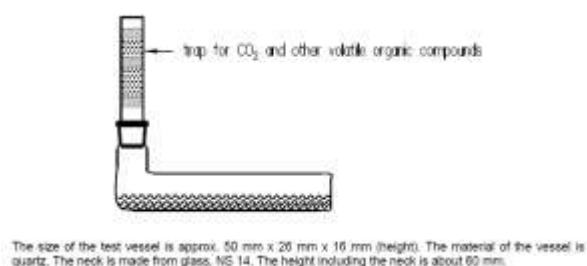
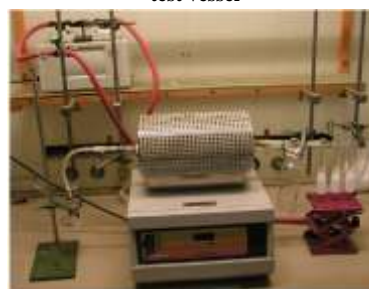
Table B.8.2.1.2.2._CA-9: The characteristic of the test medium – natural water, used in the experiment.

Parameter	Determined value
<i>Test medium</i>	River Rhine water
<i>pH</i>	8.0
<i>Suspended solids [mg/L]</i>	130
<i>Total evaporation residue [mg/L]</i>	370
<i>Oxygen saturation [%]</i>	95.3 at T = 22.5°C
<i>Conductivity [μS/cm]</i>	529
<i>Total Organic Carbon – TOC [mg/L]</i>	2
<i>Hardness [$^{\circ}$dH]</i>	10.5
<i>Total P [mg/L]</i>	0.0815
<i>Total NO₂⁻ and NO₃⁻ content [mg/L]</i>	3.1

The natural water used in the experiment was firstly filtered then sterilised by steam pressure sterilisation. The sterilisation of the test water was performed in order to avoid biological degradation of the test substance.

Its 540-mL portion was treated with 0.54 mL of the **Stock solution**, in the (sterile) Erlenmeyer flask, which afterwards was covered with aluminium foil to cut-off light and the solution was stirred under sterile conditions for ~1 hour to grant its appropriate aeration. So prepared solution was subsequently called **Test solution** and it contained 0.1% of the organic co-solvent – acetonitrile.

Next, the adequate portions of the **Test solution** – 20 mL in case of the **Main Test 1** and 19 mL in case of the **Main Test 2**, were placed in the quartz glass test vessels. Two kinds of the test vessels were prepared for the irradiated samples in the **Main Test 1** – vessels closed with the tower trap for the volatile compounds (**Test vessel type A**), shown below on figure B.8.2.1.2.2._CA-12, and those sealed with a crimped Teflon stopper (**Test vessel type B**), presented on figure B.8.2.1.2.2._CA-13. That second type of the test vessel was subsequently attached, by means of two needles piercing the Teflon stopper to the apparatus removing the volatile compounds formed in headspace and capturing them for further analysis. These samples were placed in the irradiation chamber and irradiated there, at constant temperature T = 25 ± 1°C for up to 14 days.

Test vessel with the trap tower for volatile compounds**The trap for volatile compounds in detail****Figure B.8.2.1.2.2._CA-12:** The **Test vessel type A** used in the experiment (copied from the study report).**Sealed test vessel with injection needles used to remove volatile compounds from headspace****The device for capturing the volatile compounds formed in the test vessel****Figure B.8.2.1.2.2._CA-13:** The **Test vessel type B** used in the experiment (copied from the study report).

In case of the dark control samples used in that experiment, the test vessels, same as shown on figure B.8.2.1.2.2._CA-12 (minus tower trap for volatiles) were sealed with a glass stopper. These samples were placed in the darkness, inside the climatic cabinet, and incubated at the constant temperature $T = 25 \pm 1^\circ\text{C}$ for up to 14 days.

The irradiated samples were kept in the Suntest chamber, presented below on figure B.8.2.1.2.2._CA-14, equipped with a Xenon lamp as the artificial light source. It had the following characteristic:

- emission wavelength spectrum $\lambda = 290 - 2450 \text{ nm}$, with the relevant range at $\lambda = 290 - 800 \text{ nm}$;
- light intensity: 975 W/m^2 for wavelength range $\lambda = 290 - 2450 \text{ nm}$ and 607 W/m^2 for wavelength range $\lambda = 290 - 800 \text{ nm}$;
- filters used: $<290\text{nm}$ cut-off UV filter;
- relationship to natural sunlight: constant 14-days exposure to light in suntest unit corresponded to ~38 days of natural solar irradiation (extreme conditions) in June at Phoenix, Arizona, USA – $33^\circ 26' \text{ N}$ (max daily irradiance: 31 MJ/m^2 , irradiance per 30 days: 930 MJ/m^2).

The temperature in the irradiation chamber was maintained at the constant level by using the cooling plate connected to a chiller. The device is also shown on the figure B.8.2.1.2.2._CA-14.

The Suntest unit – general view



The interior of the suntest unit with the cooling plate



Figure B.8.2.1.2.2._CA-14: The Suntest irradiation unit and its interior with the cooling plate (copied from the study report).

At the pre-designated time points the duplicate samples irradiated (one representing **Test vessels type A** and one representing **Test vessels type B**) were taken for the analysis. Those sampling points were on DAT (Days After Treatment) 1, 2, 5, 6, 8 and 14. At the same time points, and additional on DAT 0, the duplicate dark control samples were also taken for the analysis. The concentration of the test item in the solution was determined before and after introduction of the **Test solution** into the test vessels. That was done using three 0.1-mL aliquots of the solution, analysed by LSC.

The sample processing procedure used in the analysis of the irradiated samples is presented below on figure B.8.2.1.2.2._CA-15. Similar procedure was used for the dark control samples, with exception that the formation of the volatile compounds was not assessed and the solution remaining after analysis was stored in the dark in the freezer to be used as irradiated samples in the **Main Test 2**.

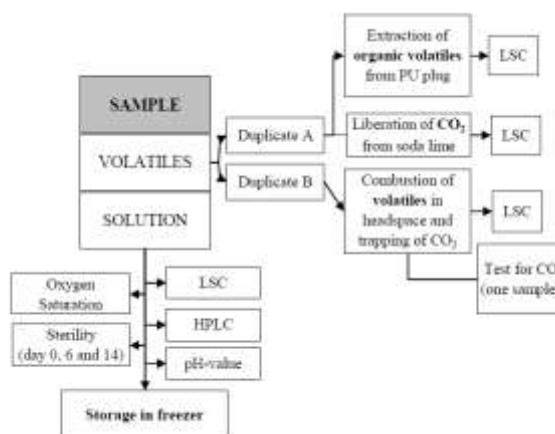


Figure B.8.2.1.2.2._CA-15: The sample-processing procedure used for irradiated samples in the **Main Test 1** (copied from the study report).

The **Main Test 2** was carried out using the test vessels containing samples that in the **Main Test 1** were used as the dark controls (as no degradation of the test item was observed in them). To carry out that experiment the vessels were sealed with crimped Teflon stopper, as were **Test vessels type B** used in the **Main Test 1**. So prepared duplicate samples were placed in the Suntest unit, shown on the figure B.8.2.1.2.2._CA-14, and irradiated for up to 14 days under the similar conditions as irradiated samples in the **Main Test 1**. The light source used in the experiment was Xenon lamp, having the following characteristic:

- emission wavelength spectrum $\lambda = 290 - 2450$ nm, with the relevant range at $\lambda = 290 - 800$ nm;
- light intensity: 958 W/m^2 for wavelength range $\lambda = 290 - 2450$ nm and 597 W/m^2 for wavelength range $\lambda = 290 - 800$ nm;
- filters used: <290nm cut-off UV filter;
- relationship to natural sunlight: constant 14-days exposure to light in suntest unit corresponded to 37.4 days of natural solar irradiation (extreme conditions) in June at Phoenix, Arizona, USA – $33^\circ 26' \text{ N}$ (max daily irradiance: 31 MJ/m^2 , irradiance per 30 days: 930 MJ/m^2).

Duplicate samples were taken for analysis at the following time points: after 1, 2, 5 8, 9 and 14 days of continuous irradiation. Additionally, prior to the start of irradiation, 2 aliquots of the test solution werer taken from one test vessel to be analysed. The samples taken for analysis at the time points listed above were processed using the procedure shown below on figure B.8.2.1.2.2._CA-16.

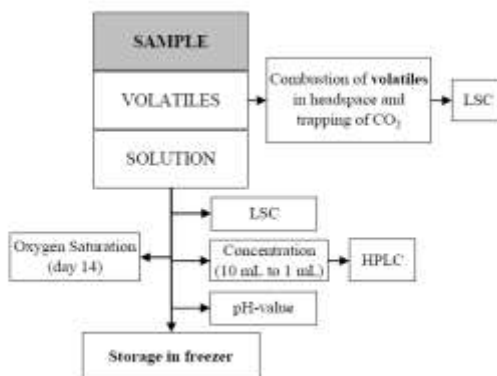


Figure B.8.2.1.2.2._CA-15: The sample-processing procedure used for irradiated samples in the **Main Test 2** (copied from the study report).

In all samples pH was determined using pH-meter Multi 340i (WTW) with a SenTix 62 electrode immediately after sampling. The sterility of the test solution was checked in DAT-0, DAT-6 and DAT-14 samples collected during the **Main Test 1**. For that purpose 20- μ L aliquots of the test solution were applied onto a sterile mixed culture medium and incubated for at least 14 days at $T = 25^{\circ}\text{C}$.

For sample collected during the **Main Test 2** such analysis was not performed as it was assumed that the sterile conditions of the samples were granted due to the high light intensity.

Samples were also monitored for aerobic conditions on DAT-0, DAT-6 and DAT-14 in case of the samples collected during the **Main Test 1** and at day 14 in case of samples collected during the **Main Test 2**. That was done using an oxygen meter Multi 340i (WTW) equipped with Celloxi 325 sensor.

All samples were analysed for radioactivity content using LSC. In case of individual liquid samples their three 0.1-mL aliquots were used in the analysis. Each was mixed with 2 mL of QuicksafeA + 5% water scintillation cocktail and analysed for radioactivity content using Beckman LS 6000LL/6500 scintillation counter. The counting time was 10 minutes, counting efficiency 86 – 92% and the background 13 – 15 cpm.

The radioactivity released from the test vessels in form of $^{14}\text{CO}_2$, either from the soda lime filling soda traps or as the combustion product of the volatile compounds present in the test vessels headspace, was absorbed in Carbosorb E/Permafluor E⁺ 1:1 scintillation cocktail. Next its 9-10-mL aliquots were analysed using LKB-Wallac 1219 LS counter. The counting time was ≤ 10 minutes, counting efficiency 74 – 90% and the background 26 – 28 cpm.

The test solutions were chromatographically analysed using RP-HPLC. The analysis was performed using Agilent 1200 HPLC system coupled with UV detector, set at $\lambda = 254$ nm, and Raytest Ramona Star radioactivity detector. Chromatographic separation was performed in a gradient mode on Purospher RP18E 250 • 4.6 mm, 5 μ m, chromatographic column placed in a chromatographic oven set at $T = 40^{\circ}\text{C}$.

The mobile phase used in the gradient elution consisted of:

- **Solvent A:** 0.1% HCOOH in Milli-Q water;
- **Solvent B:** 0.1% HCOOH in CH_3CN

The elution lasted for 34 minutes, the flow rate of the mobile phase was 1.0 mL/min and the gradient programm is shown below in the table B.8.2.1.2.2._CA-10. The volume of the sample injected was 0.15 – 0.5 mL. The identification of the test compound was performed by comparing the retention times of fractions in the analysed sample with those of the known standards. For FOE Thiadone the $R_t = \sim 23$ min.

Table B.8.2.1.2.2._CA-10: The gradient mode used in the RP-HPLC analysis.

Elution time [min]	Composition of the mobile phase	
	% Solvent A	% Solvent B
0.0	100	0
2.0	100	0
21.0	30	70
25.0	5	95
28.0	5	95
29.0	100	0
34.0	100	0

The **Stock solution** was chromatographically analysed using LC-MS method. The chromatographic analysis was carried out using Agilent HP1100 chromatographic station coupled to UV detector followed by Ramona Raytest radioactivity detector and TSQ 7000 MS Detector (Finnigan). The chromatographic separation was performed on Nucleodur C18 250 • 2, 3 μ m, chromatographic column working in the gradient mode. The mobile phase consisted of:

- **Solvent A:** 0.1% HCOOH in Milli-Q water;
- **Solvent B:** 0.1% HCOOH in CH_3CN

The elution lasted for 35 minutes, the flow rate of the mobile phase was 0.2 mL/min and the gradient programm is shown below in the table B.8.2.1.2.2._CA-11.

Table B.8.2.1.2.2._CA-11: The gradient mode used in the HPLC-MS analysis.

Elution time [min]	Composition of the mobile phase	
	% Solvent A	% Solvent B
0.0	95	5
1.0	95	5
25	5	95
35	5	95

The results – concentrations of the test compound, FOE Thiadone, in irradiated and dark-control samples in function of time, were kinetically examined in order to determine the rate of indirect photodegradation of FOE Thiadone in natural water. The analysis was performed in line with the recommendation of FOCUS Kinetics Guidance Document using KinGUI 1.1 kinetic modelling tool.

Results and their discussion:

The characteristic of artificial light used in the experiment is presented below on figure B.8.2.1.2.2._CA-16.

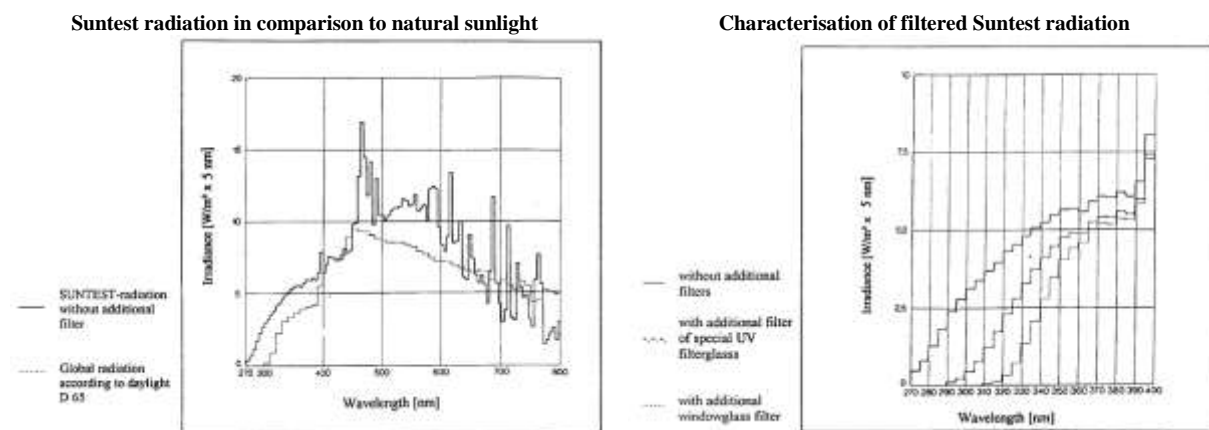


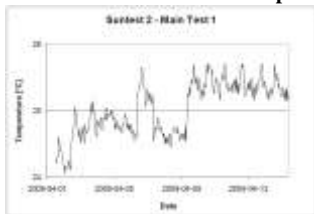
Figure B.8.2.1.2.2._CA-16: Characterisation of the artificial light used in the study (copied from the study report).

On figure B.8.2.1.2.2._CA-17 below are presented the experimental conditions – temperature, in irradiation/climatic chambers during irradiation/incubation of samples. On their basis it may be stated that:

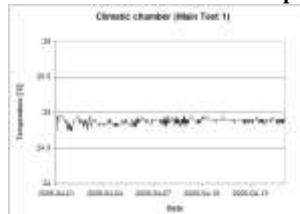
- in the Suntest chamber (irradiated samples) during the **Main Test 1** the average temperature was $T = 25.03^{\circ}\text{C}$, with min. $T = 24.05^{\circ}\text{C}$ and max. $T = 25.70^{\circ}\text{C}$;
- in the climatic chamber (dark control samples) during the **Main Test 1** the average temperature was $T = 24.90^{\circ}\text{C}$, with min. $T = 24.50^{\circ}\text{C}$ and max. $T = 25.45^{\circ}\text{C}$;
- in the Suntest chamber (irradiated samples) during the **Main Test 2** the average temperature was $T = 24.88^{\circ}\text{C}$, with min. $T = 24.75^{\circ}\text{C}$ and max. $T = 24.95^{\circ}\text{C}$.

On that basis it may be stated that during the whole study the temperature was maintained at the pre-defined level of $T = 25 \pm 1^{\circ}\text{C}$.

Main Test 1 – irradiated samples



Main Test 1 – dark-control samples



Main Test 2 – irradiated samples

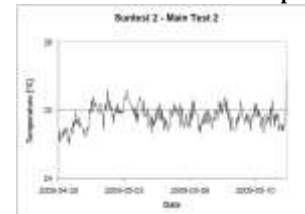


Figure B.8.2.1.2.2._CA-17: The experimental conditions – temperature, recorded in irradiation and incubation chambers during the experiment (copied from the study report).

The results of the determination of the test solution's pH, sterility and saturation with O₂ during the experiment are presented below in the table B.8.2.1.2.2._CA-12. On their basis it was stated that the samples were sterile throughout the study duration. The pH was of irradiated samples in range 7.8 – 9.0 and of the dark control ones 8.3 – 8.6. Oxygen was at the level >90%. In case of the Main Test 1 the replicate 1 of Irradiated samples represent the test vessels sealed with tower traps for volatiles, while replicate 2 – vessels capped with the crimped Teflon stopper.

Table B.8.2.1.2.2._CA-12: The results of the determination of pH, sterility and O₂ level in the test solution during experiment.

Main Test 1									
Irradiated samples					Dark control				
Sampling timepoint [DAT]	Replicate	Results of measurement			Sampling timepoint [DAT]	Replicate	Results of measurement		
		pH at T = 25°C	% O ₂	Sterility check			pH at T = 25°C	% O ₂	Sterility check
0	1	8.2	72	sterile	0	1	8.2	72	sterile
	2	----	----	sterile		2	----	----	sterile
1	1	8.7	----	----	1	1	8.5	----	----
	2	8.4	----	----		2	8.5	----	----
2	1	8.4	----	----	2	1	8.4	----	----
	2	8.6	----	----		2	8.5	----	----
5	1	9.0	----	----	5	1	8.4	----	----
	2	8.3	----	----		2	8.5	----	----
6	1	8.8	----	sterile	6	1	8.5	----	sterile
	2	8.5	----	sterile		2	8.4	----	sterile
8	1	8.7	----	----	8	1	8.5	----	----
	2	8.1	----	----		2	8.4	----	----
14	1	8.5	90.6	sterile	14	1	8.4	96.5	sterile
	2	8.6	90.4	sterile		2	8.6	92.0	sterile

Main Test 2				
Irradiated samples				
Sampling timepoint [days]	Replicate	Results of measurement		
		pH at T = 25°C	% O ₂	
1	1	8.3	----	
	2	8.4	----	
2	1	8.6	----	
	2	8.6	----	
6	1	8.6	----	
	2	8.5	----	
8	1	8.4	----	
	2	8.6	----	
9	1	8.5	----	
	2	8.4	----	
14	1	7.8	90.7	
	2	8.1	91.8	

The verification of the application rate showed that:

- in the **Main Test 1** the initial amount of the test compound – FOE Thiadone, in individual vessel was 16.44 µg, what corresponded to the concentration 0.82 mg/L;
- in the **Main Test 2** the initial amount of the test compound – FOE Thiadone, in individual vessel was 15.62 µg, what corresponded to the concentration 0.82 mg/L.

The LOQ values (LOQ stands for Limit Of Quantification) for the LSC analysis was defined as the double average instrument background count rate, which was approx. 0.25 Bq for liquid samples and approx. 0.5 Bq for combusted headspace of **Test vessels type B** samples. In case of HPLC analysis with radioactivity detection the LOD = 0.4% AR (LOD stands for the Limit Of Detection) and the LOQ = 3 • LOD = 1.2% AR.

The verification of the performance of chromatographic procedure showed that the retention time – R_t , values were well reproducible, what indicated credibility of that method of identification of the test compounds, and the recovery of injected radioactivity was very good (100.9% of radioactivity determined by LSC).

The results of the experiment – the distribution of radioactivity in test solutions in function of time, are presented below in three tables. Table B.8.2.1.2.2._CA-13 contains the results obtained for irradiated samples in the **Main Test 1**, in the table B.8.2.1.2.2._CA-14 presents the results obtained in the **Main Test 1** for the dark-control samples, and the table B.8.2.1.2.2._CA-15 provides the results obtained for irradiated samples in the **Main Test 2**. Each table is followed by the bar graph presenting the results of the examination of the distribution of radioactivity between solution and volatile-compounds fraction (figures B.8.2.1.2.2._CA-18 – B.8.2.1.2.2._CA-20). In case of irradiated samples in the **Main Test 1** two bar graphs are provided, as the test vessels were in two different variants – as vessels sealed with tower trap for volatiles (**Replicate A**) and as vessels capped with crimped Teflon stoppers. In case of the dark control samples in the **Main Test 1** and irradiated samples in **Main Test 2** on the bar graphs are presented the averages obtained for the two replicates.

Analysing them in the study report the authors stated that in case of the **Main Test 1** the use of the **Test vessels type A** resulted in losses of the radioactivity in form of the volatile compounds, what indicated the formation of the non-absorbed volatiles. The recovery of the radioactivity in the same test from **Test vessels type B** was scattered, but on the basis of these results it was decided to use that design in the definitive test with irradiated samples.

Due to the insufficient recovery levels in these samples it was decided not to use the results in the kinetic analysis carried out for FOE Thiadone.

The qualitative analysis of the test solutions showed that they contained two radiolabelled compounds/fractions – FOE Thiadone and the degradation product M1. The concentrations of FOE Thiadone in both replicates decreased with time, what indicated that the compound was photodegraded. That was conformed by the increasing amounts of the degradate M1.

In the dark control samples collected during the **Main Test 1** the analysis showed that virtually whole radioactivity was in the solution. For that reason the analysis of the volatile fraction was not carried out. The profiling of the test solutions showed that the only constituent of the solution was FOE Thiadone. On that basis it was stated that in the dark control samples the compound was stable. The determined concentrations of FOE Thiadone were used in the kinetic analysis. The analysis was performed using the concentration for individual replicates as input values.

The solutions remaining in the dark-control samples from the **Main Test 1** after LSC and chromatographic analyses were subsequently used as the irradiated samples in the **Main Test 2**. In these samples a steady build-up of the volatile compounds fraction was demonstrated, correlated with the decrease of radioactivity in the solution. The recoveries of radioactivity were, with exception of the last time point (at which the leakage in the oxidiser was observed), at the level of >90% AR.

Three radioactivity fractions were detected in solution:

- FOE Thiadone, steadily decreasing with time;
- the M1 degradation product, reaching the maximum amount, in one of replicates, of 8.4% AR, and the peak concentration, as average of two replicates, of 7.5% AR; that fraction was not further characterised, being classified in the report as minor metabolite (RMS however noticed that in both replicates it was recorded in amounts >5% AR in at least two consecutive samples);
- the diffuse radioactivity fraction representing minor degradation products, not surpassing 1.1% AR during the study.

The results obtained in the **Main Test 2** for the individual compounds/fractions identified in the experiment were presented in the study report in the graphical form. That scheme is presented as the right-hand graph on figure B.8.2.1.2.2._CA-20.

Finally, it shall be indicated that it was stated in the study report that the formed volatile products could not have been trapped directly. For that reason they were determined as the $^{14}\text{CO}_2$ formed as the result of the combustion of the headspace. RMS noticed that FOE Thiadone may be classified as a volatile compound, with $V_p = 2.05 \text{ Pa}$ at $T = 20^\circ\text{C}$ and Henry's law constant $H = 0.012 \text{ Pa} \cdot \text{m}^3 \cdot \text{mol}^{-1}$. It may be therefore possible that part of radioactivity in the headspace may be attributed to that compound, what in turn could influence the results of the kinetic analysis. The results however obtained for the dark control samples in the **Main Test 1** do not seem to confirm that – all radioactivity applied was recovered in the test solution.

Table B.8.2.1.2.2._CA-13: The numerical results obtained for irradiated samples in the **Main Test 1**.

Replicate	Parameter		Results, expressed as [%AR], obtained for the sampling point DAT (Days After Treatment):						
			0	1	2	5	6	8	14
A - vessels with tower traps for volatiles	<i>Radioactivity in solution identified as:</i>	FOE Thiadone	100.1	91.7	77.0	49.1	39.3	32.3	12.8
		Degradation product M1	Not found	Not found	2.8	6.3	6.9	6.0	3.2
		Total radioactivity in solution	100.1	91.7	79.8	55.4	46.2	38.3	16.0
	<i>Radioactivity recovered as volatile compounds</i>		Not examined	0.2	0.4	1.0	1.3	1.3	6.3
	<i>Total radioactivity recovered</i>		100.1	91.9	80.2	56.4	47.6	39.7	22.3
B – vessels capped with crimped Teflon stoppers	<i>Radioactivity in solution identified as:</i>	FOE Thiadone	99.9	89.3	76.0	49.7	43.3	31.6	12.1
		Degradation product M1	Not found	Not found	2.8	7.4	5.5	11.4	8.7
		Total radioactivity in solution	99.9	89.3	78.9	57.1	48.8	43.0	20.9
	<i>Radioactivity recovered as volatile compounds</i>		Not examined	1.2	0.6	31.1	0.2	52.2	0.2
	<i>Total radioactivity recovered</i>		99.9	90.5	79.5	88.2	48.9	95.2	21.1

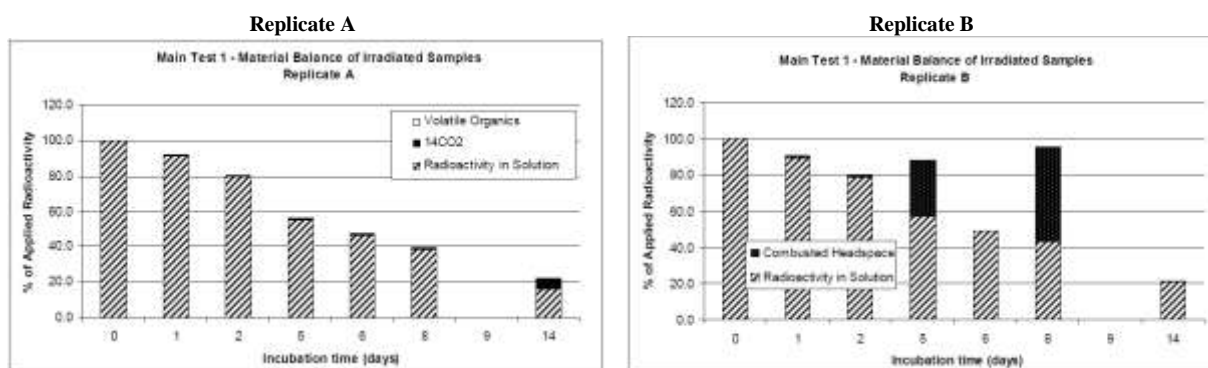


Figure B.8.2.1.2.2._CA-18: The graphical results of the determination of mass balance for irradiated samples collected in the **Main Test 1** (copied from the study report).

Table B.8.2.1.2.2._CA-14: The numerical results obtained for dark-control samples in the **Main Test 1**.

Parameter		Replicate	Results, expressed as [%AR], obtained for the sampling point DAT (Days After Treatment):						
			0	1	2	5	6	8	14
Radioactivity in solution identified as	FOE Thiadone	1	100.1	100.4	99.6	99.8	100.2	100.1	99.2
		2	99.9	99.7	99.6	99.4	100.3	100.3	100.3
		Mean	100.0	100.1	99.6	99.6	100.2	100.2	99.7
	Degradation product M1	1	n. d. ²⁾	n. d. ²⁾	n. d. ²⁾	n. d. ²⁾	n. d. ²⁾	n. d. ²⁾	n. d. ²⁾
		2	n. d. ²⁾	n. d. ²⁾	n. d. ²⁾	n. d. ²⁾	n. d. ²⁾	n. d. ²⁾	n. d. ²⁾
		Mean	n. d.²⁾	n. d.²⁾	n. d.²⁾	n. d.²⁾	n. d.²⁾	n. d.²⁾	n. d.²⁾
	Diffuse radioactivity (minor degradates)	1	n. d. ²⁾	n. d. ²⁾	n. d. ²⁾	n. d. ²⁾	n. d. ²⁾	n. d. ²⁾	n. d. ²⁾
		2	n. d. ²⁾	n. d. ²⁾	n. d. ²⁾	n. d. ²⁾	n. d. ²⁾	n. d. ²⁾	n. d. ²⁾
		Mean	n. d.²⁾	n. d.²⁾	n. d.²⁾	n. d.²⁾	n. d.²⁾	n. d.²⁾	n. d.²⁾
	Total radioactivity in solution	1	100.1	100.4	99.6	99.8	100.2	100.1	99.2
		2	99.9	99.7	99.6	99.4	100.3	100.3	100.3
		Mean	100.0	100.1	99.6	99.6	100.2	100.2	99.7
Radioactivity recovered as volatile compound¹⁾	1	n. e. ³⁾	n. e. ³⁾	n. e. ³⁾	n. e. ³⁾	n. e. ³⁾	n. e. ³⁾	n. e. ³⁾	n. e. ³⁾
	2	n. e. ³⁾	n. e. ³⁾	n. e. ³⁾	n. e. ³⁾	n. e. ³⁾	n. e. ³⁾	n. e. ³⁾	n. e. ³⁾
	Mean	n. e.³⁾	n. e.³⁾	n. e.³⁾	n. e.³⁾	n. e.³⁾	n. e.³⁾	n. e.³⁾	n. e.³⁾
Total radioactivity recovered		1	100.1	100.4	99.6	99.8	100.2	100.1	99.2
		2	99.9	99.7	99.6	99.4	100.3	100.3	100.3
		Mean	100.0	100.1	99.6	99.6	100.2	100.2	99.7

Footnotes to the table;:

- 1) Volatiles not examined, as virtually all radioactivity recovered in solution;
- 2) n. d. – not detected;
- 3) n. e. – not examined

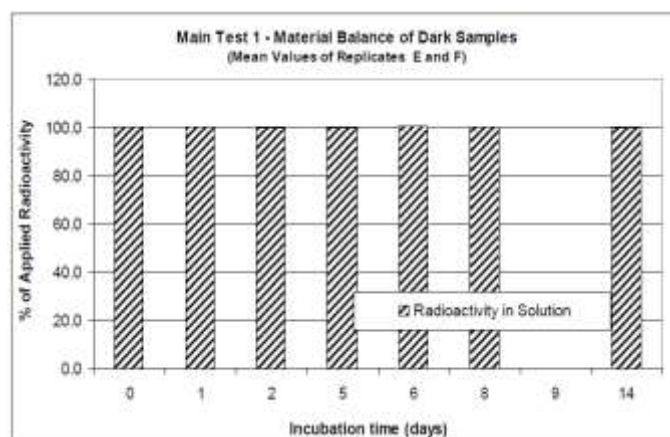
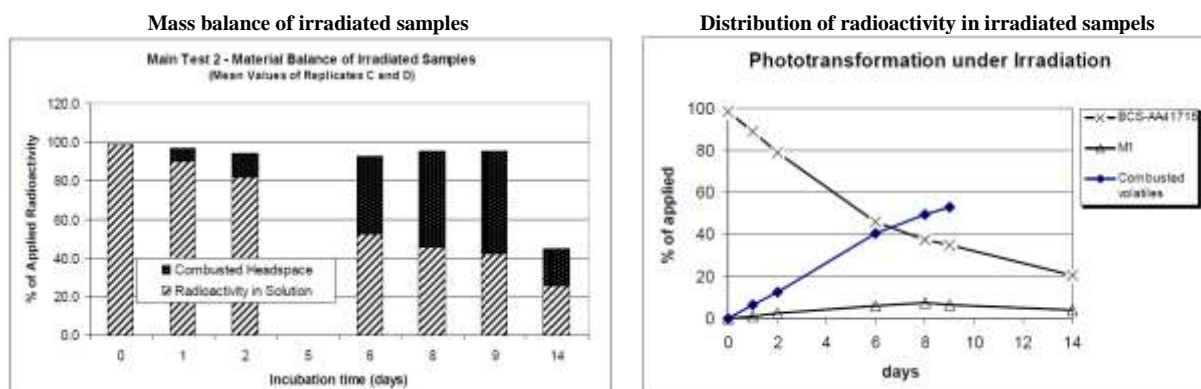
Figure B.8.2.1.2.2._CA-19: The graphical results of the determination of mass balance for dark-control samples (mean of two replicates) collected in the **Main Test 1** (copied from the study report).

Table B.8.2.1.2.2._CA-15: The numerical results obtained for irradiated samples in the **Main Test 2**.

Parameter		Replicate	Results, expressed as [%AR], obtained for the sampling point [DI] (Days of Incubation):						
			0	1	2	6	8	9	14
Radioactivity in solution identified as	FOE Thiadone	1	98.4	89.7	80.0	45.2	37.6	36.8	22.4
		2	98.5	88.1	78.2	46.3	37.1	33.0	18.4
		Mean	98.5	88.9	79.1	45.8	37.4	34.9	20.4
	Degradation product M1	1	n. d. ¹⁾	0.9	2.1	6.9	6.7	4.7	6.6
		2	n. d. ¹⁾	1.3	2.5	5.0	8.4	8.0	1.8
		Mean	n. d. ¹⁾	1.1	2.3	5.9	7.5	6.3	4.2
	Diffuse radioactivity (minor degradates)	1	0.0	0.0	0.0	0.4	0.6	0.8	1.1
		2	0.0	0.0	0.0	0.4	0.5	0.7	1.1
		Mean	0.0	0.0	0.0	0.4	0.5	0.7	1.1
	Total radioactivity in solution	1	98.4	90.6	82.1	52.5	44.8	42.2	30.2
		2	98.5	89.4	80.8	51.8	46.1	41.8	21.2
		Mean	98.5	90.0	81.4	52.1	45.4	42.0	25.7
Radioactivity recovered as volatile compound ¹⁾		1	n. e. ²⁾	5.6	11.2	39.1	50.2	52.6	37.2 ³⁾
		2	n. e. ²⁾	7.4	13.5	41.8	49.2	53.9	0.2 ³⁾
		Mean	n. e. ²⁾	6.5	12.3	40.5	49.7	53.2	18.7 ³⁾
Total radioactivity recovered		1	98.4	96.2	93.2	91.7	95.0	94.9	67.4 ⁴⁾
		2	98.5	96.8	94.2	93.5	95.3	95.6	21.5 ⁴⁾
		Mean	98.5	96.5	93.7	92.6	95.2	95.2	44.4 ⁴⁾

Footnotes to the table:

- 1) n. d. – not detected;
- 2) n. e. – not examined;
- 3) The drop of radioactivity was caused by a leak in the oxidiser;
- 4) The lost of radioactivity recovered as volatile compounds (due to the leak in the oxidiser) was the reason for low total recovery level observed for this time point.

Figure B.8.2.1.2.2._CA-20: The graphical results obtained for irradiated samples (mean of two replicates) collected in the **Main Test 2** (copied from the study report).

On the basis of the results presented above in the study report was proposed the transformation scheme for the process of photodegradation of FOE Thiadone in the natural water (indirect aquatic photolysis). It is shown below on figure B.8.2.1.2.2._CA-21. It shall be indicated that it was derived only for the compound radiolabelled in C2 position within the thiadiazole ring, so it does not address the would-be products associated with the second carbon atom within the ring – C5. That may be considered as a data gap, minor however, as possibly the photodegradation products would be similar to detected for thiadiazole group radiolabelled in C5 position in the study examining the degradation of Flufenacet in aerobic soil.

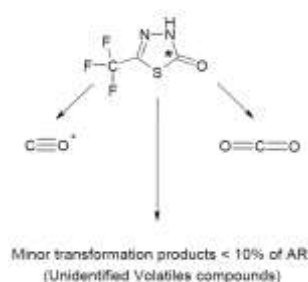


Figure B.8.2.1.2.2._CA-21: The proposed degradation pathway for FOE Thiadone radiolabelled in C2 position in the process of indirect aqueous photolysis (copied from the study report).

The data for FOE Thiadone presented in the tables B.8.2.1.2.2._CA-14 and B.8.2.1.2.2._CA-15 were subjected to the kinetic analysis carried out in line with the recommendations provided by the FOCUS Kinetics Guidance Document [Focus, 2005]. The assessment was performed using KinGUI 1.1 as a modelling tool. The data were fitted solely to the SFO kinetic model. The input data used in the analysis are presented below in the table B.8.2.1.2.2._CA-16.

Table B.8.2.1.2.2._CA-16: The input data used in the kinetic analysis of the results obtained for FOE Thiadone in the experiment examining its indirect aqueous photolysis.

Irradiated samples			Dark-control samples		
Sampling point [Days]	Concentration of FOE Thiadone [% AR]		Sampling point [Days]	Concentration of FOE Thiadone [% AR]	
	Replicate 1	Replicate 2		Replicate 1	Replicate 2
0.0	98.4	98.5	0.0	100.1	99.9
1.0	89.7	88.1	1.0	100.4	99.7
2.0	8.0	78.2	2.0	99.6	99.6
6.0	45.2	46.3	5.0	99.8	99.4
8.0	37.6	37.1	6.0	100.2	100.3
9.0	36.8	33.0	8.0	100.1	100.3
14.0	22.4	18.4	14.0	99.2	100.3

The results of the fitting are presented below, in the graphical form on figure B.8.2.1.2.2._CA-22 and in the numerical form in the table B.8.2.1.2.2._CA-17.

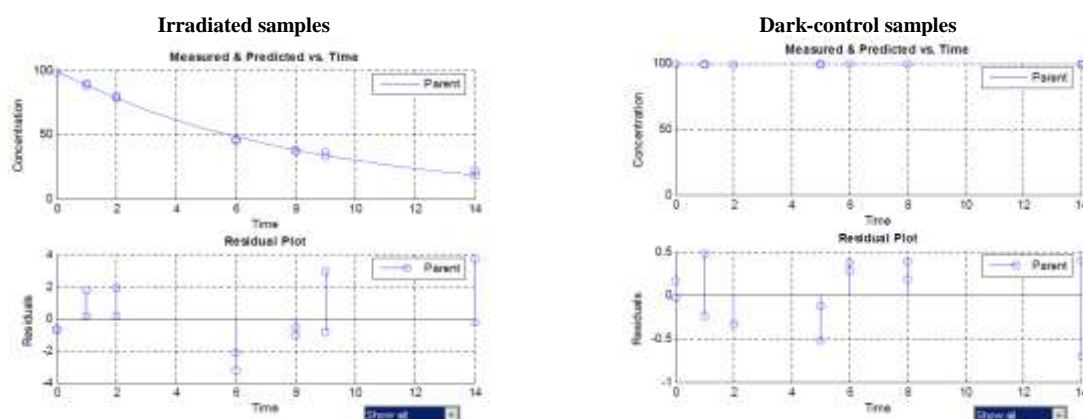


Figure B.8.2.1.2.2._CA-22: The graphical results of the kinetic fitting of the data for FOE Thiadone in irradiated and dark-control samples using SFO kinetic model (copied from the study report).

Table B.8.2.1.2.2._CA-17: The numerical results of the kinetic fitting of the data for FOE Thiadone in irradiated and dark-control samples using SFO kinetic model.

Type of samples	Kinetic model	Model parameters	Statistical evaluation of the parameter				Evaluation of the fit	
			Value	Error	Confidence intervals ¹⁾		Prob. > t	χ^2 % error
Irradiated	SFO	M ₀	99.14	1.014	----	----	----	1.972
		k	0.1194	0.0029	----	----	1.2 E-14	
Dark control	SFO	M ₀	99.93	0.160	----	----	----	0.200
		k	2.3 E-5	2.3 E-4	----	----	0.462	

Footnotes to the table:

1) Values not provided in the study report;

2) Visual assessment of the kinetic curve as proposed by the RMS.

The endpoints – DT₅₀ and DT₉₀ values, calculated by the modelling tool are presented below in the table B.8.2.1.2.2._CA-18. These results were subsequently recalculated in the study report to represent the rate of photodegradation of FOE Thiadone in natural water exposed to natural sunlight on different locations (latitudes). The results are presented on figure B.8.2.1.2.2._CA-23.

Table B.8.2.1.2.2._CA-18: The kinetic endpoints obtained in the study.

Determined parameter	Results obtained for:	
	Dark control samples	Irradiated samples
Rate constant k [days ⁻¹]	0.000023	0.1194
DT ₅₀ [days]	>1000	5.81
DT ₉₀ [days]	>1000	19.28
Kinetic model	SFO	SFO

3. Irradiation Time (8Suntest Cabinet) Transferred to Solar Days
(The spectral distribution of global irradiance is not significantly different at different latitudes and, therefore, can be extrapolated to different geographical locations by a linear correlation.)

	Monthly Average Irradiance of Natural Sunlight (Exemplary Locations) *)				
	Edmonton, Alberta (CAN)	London, Great Britain (EU)	Athens, Greece (EU)	Tokyo, Japan (Japan)	Phoenix, Arizona (USA)
Geographical Latitude	53.33 N	51.30 N	38.03 N	35.11 N	33.26 N
Month	June	July	June	April - June	June
Irradiance (MJ/m ² per day)	22	16	20	14.6	31
Irradiance (MJ/m ² per 30 days)	660	480	600	438	930
Sampling interval / Duration of Light Exposure in Suntest (days)	Corresponding to Natural Sunlight Days				
0	0.0	0.0	0.0	0.0	0.0
1	3.8	5.3	4.2	5.8	2.7
2	7.7	10.5	8.4	11.5	5.4
5	19.1	26.3	21.1	28.9	13.6
6	23.0	31.6	25.3	34.6	16.3
8	30.6	42.1	33.7	46.2	21.7
14	53.6	73.7	59.0	80.8	38.0
Calculation for DT ₅₀ [days]	22.2	30.5	24.4	33.5	15.8
5.8 **					

*) Solar radiation data from : Wypych, G.; Handbook of Material Weathering, 2nd edition; Chemtec Publishing, Ontario, Canada, 1995

**) Calculated DT₅₀ value was taken from main test 2

Figure B.8.2.1.2.2._CA-23: The rate of photodegradation of FOE Thiadone in natural water exposed to natural sunlight on different locations (latitudes) (copied from the study report).

Conclusions:

The results of the study demonstrate that FOE Thiadone is prone to photodegradation in natural water, i. e. to indirect aqueous photolysis. Light bearing characteristic identical to that of natural sunlight was demonstrated to be the main factor driving that process – the sterilisation of riverine water used in the experiment and lack of degradation observed in the dark control samples confirmed that. The degradation process, following 1st order kinetics (SFO), was relatively fast, with rate constant $k = 0.1194$ [days⁻¹] what corresponded to DT₅₀ = 5.8 days and DT₉₀ = 19.28 days in samples continuously exposed to artificial sunlight. That may indicate that FOE Thiadone could be efficiently removed in the processes of drinking water abstraction at the stage at which water is sterilised with UV radiation. The experiment was performed using the compound radiolabelled at C2 position,

for which it was possible to identify two degradation products – CO₂ and CO. There is no information about the would-be degradation products associated with the second carbon atom within the thiadiazole ring – C5, although it may be assumed that one of them could be TFA. That however may require further investigation.

When recalculated to natural conditions – exposure to sunlight at three different locations (representative), the half lives were following:

- for Phoenix, Arizona, USA, latitude 33° 26' N, in June (radiation intensity 31 MJ/m² per day and 930 MJ/m² for 30 days) **DT₅₀ = 15.8 days**;
- for Athens, Greece, EU, latitude 38° 08' N, in June (radiation intensity 20 MJ/m² per day and 600 MJ/m² for 30 days) **DT₅₀ = 24.4 days**;
- for Phoenix, Arizona, USA, latitude 33° 26' N, in July (radiation intensity 16 MJ/m² per day and 480 MJ/m² for 30 days) **DT₅₀ = 30.5 days**.

These results may indicate that the phototransformation in natural Surface Water bodies may be one of the mechanisms of the elimination of FOE Thiadone from that environmental compartment, although probably not a dominant one.

Summary – Indirect aqueous photolysis of Flufenacet

The indirect aqueous photolysis of Flufenacet was examined in four types of aqueous solutions:

- natural pond water having pH = 6.5, TOC = 20.7 mg/L and containing 160 mg/L of suspended solids (total), subsequently named Howe pond water;
- natural pond water having pH = 7.8, TOC = 1.55 mg/L and containing 9 mg/L of suspended solids, subsequently named Stilwell pond water;
- ultrapure water containing 15 ppm of humic material;
- ultrapure water containing 50 ppm KNO₃.

The samples were exposed to UV-Vis radiation generated by artificial light source, but bearing the characteristic of the natural sunlight. The irradiation conditions were similar to those recorded during the 30-days exposure to natural summer light in Phoenix, Arizona, USA. The experiment showed that Flufenacet was prone to indirect photolysis in water, although that process should not be regarded as one of the driving mechanisms in disappearance of Flufenacet from natural waters. The experiments were aimed on the determination of the kinetic parameters of the process – the rates of the indirect photodegradation of Flufenacet in water, therefore no attempt was made to identify and quantify the formed degradation products.

The calculated, net, half-lives for the indirect photodegradation of Flufenacet in water were following:

- for Howe pond water the experimentally derived (continuous irradiation) **DT₅₀ = 160.08 days**, what corresponded to **DT₅₀ = 468.53 days** for exposure to natural summer sunlight at 33° 26' N (in June at Phoenix, Arizona, USA);
- for Stilwell pond water the experimentally derived (continuous irradiation) **DT₅₀ = 281 days**, what corresponded to **DT₅₀ = 822 days** for exposure to natural summer sunlight at 33° 26' N (in June at Phoenix, Arizona, USA);
- for ultrapure water containing 15 ppm of Humic material the experimentally derived (continuous irradiation) **DT₅₀ = 114 days**, what corresponded to **DT₅₀ = 332 days** for exposure to natural summer sunlight at 33° 26' N (in June at Phoenix, Arizona, USA);
- for ultrapure water containing 50 ppm of KNO₃ the experimentally derived (continuous irradiation) **DT₅₀ = 27.5 days**, what corresponded to **DT₅₀ = 158 days** for exposure to natural summer sunlight at 33° 26' N (in June at Phoenix, Arizona, USA).

It shall be however indicated that these values were determined using the results obtained in non-GLP experiments (being an additional part of a GLP study aimed on the examination of the direct aqueous photolysis of Flufenacet). For that reason RMS decided to consider them as only indicative and not to include them into the EU List of Endpoints.

Additionally, in a separate experiment, was examined the indirect aqueous photolysis of FOE Thiadone – the major soil and aquatic degradation product of Flufenacet. The test medium was sterilised natural (riverine) water. The samples were exposed to UV-Vis radiation generated by artificial light source, but bearing the characteristic of the natural sunlight. The irradiation conditions were similar to those recorded during the 30-days exposure to natural summer light in Phoenix, Arizona, USA. The experiment showed that FOE Thiadone was prone to indirect photolysis in water, although that process should not be regarded as one of the driving mechanisms in disappearance of Flufenacet from natural waters. The experiment was performed with the test compound radiolabelled at C2 position in thiadiazole ring, what resulted in identification only CO and CO₂ as degradation

products. Therefore it remains unknown what are the degradation products associated with the second carbon atom within the thiadiazole ring – C5. However, it may be assumed that one of such products could be TFA. The calculated, net, rate of indirect photodegradation of FOE Thiadone in water was $k = 0.1194 \text{ [days}^{-1}\text{]}$, corresponding to $\text{DT}_{50} = 5.8 \text{ days}$ in samples continuously irradiated with artificial sunlight. When recalculated to the natural conditions that value corresponded to:

- $\text{DT}_{50} = 15.8 \text{ days}$ determined for summer sunlight conditions (June) in Phoenix, Arizona, USA ($33^{\circ} 26' \text{N}$);
- $\text{DT}_{50} = 24.4 \text{ days}$ determined for summer sunlight conditions (June) in Athens, Greece, EU ($38^{\circ} 03' \text{N}$);
- $\text{DT}_{50} = 30.5 \text{ days}$ determined for summer sunlight conditions (July) in London, UK, EU ($51^{\circ} 30' \text{N}$).

These results were reported in the EU List of EndPoints for Flufenacet.

The results of the examination of the indirect aqueous photolysis of FOE Thiadone, in format recommended for reporting the regulatory endpoints in the EU, are presented below.

Aqueous photochemical degradation (Regulation (EU) N° 283/2013, Annex Part A, points 7.2.1.2 / 7.2.1.3)

Photolytic degradation of active substance and metabolites above 10 % - [results for Flufenacet, indirect photolysis](#)

Fully reliable results not available

Photolytic degradation of active substance and metabolites above 10 % - [results for FOE Thiadone, indirect photolysis](#)

DT_{50} : *5.8 days*
 Estimated DT_{50} at $33^{\circ} 26' \text{N}$ (*Phoenix, AZ, USA*) *15.8 days (June)*
 Estimated DT_{50} at $38^{\circ} 03' \text{N}$ (*Athens, Greece, EU*) *24.4 days (June)*
 Estimated DT_{50} at $51^{\circ} 30' \text{N}$ (*London, UK, EU*) *30.5 days (July)*

B.8.2.2. – Route and rate of biological degradation in aquatic systems

The assessment in that area covered the following issues:

- examination of the ready biodegradability;
- examination of the aerobic mineralisation in surface water;
- examination of the fate and behaviour of Flufenacet in aerobic water/sediment systems;
- examination of the fate and behaviour of Flufenacet in irradiated aerobic water/sediment systems;
- examination of the degradation of Flufenacet in saturated zone (anaerobic water/sediment system).

Each of these problems is addressed below, under the relevant data point.

B.8.2.2.1. – Ready biodegradability

The Applicant has not submitted any study report presenting the results of the examination of ready biodegradability of Flufenacet. Instead the following justification for non-submission was provided:

“Flufenacet was stated to be not ready biodegradable. This was accepted by the European Commission (7469/VI/98-Final -3rd July 2003). Therefore no additional study was performed for the flufenacet renewal of approval.”

The justification for non-provision of the adequate study may be considered acceptable. RMS examining the submitted documentation stated that the Applicant submitted a study examining the degradation of Flufenacet in natural water. Also are available two studies examining the fate and behaviour of Flufenacet in aerobic water/sediment systems. These studies provided information on the mineralisation of Flufenacet in aquatic environment. Their results confirm that Flufenacet shall be classified as not readily biodegradable, hence the conclusion drawn during the previous evaluation of Flufenacet for its authorisation in the EU remains valid.

The outcome of that evaluation, in format recommended for reporting the regulatory endpoints in the EU, is presented below.

‘Ready biodegradability’ (Regulation (EU) N° 283/2013, Annex Part A, point 7.2.2.1)

Readily biodegradable
(yes/no)

<i>No data submitted, substance considered not readily biodegradable</i>
--

B.8.2.2.2. – Aerobic mineralisation in surface water

To address this data requirement the Applicant submitted two study reports, one examining the biotransformation of Flufenacet in natural water and the second one containing the results of the kinetic examination of the data obtained in the first study. Additionally was submitted the position paper presenting the compliance of the study examining the biological transformation of Flufenacet in water with the provisions of the OECD Guideline 309 – “Aerobic Mineralisation in Surface Water – Simulation Biodegradation Test.”.

All three submitted documents are summarised below as *Studies 1-3*.

Study 1:

Report: Schocken M. J., Yen P. Y., Widmer S. L., (1995): “[Phenyl-U-¹⁴C]FOE 5043 – Determination of Aerobic Aquatic Biotransformation at 25°C.”; Springborn Laboratories Inc., Environmental Sciences Division, 790 Main Street, Wareham, Massachusetts 02571-1075, USA (performing laboratory) for Bayer Corporation (formerly Miles Inc.), Agriculture Division, Research and Development Department, P. O. Box 4913, Kansas City, MO 64120, USA; Springborn Laboratories Report No. 95-4-5785; study No. F3042404 (Bayer); Bayer Report No. BR106961; 27 December 1995; study reference number M-002210-01-1;

Guidelines: The study was performed to comply with the following Guidelines:

- Canadian Guidelines T-1-255 for Determining Environmental Chemistry and Fate of Pesticides (Agriculture Canada), 30 October 1987.

GLP: Yes;

RMS comments: This is a newly submitted study. For the purpose of the present assessment it was evaluated for its compliance with the following Guidelines:

- OECD Guideline for the Testing of Chemicals No. 309: “Aerobic Mineralisation in Surface Water – Simulation Biodegradation Test.”, adopted 13 April 2004;

That evaluation of compliance was based on the results of the position paper submitted by the Applicant and summarised immediately after the summary of this study as *Study 2*.

RMS stated that, despite some deficiencies and deviations from the reference Guideline OECD 309, the study may be considered acceptable and used in the current assessment. It is summarised below.

Summary:

The aim of the study was to examine aerobic aquatic metabolism of Flufenacet (compound uniformly radiolabelled in phenyl ring) in order to:

- 1) determine the degradation kinetics of that compound;
- 2) to identify the major degradation products (>10% of the applied dose) and to establish their patterns of formation and decline over the course of one year.

The test compound used in the experiment was [Phenyl-U-¹⁴C]Flufenacet, having radiochemical purity of ≥ 99.0% and specific activity of 66.5 mCi/mmol. Its structural formula is shown below on figure B.8.2.2.2._CA-1. The radiolabelling position is indicated by an asterisk.

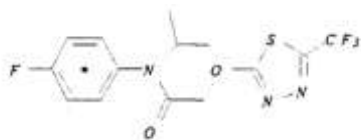


Figure B.8.2.2.2._CA-1: The structural formula of the test compound used in the study. Radiolabelling position is marked by an asterisk (copied from the study report).

The test compound was delivered in two separate vials, the content of which was used to prepare two stock solutions.

First vial, delivered on the 19 November 1993, was used to prepare the **Stock solution A**, used as application solution in an aborted study. That solution was prepared by dissolving the entire content of the vial with 100 mL of CH₃CN, what resulted in solution having the concentration of the test compound 0.165 mg/mL and specific activity of 406458 dpm/μL.

The second vial, received in the test facility on 18th February 1994, was used to prepare the **Stock solution B**. That was done by dissolving the entire content of that vial in 50 mL of CH₃CN and then combining so obtained solution with the remaining amount of the **Stock solution A**, in a volumetric flask. The so prepared solution had the concentration of the test compound 0.087 mg/mL and specific activity of 406358 dpm/μL (35211866 dpm/mL). It was used to prepare the application solution for fortification of the test samples. That was done by adding 3.177 mg of the non-radiolabelled Flufenacet with 77.151 mL of the **Stock solution B**. So prepared **Application solution** had the following estimated (calculated) parameters:

- concentration 0.128 mg/mL,
- radioactivity content 34861893 dpm/mL,
- specific activity 272614 dpm/μg.

The specific activity of the solution, determined experimentally (using HPLC), was 274661 dpm/μg and its radiochemical purity was 99.9%.

The experiment was performed using the natural pond water as a test medium. The test water was collected on the 25th October 1993 from a pond near Branchton/St. George, Ontario, Canada, from a depth of 30-60 cm below the surface. The sampling water body was representative for the areas of the intended use of Flufenacet. After delivery to the test facility the test water was stored at T = 5⁰C until being used. The characteristic of the non-sterilised test water is presented below in the table B.8.2.2.2._CA-1. It was carried out shortly before the initiation of the experiment.

Table B.8.2.2.2._CA-1: The characteristic of the tes water used in the experiment.

Determined parameter		Information/Value
<i>Data on sampling</i>	Location of the sampling site	Brachton/St. George, Ontario, Canada
	Type of water body	Pond
	Type of water sample	Pelagic water
	Sampling depth [cm below the surface]	30-60
<i>Physico-chemical properties of test water</i>	pH	7.5
	Total alkalinity [mg/L as CaCO ₃]	230
	Total hardness [mg/L as CaCO ₃]	329
	Specific conductivity [μmhos/cm]	500
	Dissolved oxygen [mg/L]	9.6
	Suspended solids [mg/L]	8.5
<i>Biological properties of test water – microbial activity</i>	Microbial population expressed as Colony Forming Units in 1 mL of test water [CFU/mL]	5.9 E3

The experiment was carried out in two variants – in sterile and non-sterile conditions. In case of sterile conditions the test water samples and all glassware used in the experiment was sterilised by autoclaving. Also sterilised in the same manner was glassware used in the experiment under non-sterile conditions.

The test system used in the experiment for individual samples was a flow-through system presented below on figure B.8.2.2.2._CA-2. It consisted of the 250-mL Erlenmeyer flask fitted with glass Dreschel cap equipped with inlet and outlet port, connected to a system delivering sterilised air (inlet port) and the system of trapping vessels to collect volatile compounds formed in the system during experiment (outlet port), at the end of which was placed a vacuum pump providing a flow of air through the system, for 30 minutes on each day of the experiment at rate 1-2 bubbles/second.

Each Erlenmayer flask was filled with 150 mL of sterilised or non-sterile test water. In total 36 such test systems were prepared – 24 for non-sterile experiment (2 replicates per each sampling point) and 12 for the sterile experiment (single replicates for each sampling point).

The test systems for sterile samples were assembled and treated with the test substance under the laminar-flow hood and those for non-sterile samples in an environmental fate laboratory.

After treatment all test systems were incubated under aerobic conditions in an environmental chamber at constant temperature T = 25 ± 1⁰C and standard daily light regime of 16 hours light and 8 hours darkness

(Sylvania GTE fluorescent lights of the type recommended for plant cultivation; light intensity 7.34 W/m^2 – 7.49 W/m^2) for up to 368 days.

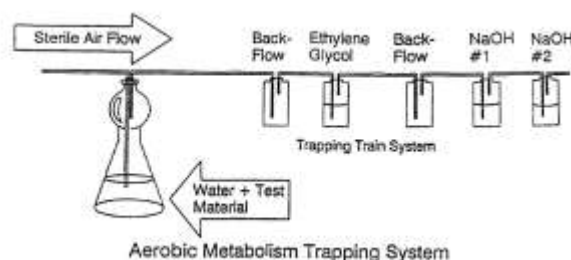


Figure B.8.2.2.2._CA-2: The test system for the individual samples used in the experiment (copied from the study report).

The test samples were treated with the test compound at application rate 1.3 mg/L , by adding 1.5 mL of the **Application solution** characterised above. That fortification rate was determined assuming the complete run-off from 1-acre field treated at application rate $1 \text{ kg Flufenacet/ha}$, soil bulk density of 1.5 g/cm^3 and the thickness of the treated soil layer of 5 cm . The **Application solution** was delivered using the gas-tight syringe below the surface of the test water in the given flask.

During the incubation period the water levels in all test vessels were constantly monitored and in non-sterile samples requiring the addition of water, that was done on day 102nd of incubation by addition of sterilised test water using 10-mL graduated pipet.

All test vessels were aerated by a daily purge, characterised above. The microbial activity of the test water was examined in non-sterile samples, by determining the size of microbial population, 7 days before the initiation of the experiment, on Day 0, day 278 and Day 368 (terminal) of the experiment. In case of the sterilised samples that was done on 7th day before the initiation of the experiment and on Days 278 and 368 of the incubation.

The non-sterile and sterilised samples were collected for the analysis on DAT (Days After Treatment with the test compound) 0, 4, 7, 15, 29, 60, 95, 188, 278 and 368. At these sampling points duplicate non-sterile samples and single sterilised samples were collected for analysis. The test systems collected for analysis were aerated for 30 minutes before being removed from the incubation chamber. Next each collected flask was gently swirled and, from pre-designated samples, $\sim 6\text{-mL}$ aliquot of the test water were taken for the analysis of microbial activity. The remaining sample was transferred to graduated cylinder and its volume recorded. Then three 1-mL aliquots were taken for LSC analysis, after mixing each of them with 15 mL of the scintillation cocktail, and 2-mL or 4-mL aliquots transferred to amber vials for radio-HPLC analysis. The remaining sample was stored in the freezer in Nalgene bottles.

At these sampling intervals the traps for volatile compounds – ethylene glycol- traps NaOH-traps, in all samples were replaced with fresh ones. Additional sampling of the traps for volatiles took place on DATs 153, 215, 243, 312 and 337.

The volumes of ethyl glycole and NaOH_{aq} from collected traps were recorded and duplicate 1-mL aliquots of each solution analysed, after mixing with 15 mL of the scintillation cocktail, by LSC.

Also, when it was necessary, the backflow traps were analysed for the radioactivity content.

The LSC analysis of all samples was performed using Beckman LS 1801 TD LS Counter or Packard 1600CA LS Counter. The maximum counting time was 5 minutes or until 2σ error of 5% was attained. The LOD was in range $30 - 60 \text{ cpm}$.

The chromatographic analysis was aimed at:

- the determination of the radiopurity and specific activity of the **Stock** and **Application** Solutions;
- the profiling of Flufenacet and its degradation products in collected samples (identification and quantitation);
- confirmatory analysis for the identification of degradation products of Flufenacet – FOE Alcohol, FOE Oxalate and FOE Sulfonic acid.

The determination of radiopurity and specific activity of the **Stock** and **Application** solutions was performed by means of HPLC analysis. It was carried out on Waters HPLC system, coupled with Beckman Model 171 radioactivity detector, equipped with Hamilton PRP-1 $250 \text{ mm} \times 4.1 \text{ mm}$, $10 \mu\text{m}$, chromatographic column working in the gradient mode.

The mobile phase consisted of: 0.4% CH₃COOH in HPLC-grade water as **Solvent A** and 0.4% CH₃COOH in CH₃CN as **Solvent B**. The flow rate of the mobile phase was 2.0 mL/minute and the gradient mode is presented below in the table B.8.2.2.2._CA-2. The elution lasted for 90 minutes.

Table B.8.2.2.2._CA-2: The gradient mode used in the analysis.

Elution time [min]	Composition of the mobile phase	
	% Solvent A	% Solvent B
0	100	0
15	70	30
65	40	60
70	0	100
80	0	100
81	100	0
90	100	0

The chromatographic profiling of Flufenacet and its degradation products in test water samples was performed by means of HPLC analysis, using Shimadzu SLC-6A HPLC system coupled with Raytest Ramona 90 radioactivity detector, equipped with Alltech Econsoil C18 250 mm • 4.6 mm chromatographic column working in the gradient mode.

The mobile phase consisted of: 0.1% CH₃COOH in HPLC-grade water as **Solvent A** and CH₃CN as **Solvent B**. The flow rate of the mobile phase was 1.0 mL/minute and the gradient mode is presented below in the table B.8.2.2.2._CA-3. The elution lasted for 45 minutes.

Table B.8.2.2.2._CA-3: The gradient mode used in the analysis.

Elution time [min]	Composition of the mobile phase	
	% Solvent A	% Solvent B
0	100	0
40	0	100
45	0	100

The identification was carried out by means of the comparison of the retention times of detected fractions with those of the known standards and the quantitative analysis by means of calibration curve.

The confirmatory analysis of the identity of the degradation compounds was performed in DAT-278 non-sterile samples and DAT-368 non-sterile samples.

The DAT-278 non-sterile samples were used to carry out the confirmatory analysis for FOE Alcohol and FOE Oxalate. The analysis was performed using GC-MS method. In case of FOE Alcohol the analysis was performed directly, without derivatisation, while FOE Oxalate was analysed after derivatisation as the methyl-ester.

The chromatographic analysis was performed on HP 5890 series II gas chromatograph coupled with HP 5970 MS detector. The GC column used in the analysis was Restec Rtx-1 GC column, 30-m long with 0.25 mm internal diameter and 0.5 df. The carrier gas was helium and the oven programme was following: start at T = 100°C, hold at that level for next 4 minutes then increase at rate 5°C/min up to T = 260°C and hold at that level for next 4 minutes. The ionisation mode was EI (electron impact) at 70 eV. The solvent delay was in case of Flufenacet 4 minutes, for FOE Alcohol – 10 minutes and for FOE Oxalate methyl ester – 14 minutes.

The confirmatory analysis for FOE Sulfonic acid was carried out in DAT-368 non-sterile samples using LC-TSP/MS method.

The chromatographic analysis was performed in a linear gradient mode on Varian HPLC system, coupled with Finnigan MAT 90 MS detector, equipped with Novapack C-18 150 mm • 3.9 mm, 5 µm, chromatographic column. The flow rate of the mobile phase was 0.8 mL/min. The gradient mode was defined as “5% methanol to 100% methanol in 20 minutes”. It was also indicated that the buffer solution – 0.1M CH₃COONH₄ in water was added “post column at a rate 0.5 mL/min.

The examination of the microbial activity in test water samples was carried out in the following way: each 6.0-mL sample of water vortexed twice: before diluting and after diluting, before placing on the plates. Next, serial dilutions 1:10 in 9.0 mL of the sterile water were performed. 0.1-mL aliquots of diluted water samples were placed in triplicate sterile 100 • 15 mm Petri plates and nutrient agar was poured. Then, when agar

solidified, plates were placed in the incubator set at $T = 35 - 37^{\circ}\text{C}$ and incubated there for 48 hours. The number of colony forming units per mL (cfu/mL) was determined by counting the visible colonies on each plate and dividing by dilution factor.

Finally, the obtained results – concentration of Flufenacet in solution in function of time, were kinetically examined using the linear regression method.

Results and their discussion:

The temperature in the incubation chamber during the experiment ranged from $T = 15.8^{\circ}\text{C}$ to $T = 28.8^{\circ}\text{C}$, with mean minimum $T = 23.1^{\circ}\text{C}$ and mean maximum $T = 24.4^{\circ}\text{C}$. In the study report it was indicated that that range was outside the protocol specification of $T = 25 \pm 1^{\circ}\text{C}$, but the deviation was not considered to have had an impact on the kinetics of the degradation of Flufenacet in water. The mean incubation temperature, estimated by the RMS, was $T = 23.75^{\circ}\text{C}$.

The intensity of light in the incubation chamber was determined to be 7.34 W/m^2 on the top shelf and 7.49 W/m^2 on the bottom shelf. The graphical results of the determination of that parameter are presented below on figure B.8.2.2.2._CA-3.

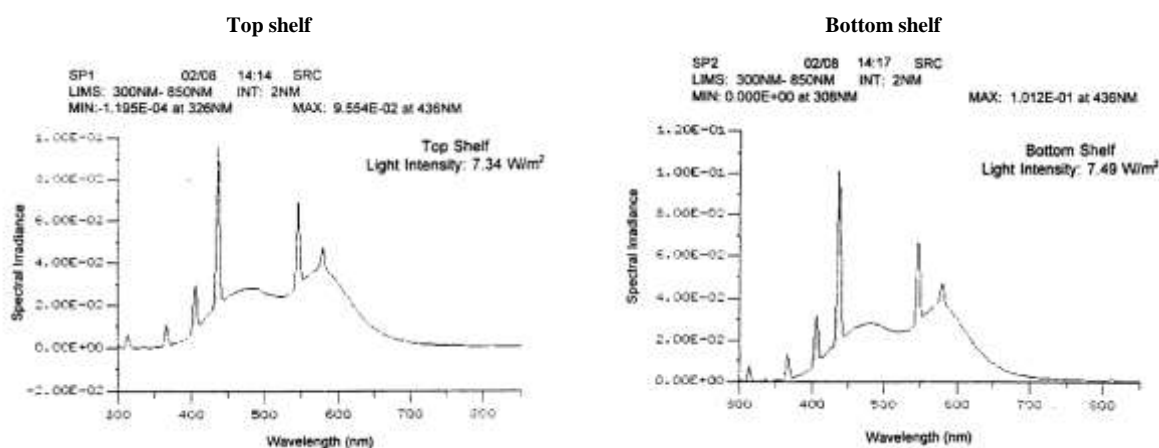


Figure B.8.2.2.2._CA-3: The results of the determination of the light intensity in the incubation chamber (copied from the study report).

The results of the examination of the biological viability of the non-sterile and sterilised pond water used in the experiment are presented below in the table B.8.2.2.2._CA-4. On their basis it may be stated that the non-sterile water retained its biological viability throughout the whole study period. The sterility of the sterilised water was compromised, what indicate the results obtained for DAT-278 sample of the test water, but it is not possible to determine when that occurred. However, according to the Applicant the results of the determination of radioactivity in the sterile samples may indicate that the lack of sterility detected in sterilised samples at the later time points had no significant impact on the results of the study (the degradation of Flufenacet in sterilised samples started to be observed on DAT 188, long after it was recorded for the first time in non-sterile samples – DAT 60).

Table B.8.2.2.2._CA-4: The results of the determination of the biological activity in the test medium – pond water, during the experiment.

Sampling time point (DAT = Days After Treatment)	Microbial viability of the test medium – pond water, determined in Colony Forming Units/mL [CFU/mL], of:		
	Non-sterilised test water		Sterilised test water
	Replicate 1	Replicate 2	
7 days before the test initiation	5.9 E3	----	0
DAT 7	3.0 E5	----	----
DAT 278	3.0 E3	3.0 E3	3.3 E2
DAT 368	1.7 E3	3.8 E2	2.0 E2

The results of the examination of the distribution and profiling of radioactivity in the non-sterilised samples are presented below in the table B.8.2.2.2._CA-5. In the next table – B.8.2.2.2._CA-6, are presented the results of the distribution and profiling of radioactivity obtained for the sterilised samples

Table B.8.2.2.2._CA-5: The results of the determination and profiling of radioactivity in the non-sterile samples collected during the experiment.

Parameter		Results – [% Applied dose] determined for the sampling time point – DAT (Days After Treatment)										
Radioactivity in:		Repli- cate	0	4	7	15	29	60	95	188 ¹⁾	278	368
<i>Water; Total recovered</i>		1	100.0	107.2	108.3	104.0	105.0	109.1	96.5	78.4	100.5	97.6
		2	99.7	109.6	107.3	106.9	102.4	106.0	105.7	96.9	99.7	97.9
		mean	99.8	108.4	107.8	105.4	103.7	107.6	101.1	87.7	100.1	97.8
<i>Water, identified as:</i>	Flufenacet	1	100.0	106.6	107.5	103.5	105.0	104.0	88.0	60.2	77.0	57.2
		2	99.7	108.5	107.3	106.9	102.4	100.4	97.3	87.0	71.4	57.5
		mean	99.8	107.5	107.4	105.2	103.7	102.2	92.6	73.6	74.2	57.4
	FOE Oxalate	1	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	1.4	3.9	4.1	15.7	22.2
		2	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	2.7	5.9	7.8	11.9	25.7
		mean	n. d.⁴⁾	n. d.⁴⁾	n. d.⁴⁾	n. d.⁴⁾	n. d.⁴⁾	2.1	4.9	5.9	13.8	24.0
	FOE Alcohol	1	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	2.7	4.6	3.9	3.1	4.4
		2	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	2.9	2.5	1.5	3.9	4.5
		mean	n. d.⁴⁾	n. d.⁴⁾	n. d.⁴⁾	n. d.⁴⁾	n. d.⁴⁾	2.8	3.6	2.7	3.5	4.4
	FOE Sulfonic acid	1	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	3.6	9.1
		2	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	9.4	8.0
		mean	n. d.⁴⁾	n. d.⁴⁾	n. d.⁴⁾	n. d.⁴⁾	n. d.⁴⁾	n. d.⁴⁾	n. d.⁴⁾	n. d.⁴⁾	6.5	8.6
	Unknown ¹ 2)	1	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	1.4	n. d. ⁴⁾
		2	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	1.0	n. d. ⁴⁾
		mean	n. d.⁴⁾	n. d.⁴⁾	n. d.⁴⁾	n. d.⁴⁾	n. d.⁴⁾	n. d.⁴⁾	n. d.⁴⁾	n. d.⁴⁾	1.2	n. d.⁴⁾
	Unknown ² 3)	1	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
		2	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾	n. d. ⁴⁾
		mean	n. d.⁴⁾	n. d.⁴⁾	n. d.⁴⁾	n. d.⁴⁾	n. d.⁴⁾	n. d.⁴⁾	n. d.⁴⁾	n. d.⁴⁾	n. d.⁴⁾	n. d.⁴⁾
	Total	1	100.0	106.6	107.5	103.5	105.0	108.2	96.5	68.1	100.7	92.8
		2	99.7	108.5	107.3	106.9	102.4	106.0	105.7	96.3	97.5	95.8
		mean	99.8	107.5	107.4	105.2	103.7	107.1	101.1	---- ⁶⁾	99.1	94.3
<i>Volatile compounds fraction in:</i>	Ethylene glycol trap	1	n. a. ⁵⁾	0.0	0.0	0.0	0.0	0.0	0.1	0.3	0.1	0.4
		2	n. a. ⁵⁾	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.1	0.2
		mean	n. a.⁵⁾	0.0	0.0	0.0	0.0	0.0	0.1	0.2	0.1	0.3
	NaOH trap	1	n. a. ⁵⁾	0.0	0.0	0.0	0.0	0.2	0.2	0.7	1.7	2.8
		2	n. a. ⁵⁾	0.0	0.0	0.0	0.0	0.2	0.3	1.0	1.5	3.1
		mean	n. a.⁵⁾	0.0	0.0	0.0	0.0	0.2	0.3	0.9	1.6	3.0
<i>Total radioactivity recovered</i>		1	100.0	107.2	108.3	104.0	105.1	109.3	96.8	79.4	102.2	100.9
		2	99.7	109.6	107.3	106.9	102.4	106.2	106.0	98.0	101.3	101.1
		mean	99.8	108.4	107.8	105.5	103.7	107.8	107.8	88.7	101.7	101.0

Footnotes to the table:

- 1) For that time point the results obtained for the *Replicate 1* are reported but not further used being considered as non-representative ones due to the inadvertent sample loss during aeration;
- 2) The fraction detected at $R_t = 5.3$ minutes in HPLC analysis;
- 3) The fraction detected at $R_t = 13.9$ minutes in HPLC analysis;
- 4) n. d. =not detected;
- 5) n. a. = not analysed – the traps for volatile compounds were not set for these samples;
- 6) The mean value was not calculated.

Table B.8.2.2.2._CA-6: The results of the determination and profiling of radioactivity in the sterile samples collected during the experiment.

Radioactivity in:		Results – [% Applied dose] determined for the sampling time point – DAT (Days After Treatment)									
		0	4	7	15	29	60	95	188	278	368
Water; Total recovered		98.9	106.0	108.2	103.2	105.2	107.2	101.9	104.3	101.6	102.0
Water, identified as:	Flufenacet	98.9	105.3	107.3	103.2	105.2	107.2	101.9	99.8	95.5	93.1
	FOE Oxalate	n. d. ³⁾	n. d. ³⁾	n. d. ³⁾	n. d. ³⁾	n. d. ³⁾	n. d. ³⁾	n. d. ³⁾	n. d. ³⁾	n. d. ³⁾	n. d. ³⁾
	FOE Alcohol	n. d. ³⁾	n. d. ³⁾	n. d. ³⁾	n. d. ³⁾	n. d. ³⁾	n. d. ³⁾	n. d. ³⁾	4.5	4.8	6.8
	FOE Sulfonic acid	n. d. ³⁾	n. d. ³⁾	n. d. ³⁾	n. d. ³⁾	n. d. ³⁾	n. d. ³⁾	n. d. ³⁾	n. d. ³⁾	n. d. ³⁾	n. d. ³⁾
	Unknown 1 ¹⁾	n. d. ³⁾	n. d. ³⁾	n. d. ³⁾	n. d. ³⁾	n. d. ³⁾	n. d. ³⁾	n. d. ³⁾	n. d. ³⁾	n. d. ³⁾	n. d. ³⁾
	Unknown 2 ²⁾	n. d. ³⁾	n. d. ³⁾	n. d. ³⁾	n. d. ³⁾	n. d. ³⁾	n. d. ³⁾	n. d. ³⁾	n. d. ³⁾	n. d. ³⁾	1.3
	Total	98.9	105.3	107.3	103.2	105.2	107.2	101.9	104.3	100.2	101.2
Volatile compounds fraction in:	Ethylene glycol trap	n. a. ⁴⁾	0.0	0.0	0.0	0.0	0.0	0.6	0.0	0.1	0.0
	NaOH trap	n. a. ⁴⁾	0.0	0.0	0.0	0.0	0.1	0.2	0.6	0.8	0.8
Total radioactivity recovered		98.9	106.0	108.2	103.2	105.2	107.3	102.2	105.0	102.5	102.8

Footnotes to the table:

- 1) The fraction detected at $R_t = 5.3$ minutes in HPLC analysis;
- 2) The fraction detected at $R_t = 13.9$ minutes in HPLC analysis;
- 3) n. d. = not detected;
- 4) n. a. = not analysed – the traps for volatile compounds were not set for these samples.

The results obtained for Flufenacet in the non-sterile samples (mean values) and sterilised ones were subsequently subjected to the kinetic analysis after being logarithmically transformed (ln was calculated). The kinetic analysis presented in the study report was not accepted by the RMS, and therefore not presented in the summary, as it was carried out using the linear regression. The Applicant repeated the kinetic analysis of the results using the approach recommended by FOCUS. The results of that analysis, presented in the separate study, are summarised as **Study 3**.

Analysing the obtained results the Applicant stated that the degradation of Flufenacet was predominantly biologically-mediated, while the abiotic processes, such as hydrolysis or photolysis, played only a minor role.

The level of mineralisation, determined on the basis of the amount of the radioactivity in the traps for volatile compounds, and that containing aqueous solution of sodium hydroxide in particular, was very low, not surpassing 3% in biologically viable samples. That may indicate that Flufenacet should be classified as not readily biodegradable.

Analysing the results the Applicant indicated that the degradation of Flufenacet in water was retarded – during initial 60 days no degradation was observed. The reasons however of that 60-days lag phase were not explained.

In non-sterile samples three degradation products were identified: FOE Alcohol (in amounts up to 4.4% of applied parent), FOE Oxalate (up to 24% of the applied parent) and FOE Sulfonic acid (up to 8.6% of the applied parent compound). It shall be indicated that while FOE Oxalate and FOE Alcohol were both observed since the estimated beginning of the process of degradation of Flufenacet (DAT 60), FOE Sulfonic acid was formed much later. The amounts of all three degradation products were increasing at the end of the experiment, what may indicate that all three degradates should be considered as potentially major transformation products of Flufenacet in natural water.

The Applicant stated that despite the low level of mineralisation it may be stated that Flufenacet in water will undergo the degradation, predominantly biologically mediated, although that process will be slow.

On the basis of the obtained results the transformation pathway of Flufenacet in natural water was postulated, which is presented below on figure B.8.2.2.2._CA-4. It should be indicated however that it fully covers only the part of the molecule containing fluorophenyl moiety, while the subsequent transformation of the part of the molecule containing thiadiazole moiety was not further examined.

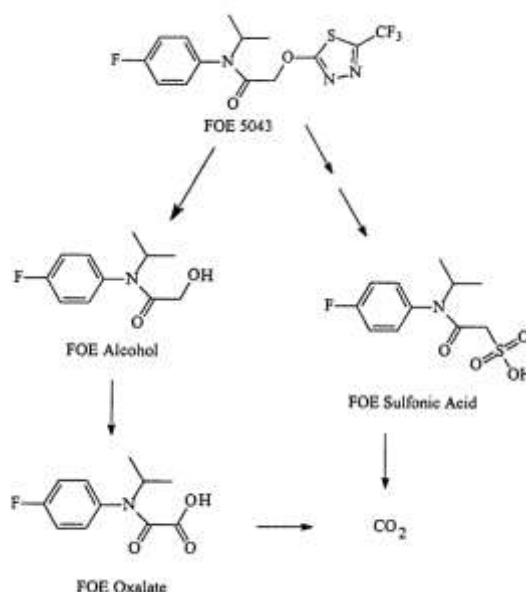


Figure B.8.2.2.2_CA-4: The proposed transformation pathway of Flufenacet, radiolabelled in fluorophenyl ring, in natural water (copied from the study report).

Conclusions:

The degradation of Flufenacet in natural water was examined using the test compound radiolabelled in fluorophenyl ring and non-sterilised pond water as the test medium. It was demonstrated that Flufenacet in natural water would undergo degradation, although that process would be slow. The postulated transformation pathway may indicate that the mechanism of the break-down of the molecule would be similar to that determined for Flufenacet in aerobic soil. The comparison of the results obtained in non-sterilised and sterilised samples demonstrated that the process of degradation of Flufenacet in water will be predominantly biologically-mediated. The identified degradation products – FOE Alcohol, FOE Oxalate and FOE Sulfonic acid, were specific for the radiolabelling position assumed in this study. It shall be indicated that no new degradation products for that specific radiolabelling position, other than those detected in aerobic soil, were identified, what clearly indicates that the transformation pathway of Flufenacet within the moiety containing fluorophenyl ring would be very similar to that determined in soil.

The process of degradation was demonstrated to be very slow, with the lag phase, what may indicate that in natural water bodies the degradation of Flufenacet in water phase may play only a secondary role in comparison to other dissipation processes, such as migration to the sediment.

The low level of mineralisation indicated that Flufenacet cannot be considered as readily biodegradable.

RMS is of the opinion that the study provides the relevant information in the area of the persistence of Flufenacet in water and its ready biodegradability. However it does not provide full information with regard to the transformation pathways in that compartment, as there is no information on the fate of the thiadiazole moiety.

Study 2:

Report: Hein E. – M., (2013): “Evaluation of the Study: [*Phenyl-U-¹⁴C*] FOE 5043 – Determination of Aerobic Aquatic Biotransformation at 25⁰C.”; Bayer CropScience AG, Environmental Fate, BCS AG – R&D-D-EnSa-Efate, Alfred-Nobel-Str. 50, D-40789 Monheim, Germany; unpublished report No. EnSa-13-0268; 03. 04. 2013; study reference number M-450131-01-1;

Guidelines: None declared, the study however examined the compliance of another study with the provisions of the following OECD Guideline:

- OECD Guideline for the Testing of Chemicals No. 309: “Aerobic Mineralisation in Surface Water – Simulation Biodegradation Test.”, adopted 13 April.

GLP: No, not required, the study is a position paper;

RMS comments: This is a new study, submitted in support of the study by [Schocken, Yen and Widmer; 1995] (study reference number M-002210-01-1) that examined the biological transformation of Flufenacet in natural water. It has a form of position paper presenting the compliance, in tabularised form, of the key features of the evaluated study with the provisions of the OECD Guideline 309. RMS examined that evaluation and found it acceptable. Therefore the study is summarised below, in format proposed by the Applicant, with comments to the assessment given by the RMS.

Summary:

The aim of the study was to evaluate the essential experimental facts of the study “[*Phenyl-U-¹⁴C*]FOE 5043 – Determination of Aerobic Biotransformation at 25⁰C.” by [Schocken, Yen and Widmer; 1995] against the requirements set by the OECD Test Guideline 309 “Aerobic Mineralisation in Surface Water – Simulation Biodegradation Test”. The results of the evaluation were presented in form of a table containing test parameter, requirement set by the OECD Guideline 309, solution in the study and evaluation by the Applicant. That table is reproduced below as the Table B.8.2.2.2._CA-6. RMS added one additional column containing RMS’s own remarks and assessment of the evaluated issue.

Table B.8.2.2.2._CA-6: The results of the evaluation of the study M-002210-01-1 for its compliance with the provisions of the OECD Guideline 309.

Test feature	Requirement of the OECD 309 Guideline	In the evaluated study	Evaluation by the Applicant	RMS's comments and evaluation
<i>Test Design</i>	Pelagic or Suspended Sediment	Pelagic	OK	Checked, conformed
<i>Lighting Conditions</i>	Dark (preferred) or diffuse light	16h light + 8h dark	The used lighting conditions are considered acceptable by BCS	RMS carried out the comparative analysis of the evaluated study with that examining the direct and indirect photolysis of Flufenacet. It was demonstrated that Flufenacet was not prone to direct photolysis in water, while indirect photolysis in natural pond water may play some role in the degradation of that compound in SW bodies. It was stated that the water used in the experiment bore similar characteristic to that from Stilwell pond used to examine the indirect aqueous photolysis. Additionally the intensity of light in the assessed experiment was much lower 7.34 -749 W/m ² v/s 680 W/m ² in the experiment examining the aqueous photolysis of Flufenacet. In the Stilwell pond water the rate of indirect photolysis was estimated to be DT ₅₀ = 822 Natural Sunlight Days. Therefore, on the basis of the similarity of the experimental solutions and intensity of light, RMS stated that light conditions will have a minimal influence on the overall rate of degradation of Flufenacet in that experiment, hence the justification provided by the Applicant may be considered valid.
<i>Temperature</i>	20-25°C (Keep constant at ± 2°C)	25 ± 1°C	OK	Checked, in the study report it was stated that the temperature during the experiment was in range 15.8 – 28.8°C (extremes) with averages in range 23.1 – 24.4°C. The mean incubation temperature, estimated by the RMS was T = 23.75°C.

Test feature	Requirement of the OECD 309 Guideline	In the evaluated study	Evaluation by the Applicant	RMS's comments and evaluation
<i>Study duration</i>	max. 60 days (up to max. 90 days, if degradation of test item starts within first 60 days)	1 year (368 days)	6 sampling intervals were taken within a period of 60 days and 7 sampling intervals were taken within a period of 95 days (degradation of test item starts between DAT-29 and DAT-60). Remark: Re-evaluation of the first study period possible, if required.	The study lasted for 1 year, significantly longer than recommended by the Guideline. RMS however noted that the analysis of the biological viability of the non-sterile samples, performed 7 days before the beginning of the experiment, on DAT 7, DAT 278 and DAT 368 confirmed its biological viability
<i>Sampling intervals</i>	Not stated	DAT-0, DAT-4, DAT-7, DAT-15, DAT-29, DAT-60, DAT-95, DAT-188, DAT-278, DAT-368		Number of sampling points and sampling intervals confirmed.
<i>Test item concentration</i>	Two different concentrations which represent the expected range in the environment (differ by factor of 5 to 10) e.g. 10 µg/L to 100 µg/L e.g. 1 µg/L to 10 µg/L	One concentration 1.3 mg/L	The used test item concentration is considered acceptable by BCS as it covers the following worst case scenario: - use of max. field application rate of 1 kg/ha - complete run-off - soil depth 5 cm, bulk density 1.5 g/cm ³ The prolonged study duration of 368 days combined with a higher test concentration enables to propose a valid degradation pathway of the test item and reflects also a worst case scenario referred to the kinetic behaviour of the test item under the tested conditions (DT ₅₀ values).	The concentration of the test item was an order of magnitude higher than that recommended by the Guideline. However, that enabled the identification and quantitation of the degradation products. Therefore RMS is of the opinion that that deviation should not have an impact on the validity and acceptability of the study. Also the justification provided by the Applicant is acceptable.
<i>Test system</i>	Flow through or static system	Flow-through system	OK	Checked, confirmed
<i>Traps for Volatiles</i>	Direct or indirect determination of carbon dioxide	Direct determination of volatiles using ethylene glycol (1x) and sodium hydroxide traps (2x)	OK	Checked, confirmed
<i>No of replicates</i>	Duplicate samples	Duplicate samples	OK	Checked, confirmed; RMS noticed that the only non-sterile samples were collected as duplicate samples per sampling point, while sterile samples were collected in single replicates per sampling point.
<i>Aeration</i>	By continuous stirring or shaking	By daily purge	The used method is considered acceptable for aeration of the test system.	Checked, confirmed – the system was aerated every day for 30 minutes with sterilised moist air
<i>Agitation</i>	By continuous stirring or shaking	By daily purge	Test systems were agitated by daily purge. However, this point is not assumed to have an impact on the validity of the study.	Checked, confirmed – the purging method caused agitation of the solution in the test vessels.

Test feature	Requirement of the OECD 309 Guideline	In the evaluated study	Evaluation by the Applicant	RMS's comments and evaluation
<i>Kinetics</i>	SFO	SFO	OK	Kinetic analysis of the results, in line of the provisions of the FOCUS Kinetics Guideline, in a separate report.
<i>Sterile samples</i>	Yes (autoclaving, HgCl ₂ or γ -irradiation)	Yes (autoclaving)	OK	Checked, confirmed; the initial sterility of test system confirmed, but the sterility during the experiment, in particular at later time points seems to be compromised; that deviation however does not seem to have an impact on the acceptability of the study.
<i>Reference substance</i>	Yes (aniline or sodium benzoate)	No	Microbial activity of the system was proven by plate count assay and by degradation of the test item (including total degradation/mineralization to carbon dioxide).	The design of the test system resulted in not meeting that requirement. RMS is of the opinion that that deviation from the OECD Guideline does not invalidate the study.
<i>Measurement of pH and O₂ concentration</i>	Yes	No	This point is not assumed to have an impact on the validity of the study.	Justification of that deviation provided by the Applicant is acceptable.
<i>Establish Material Balance</i>	Yes	Yes Non-sterile samples: 96.8 to 109.6% AR (mean 103.8% AR) Sterile samples 98.9 to 108.2% AR (mean 104.1% AR)	OK	Checked, confirmed
<i>Degradation Product Identification Trigger</i>	2 x >5% AR, 1 X >10% AR or >5% AR increasing at study end	2 x >5% AR, 1 X >10% AR or >5% AR increasing at study end	OK	Checked, confirmed

The Applicant, on the basis of the results of evaluation presented above stated that: “Bayer CropScience is of the opinion that the study “[Phenyl-U-¹⁴C]FOE 5043 – Determination of Aerobic Aquatic Transformation at 25⁰C” conducted according to the Canadian guideline T-1-255, is suitable to address the fate of Flufenacet in open water as required according to regulation (EC) No. 1107/2009, as the applied test conditions cover a worst case scenario.

RMS confirms the validity of that conclusion.

Study 3:

Report: Reinken G., Maassen K., (2014): “Kinetic Evaluation for Calculating Refined Half-life Times of [Phenyl-UL-¹⁴C]Flufenacet in Natural Pond-water According to FOCUS Kineitscs Using the KinGUI 2 Tool.”; Bayer CropScience AG, Environmental Safety, Alfred-Nobel-Strasse 50, 40789 Monheim, Germany; Study report No. En-Sa-13-0970; 18. 02. 2014; study reference number: M-478212-01-1.

Guidelines: The study was performed to comply with the following Guidelines:

- FOCUS (2006): “Guidance Document on Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration.”; Report of the Work Group on Degradation Kinetics, EC Document Reference SANCO/10058/2005, version 2.0, 434 pp.;
- FOCUS (2011): “Generic Guidance for Estimating Persistence and Degradation Kinetics from Environmental Fate Studies in EU Registration, version 1.0, 436 pp.

GLP: No, not required – modelling study;

RMS comments: This is a newly submitted study, evaluated for the purpose of the current assessment. RMS evaluated it for its compliance with the Guidelines listed as the reference Guidelines. That evaluation showed that the Applicant reduced the data base for which the assessment was performed by eliminating the time points after DAT 95. That was explained by the necessity to comply with the provisions of the OECD 309 Guideline, recommending that the study should not last longer than 60 days unless no degradation was observed within that period, and in such case it can be extended to 90 days. It shall be indicated that in the source study it was stated that the degradation of Flufenacet in non-sterilised water was delayed by at least 29 days after application of the test compound and the first time point at which the degradation of Flufenacet, demonstrating itself as the formation of the degradation products, was observed was DAT 60. That may indicate the lag-phase with the break-point occurring somewhere between DAT-29 and DAT-60 time points, the fact that was not taken into account by the Applicant in the performed kinetic analysis. It shall be pointed out that if the lag-phase indeed occurred the number of the data points for which the degradation of Flufenacet was observed, used by the Applicant in the kinetic analysis, was only two, a number too small to return the reliable kinetic endpoints.

It is also worth of noticing that the amounts of radioactivity recovered during the experiment in the non-sterilised samples were generally above 100% of the amount theoretically applied. These levels were in general within the acceptable range of 90 - 110%, therefore not having the influence on the validity of the study. However in terms of the kinetic analysis at early time points the recoveries of radioactivity >100% TAR, which was in addition identified as solely Flufenacet, caused some problems with fitting, in particular because the concentrations of that compound at the time points between DAT 0 and DAT 60 were higher than those recorded on DAT 0.

All that was not taken into account by the Applicant in the kinetic analysis.

Finally, it shall be indicated that in the study report only the results obtained for the non-sterilised samples, while for the sterile ones no such analysis was performed (which would be useful to demonstrate that in natural biologically viable water the degradation of that compound is indeed due to biologically-mediated transformation and abiotic processes play only minimal role.

As a result, RMS decided to repeat the kinetic analysis using for the non-sterile samples the whole data set and assuming that either lag phase occurred or such phenomenon was not observed. In parallel the data obtained for the sterilised samples were kinetically analysed using the same approach.

RMS decided, for comparative purpose, to present the kinetic analysis performed by the Applicant. It shall be indicated however that these results will not be further used in the assessment.

Summary:

The aim of the study was to kinetically examine the results obtained for Flufenacet in the study by [Schocken, Yen and Widmer; 1995], aimed on the examination of aerobic transformation of that compound in natural pelagic water. The kinetic analysis followed the procedure outlined in the FOCUS Kinetics Guidance Document

[FOCUS; 2006], [FOCUS; 2011]. As the initial step the data presented in the experimental data presented in the source study were pre-processed according to the recommendations of the FOCUS Kinetics Work Group. In particular:

- the DAT-0 values were included as provided in the study report, but for optimal goodness of fit they were allowed to be estimated by the model;
- values between LOD and LOQ were set to measured values (**N. b.:** RMS noticed that such values for Flufenacet did not appear in the study);
- values <LOD or the “non-detects” were processed in line with FOCUS recommendations (**N. b.:** once again RMS did not identify such values for Flufenacet in the analysed data set);
- to maintain the consistency with the provisions of the OCED test guideline No. 309 all values obtained after the time point DAT-95 were not used in the analysis.

The resulting data set used as input for the kinetic analysis is presented below in the table B.8.2.2.2._CA-7.

Table B.8.2.2.2._CA-7: The data set used in the kinetic analysis of the degradation of Flufenacet in the non-sterilised natural pelagic (pond) water.

Sampling time-point [Days After Treatment]		DAT						
		0	4	7	15	29	60	95
Concentration of Flufenacet [%TAR]	Replicate 1	100.0	106.6	107.5	103.5	105.0	104.0	88.0
	Replicate 2	99.7	108.5	107.3	106.9	102.4	100.4	97.3

The kinetic analysis was carried out using the single compartment approach (PI). The Applicant used two kinetic models – SFO and FOMC. The modelling tool used in the assessment was KinGUI version 2 software. The optimisation algorithm was IRLS (Iteratively Reweighed Nonlinear Least Squares).

The assessment of the acceptability of the kinetic analysis was based on:

- the assessment of the goodness of fit;
- the assessment of the reliability of the kinetic parameters.

The assessment of the goodness of fit was based on the results of the χ^2 -significance test and the visual assessment of the decline curve – conformity of the determined curve with the measured values and the levels and distribution of the residuals.

The assessment of the reliability of the kinetic parameters was indicated to be based on the examination of their statistical significance.

The whole assessment procedure was identical to that characterised for the kinetic assessment of the data obtained in soil, presented in details in this section of the Renewal Assessment Report report under the data point B.8.1.1.2.1.1.

The results of the kinetic assessment performed by the Applicant are presented below, in numerical form in the table B.8.2.2.2._CA-8 and in graphical form on figure B.8.2.2.2._CA-5. On their basis the Applicant proposed to consider the SFO as returning the reliable kinetic fit and the kinetic endpoints – DT₅₀ and DT₉₀ values.

Table B.8.2.2.2._CA-8: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	Visual assessment ¹⁾
				Lower	Upper			
SFO	M ₀	106.1	5.395	95.52	116.67	8.5 E-11	2.37	Good fit; R ² = 0.502
	k	0.001121	4.994 E-4	1.424 E-4	0.002	0.0222		
FOMC	M ₀	106.76	1.21	104.39	109.10	<2 E-16	2.63	Bad fit
	α	68.09	320.56	-560.18	696.40	0.418		
	β	50438.39	237614.71	-415277.88	516154.70	0.418		

Footnotes to the table:

1) Visual assessment of the kinetic curve as proposed by the Applicant.

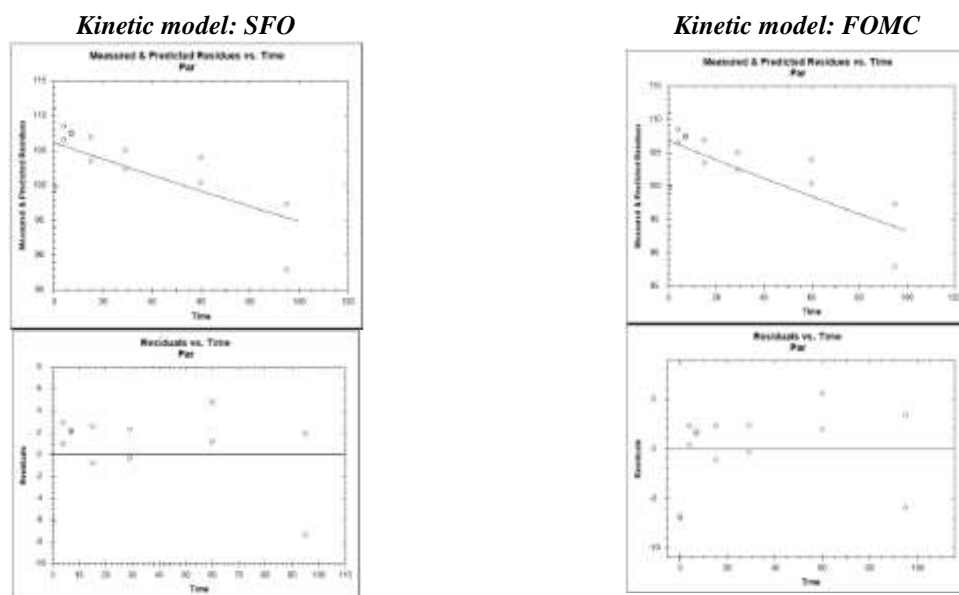


Figure B.8.2.2.2._CA-5: The graphical results of the kinetic analysis (copied from the study report).

The reliable kinetic endpoints determined in this analysis are: $k = 0.001121$ [days⁻¹], $DT_{50} = 618.25$ [days], $DT_{90} = 2053.8$ [days], kinetic model: **SFO**.

RMS however decided to repeat the kinetic analysis due to the fact that the approach adopted by the Applicant, consisting on the removal of the data obtained after the time point DAT-95, also in light of the postulated lag-phase observed in non-sterilised samples, does not seem appropriate, even though it may comply with the recommendations of the OECD test Guideline 309. The results of that analysis are presented below.

The kinetic analysis of the results of the study [Schocken, Yen and Widmer; 1995] performed by the RMS

The analysis was performed for the non-sterile and sterilised samples using the data sets presented below in the table B.8.2.2.2._CA-9. The pre-processing of the data followed the same procedure as used by the Applicant, with exception that the whole data sets generated in the study by [Schocken, Yen and Widmer; 1995] were used in the analysis.

Table B.8.2.2.2._CA-9: The data sets used in the repeated kinetic analysis performed by the RMS.

Sampling Time Point – Days After Treatment [DAT]	Concentration of Flufenacet – [% TAR ¹⁾] in:		
	Non-sterilised samples		Sterilised samples
	Replicate 1	Replicate 2	
0	100.0	99.7	98.9
4	107.5	108.5	105.3
7	103.5	107.3	107.3
15	105.0	106.9	103.2
29	104.0	102.4	105.2
60	88.0	100.4	107.2
95	---- ²⁾	97.3	101.9
188	77.0	87.0	99.8
278	71.4	71.4	95.5
368	57.2	57.5	93.1

Footnotes to the table:

- 1) TAR stands for Theoretically Applied Radioactivity;
- 2) For this sampling point in this replicate the Applicant indicated the inadvertent sample loss due to aeration, therefore, although the value was provided RMS decided not to use it in the kinetic analysis.

The values presented above were subjected to the kinetic analysis in order to determine the kinetic endpoints representing the degradation of Flufenacet in the non-sterile natural pelagic freshwater and the sterilised natural pelagic freshwater.

The kinetic analysis was performed using CAKE ver. 3.1 modelling tool, developed by Tessella. The optimisation was performed using IRLS (Iteratively Reweighed Nonlinear Least Squares) algorithm. The settings of the optimiser were the defaults of the tool:

- maximum iterations: 100,
- maximum reweighing: 10,
- SANN maximum iterations: 10000,
- convergence tolerance: 1 E-5,
- error variance tolerance: 1 E-5,
- extra solver: yes, if required.

The analysis performed for the data obtained in the non-sterilised samples was carried out in line of the procedure outlined in the FOCUS Kineitcs Guidance Document [FOCUS, 2006]. It consisted of two step. At first step the data were fitted as if no lag-phase occurred. Two kinetic models were used in that assessment – SFO and FOMC. At second step the kinetic analysis was performed with assumption that the lag-pahse, postulated in the source study report by [Schocken, Yen and Widmer; 1995] occurred. In this assessment, performed in line with the recommendations of the Guidance Document evoked above, RMS used the reversed HS model, with the k_l set to zero. The analysis was performed in two variants: with $k_l = 0.0$ not fixed but left to be optimised by the modelling tool and with $k_l = 0.0$ defined as a fixed value.

Additionally, parametrising the model, RMS assumed the $M_0 = 110.0$, what was in line with the values observed for the time points between DAT-4 and DAT-60. That value however was not defined as a fixed value, but was left to be optimised by the model. Finally, for each time point the values for individual replicates were used as the input data.

Exactly the same fitting procedure was used for the results obtained in sterilised samples. RMS decided to perform the analysis assuming the occurrence of the lag-phase, although that was not postulated for the sterilised samples in the source study report. That was done however to maintain the coherence of the performed kinetic analysis.

The results of the kinetic assessment are presented below.

1) Results of the kinetic analysis performed for the non-sterilised samples:

a) Analysis assuming no lag-phase:

The kinetic analysis was carried out using two kinetic models: SFO and FOMC – the same as used by the Applicant. RMS noticed that the concentrations of the test item – Flufenacet at the end of the experiment were well above the 10%, therefore FOMC model may not be fully appropriate. It was however used in order to verify whether other bi-phasic models should be checked in the analysis.

The results of the fitting are presented below, in the numerical form in table B.8.2.2.2._CA-10 and in the graphical form on figure B.8.2.2.2._CA-6. The kinetic endpoints obtained using each kinetic model tested are presented in the table B.8.2.2.2._CA-11.

Table B.8.2.2.2._CA-10: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	Visual assessment/ R value
				Lower	Upper			
SFO	M_0	107.2	1.352	104.9	109.6	----	3.22	Good fit; R = 0.934
	k	0.001464	1.09 E-4	0.001276	0.001653	8.12 E-11		
FOMC	M_0	108.4	1.494	105.8	111.0	----	3.40	Good fit; R = 0.934
	α	37.05	2.677	32.37	41.72	----		
	β	22500	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	----		

Footnotes to the table:

- 1) n. d. = not determined – in the report returned by the modelling tools it was stated that these values “could not be calculated because the covariance matrix could not be created”.

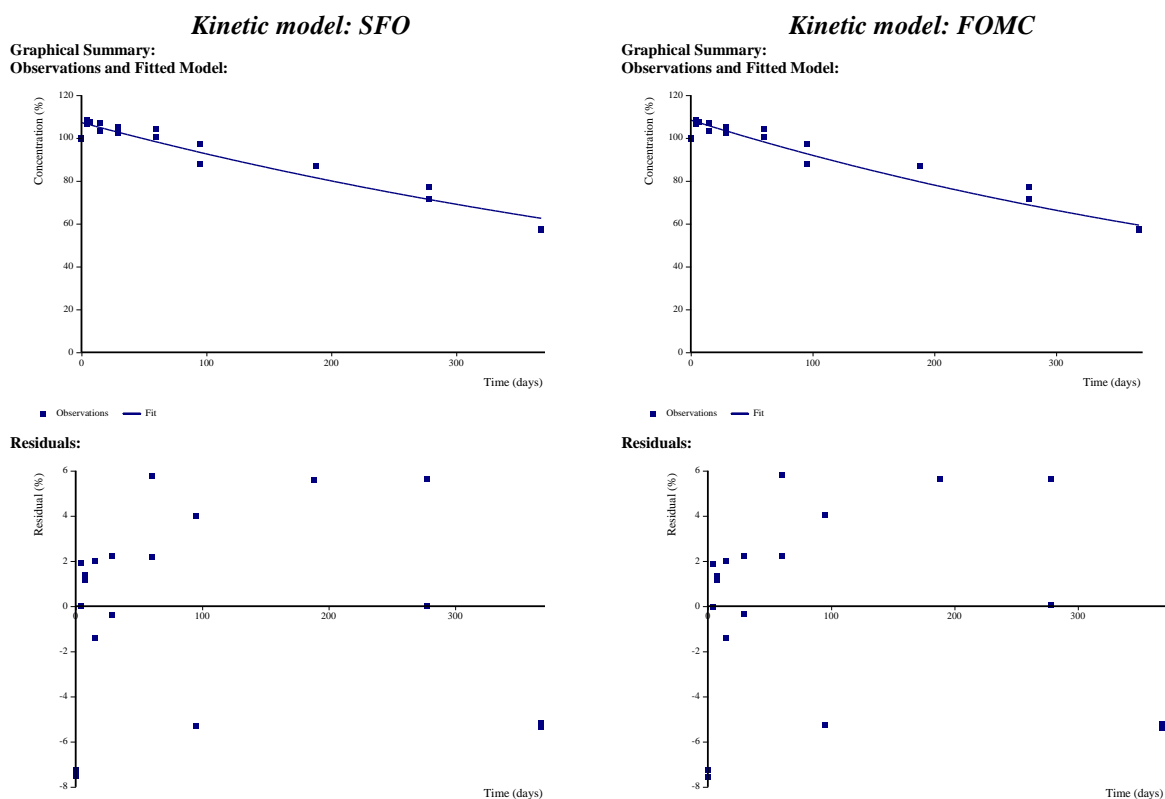


Figure B.8.2.2.2._CA-6: The graphical results of the kinetic analysis.

Table B.8.2.2.2._CA-11: The determined kinetic endpoints

Kinetic model	Determined parameters				
	Kinetic parameters		Kinetic endpoints		
			DT ₅₀ [days]	DT ₉₀ [days]	t_FOMC [days] (pseudo-SFO DT ₅₀)
<i>SFO</i>	$k = 0.001464$ [days ⁻¹]		473	1570	not applicable
<i>FOMC</i>	$\alpha = 37.05$	$\beta = 22500$	424	1440	434

Both kinetic models returned visually very similar fits. The value of χ^2 -error indicate that the SFO fit was statistically slightly better, therefore it should be selected as the first option. The analysis of the reliability of the kinetic parameters showed that while the rate constant k determined for the SFO model passed the reliability criteria, the kinetic parameters determined for FOMC model cannot be considered reliable – for β it was not possible to calculate either the error – σ , or the CI values. Finally, it shall be indicated that both models returned very similar kinetic endpoints, with DT₉₀ in FOMC being shorter than its SFO counterpart. Therefore SFO seems to be the appropriate kinetic model in this analysis.

b) Analysis assuming the occurrence of the lag-phase:

The kinetic analysis was carried in line with recommendations provided by the FOCUS Kinetics Guidance document, assuming the rate constant k_l set to 0.0. RMS decided to test two options:

- 1) with the rate constant k_l set to the value 0.0, but not fixed and left to be optimised by the modelling tool;
- 2) with k_l value fixed to the pre-defined value 0.0 and fixed, what resulted in switching off the optimisation performed by the modelling tool.

The second option was selected by the RMS because it simulated the lag-phase with no degradation of the test compound occurring, while the first option, assumed some, although minimal, level of degradation.

The results of the fitting are presented below, in the numerical form in table B.8.2.2.2._CA-12 and in the graphical form on figure B.8.2.2.2._CA-7. The kinetic endpoints obtained using each kinetic model tested are presented in the table B.8.2.2.2._CA-13.

Table B.8.2.2.2._CA-12: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	Visual assessment/ R value
				Lower	Upper			
HS, k_1 optimised	M_0	104.7	1.9	101.4	108.1	----	3.00	Good; R = 0.9494
	k_1	1.77 E-198	0.001206	-0.002114	0.002114	0.5		
	k_2	0.001654	1.51 E-4	0.00139	0.001918	7.15 E-4		
	t_b	40.81	25.78	-4.379	85.99	----		
HS, k_1 fixed	M_0	105.0	1.377	102.6	107.4	----	2.69	Good; R = 0.9511
	k_1	0.0	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾		
	k_2	0.001624	1.28 E-4	0.001401	0.001847	4.42 E-10		
	t_b	27.01	15.49	-0.02676	54.05	----		

Footnotes to the table:

1) n. d. = not determined – the k_1 value was fixed.

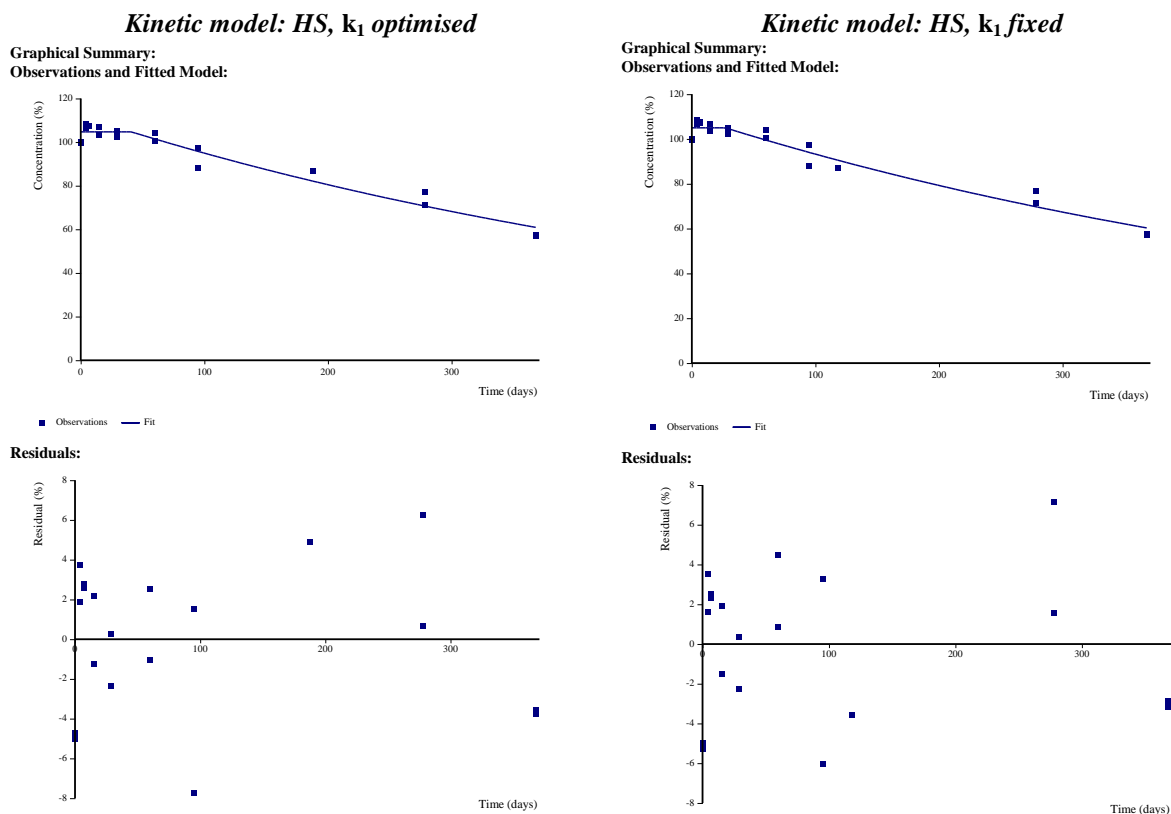


Figure B.8.2.2.2._CA-7: The graphical results of the kinetic analysis.

Table B.8.2.2.2._CA-13: The determined kinetic endpoints

Kinetic model	Determined parameters					
	Kinetic parameters		Kinetic endpoints			
	k_1 [days ⁻¹]	k_2 [days ⁻¹]	DT ₅₀ [days]	DT ₉₀ [days]	DT ₅₀ [days] for k_1	DT ₅₀ [days] for k_2
HS, k_1 optimised	1.77 E-198	0.001654	460	1430	> 10000	419
HS, k_1 fixed	----	0.001624	454	1440	> 10000	427

Both kinetic fits were visually very good and classified as good. The values of the χ^2 -error indicate that statistically slightly better fit was obtained when the k_1 value was fixed. Additionally it was noticed that the k_1

value optimised by the model lacked the reliability. As a result, the solution with fixed k_l value seems to be better fitting solution. At the same time it shall be indicated that the lack of reliability of the model-optimised k_l value may be due to the fact that it was extremely low, indicating this way virtually no degradation during the lag phase. That may indicate the appropriateness of the fixing of the k_l value in the repeated fitting.

The k_2 value was demonstrated to be reliable in both variants of the kinetic analysis.

The results of the determination of t_b value for the fit with fixed k_l value show that the lag phase was not very prolonged and it may be assumed that the degradation process was initiated already around DAT 29.

Finally, it shall be indicated that the DT_{50} values obtained for the second phase of HS kinetic curve, with both k_l value optimised by the model and fixed, are similar to those obtained for the SFO fit, without assuming the lag phase (they are even shorter). That may indicate that despite the postulated in the source study report lag phase, SFO model may be considered a good representation of the kinetic behaviour of Flufenacet in natural pelagic (pond) water.

Conclusion of the assessment:

The results of the performed analysis showed, that the degradation of Flufenacet in natural pelagic (pond) water was well described by the SFO kinetic model without assuming the lag phase. The analysis of the data assuming lag phase, performed using the reversed HS model returned the rate constant k and the kinetic parameters – DT_{50} and DT_{90} similar to those obtained using SFO model.

The average duration of the lag phase may be estimated to be around 29 days, however the longest possible value could be 40 days.

As the rate constant k and the kinetic parameters – DT_{50} and DT_{90} values obtained for the second phase of the reversed HS fit were shorter than their counterparts obtained with SFO model, it can be therefore stated that the results of the SFO fit without lag phase are the good representation of the degradation kinetics of Flufenacet in natural pelagic (pond) water. RMS proposes therefore to use them as the endpoint values in the assessment.

Therefore the proposed kinetic endpoints for the degradation of Flufenacet in the non-sterilised pelagic (pond) water are following: $k = 0.001464$ [days⁻¹], $DT_{50} = 473$ [days], $DT_{90} = 1570$ [days], kinetic model: **SFO**. The values were determined in the test system incubated at the mean temperature $T = 23.75^{\circ}\text{C}$. Therefore RMS decided to normalise them to the standard conditions – $T = 20^{\circ}\text{C}$. That was done using the Arrhenius equation, assuming the activation energy $E_a = 65.4$ kJ/mol (in line with the recommendations of EFSA PPR Panel). The normalised kinetic endpoints following: $k = 0.001044$ [days⁻¹], $DT_{50} = 664$ [days], $DT_{90} = 2204.1$ [days], kinetic model: **SFO**.

2) Results of the kinetic analysis performed for the sterilised samples:

a) Analysis assuming no lag-phase:

The kinetic analysis was carried out using two kinetic models: SFO and FOMC – the same as used by the Applicant. RMS noticed that the concentrations of the test item – Flufenacet at the end of the experiment were well above the 10%, therefore FOMC model may not be fully appropriate. It was however used in order to verify whether other bi-phasic models should be checked in the analysis.

The results of the fitting are presented below, in the numerical form in table B.8.2.2.2._CA-14 and in the graphical form on figure B.8.2.2.2._CA-8. The kinetic endpoints obtained using each kinetic model tested are presented in the table B.8.2.2.2._CA-15.

Table B.8.2.2.2._CA-14: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	Visual assessment/ R value
				Lower	Upper			
SFO	M_0	105.0	1.198	102.8	107.2	----	2.02	Acceptable; R = 0.6925
	k	3.11 E-4	7.50 E-5	1.71 E-4	4.50 E-4	0.001622		
FOMC	M_0	105.1	1.338	102.6	107.7	----	2.18	Acceptable; R = 0.6762
	α	0.296	0.07197	0.1596	0.4323	----		
	β	808.4	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾		

Footnotes to the table:

- 1) n. d. = not determined – in the report returned by the modelling tools it was stated that these values “could not be calculated because the covariance matrix could not be created”.

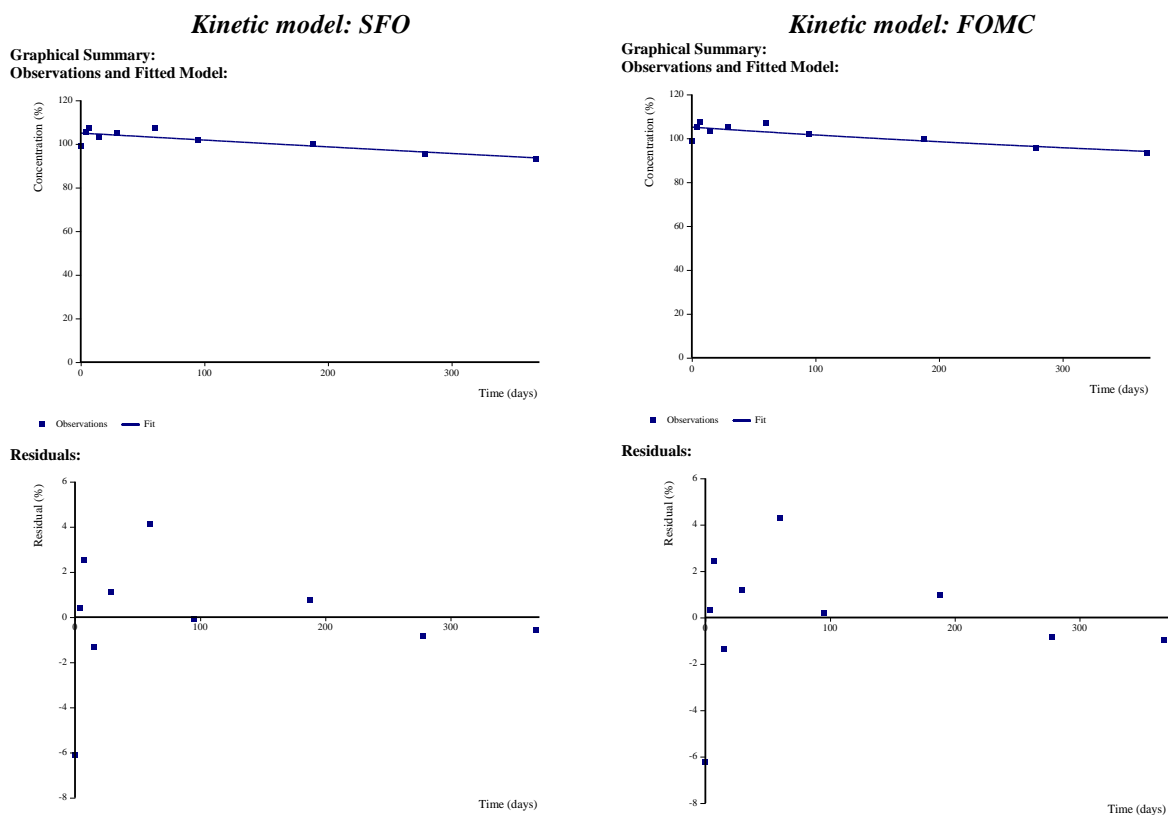


Figure B.8.2.2.2._CA-8: The graphical results of the kinetic analysis.

Table B.8.2.2.2._CA-15: The determined kinetic endpoints

Kinetic model	Determined parameters				
	Kinetic parameters	Kinetic endpoints			
		DT ₅₀ [days]	DT ₉₀ [days]	t_FOMC [days] (pseudo-SFO DT ₅₀)	
<i>SFO</i>	$k = 3.11 \text{ E-4} [\text{days}^{-1}]$	2230	7410	not applicable	
<i>FOMC</i>	$\alpha = 0.296$ $\beta = 808.4$	7600	> 10000	> 10000	

Both kinetic models returned visually very similar fits. The value of χ^2 -error indicate that the SFO fit was statistically slightly better, therefore it should be selected as the first option. The analysis of the reliability of the kinetic parameters showed that while the rate constant k determined for the SFO model passed the reliability criteria, the kinetic parameters determined for FOMC model cannot be considered reliable – for β it was not possible to calculate either the error – σ , or the CI values. Finally, it shall be indicated that both models returned very similar kinetic endpoints, with DT₉₀ in FOMC being shorter than its SFO counterpart. Therefore SFO seems to be the appropriate kinetic model in this analysis.

b) Analysis assuming the occurrence of the lag-phase:

The kinetic analysis was carried in line with recommendations provided by the FOCUS Kinetics Guidance document, assuming the rate constant k_l set to 0.0. RMS decided to test two options:

- 1) with the rate constant k_l set to the value 0.0, but not fixed and left to be optimised by the modelling tool;
- 2) with k_l value fixed to the pre-defined value 0.0 and fixed, what resulted in switching off the optimisation performed by the modelling tool.

The second option was selected by the RMS because it simulated the lag-phase with no degradation of the test compound occurring, while the first option, assumed some, although minimal, level of degradation.

The results of the fitting are presented below, in the numerical form in table B.8.2.2.2._CA-16 and in the graphical form on figure B.8.2.2.2._CA-9. The kinetic endpoints obtained using each kinetic model tested are presented in the table B.8.2.2.2._CA-17.

Table B.8.2.2.2._CA-16: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	Visual assessment/ R value
				Lower	Upper			
HS, k_l optimised	M_0	104.3	1.563	101.3	107.3	----	2.01	Good; R = 0.752
	k_l	9.95 E-6	3.78 E-4	-7.25 E-4	7.45 E-4	0.4899		
	k_2	3.96 E-4	1.17 E-4	1.69 E-4	6.22 E-4	0.00727		
	t_b	74.27	0.2369	73.81	74.73	----		
HS, k_l fixed	M_0	105.1	1.203	102.8	107.3	----	2.37	Poor; R = 0.0479
	k_l	0.0	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾	n. d. ¹⁾		
	k_2	8.99 E-5	1.33 e-4	-1.62 E-4	3.42 E-4	0.2603		
	t_b	151.3	n. d. ²⁾	n. d. ²⁾	n. d. ²⁾	n. d. ²⁾		

Footnotes to the table:

1) n. d. = not determined – the k_l value was fixed.

2) n. d. = not determined – in the report returned by the modelling tools it was stated that these values “could not be calculated because the covariance matrix could not be created”.

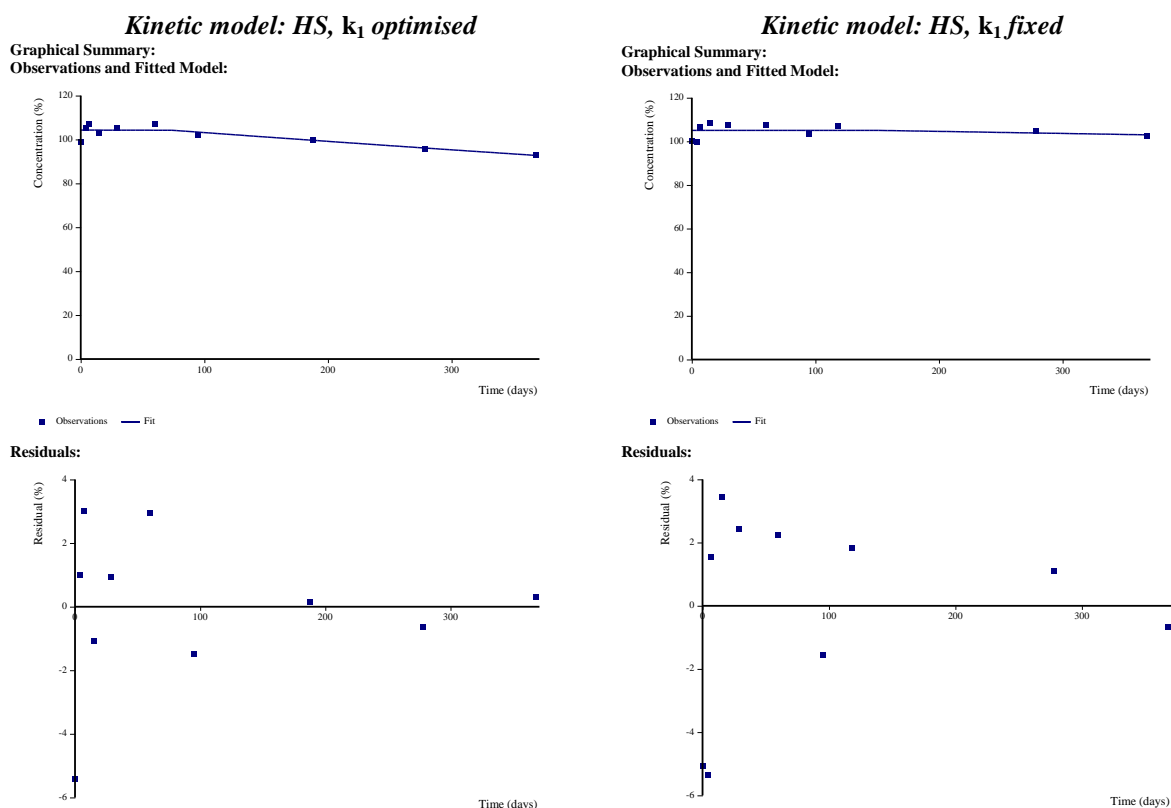


Figure B.8.2.2.2._CA-9: The graphical results of the kinetic analysis.

Table B.8.2.2.2._CA-17: The determined kinetic endpoints

Kinetic model	Determined parameters					
	Kinetic parameters		Kinetic endpoints			
	k_1 [days ⁻¹]	k_2 [days ⁻¹]	DT ₅₀ [days]	DT ₉₀ [days]	DT ₅₀ [days] for k_1	DT ₅₀ [days] for k_2
HS, k_1 optimised	9.95 E-6	3.69 E-4	1820	5890	> 10000	1750
HS, k_1 fixed	0.0	8.99 E-5	7860	> 10000	> 10000	7710

It was not possible to obtain fully reliable kinetic fits. Although visually fits seem to be acceptable, only the reversed HS fit with optimised k_1 value may be considered good, while that with fixed k_1 value is poor because of the low R value. Also the distribution of the residuals in this fit indicates its lack of appropriateness, because they are not distributed randomly, what is observed in case of the fit with the optimised k_1 value. Finally, it shall be indicated that, although the value of χ^2 -error was well <15%, it was higher for the fit with the fixed k_1 value. As a result, from the point of view of the appropriateness of the visual fit, only the reversed HS fit with the k_1 value can be considered acceptable.

At the same time it shall be indicated that also that fit cannot be considered acceptable because of the lack of reliability of the k_1 value, which did not pass the T-test (the *Prob.* > *t* is at the level 0.4899 therefore much higher than the recommended threshold value of 0.05).

As a result, it shall be indicated that the kinetic analysis of the data for Flufenacet in the sterilised natural pelagic (pond) water assuming the occurrence of the lag phase is not an appropriate option.

Conclusion of the assessment:

The results of the performed analysis showed, that the degradation of Flufenacet in sterilised natural pelagic (pond) water was well described by the SFO kinetic model without assuming the lag phase. The analysis of the data assuming lag phase, performed using the reversed HS model, showed that probably no lag phase occurred.

That also may indicate that the possible change of the conditions in the test system from sterile to the non-sterile, taking place at some point during the experiment, had no visible impact on the degradation kinetics of Flufenacet in sterilised test medium. It cannot be also excluded that the contamination of the test vessels occurred not during incubation, but during their processing.

RMS therefore proposes to consider that the degradation of Flufenacet in sterilised natural pelagic (pond) water follows the SFO kinetics and the proposed kinetic endpoints for the degradation of Flufenacet in the sterilised pelagic (pond) water are following: $k = 0.000311$ [days⁻¹], $DT_{50} = 2230$ [days], $DT_{90} = 7410$ [days], kinetic model: **SFO**. The values were determined in the test system incubated at the mean temperature $T = 23.75^{\circ}\text{C}$. Therefore RMS decided to normalise them to the standard conditions – $T = 20^{\circ}\text{C}$. That was done using the Arrhenius equation, assuming the activation energy $E_a = 65.4$ kJ/mol (in line with the recommendations of EFSA PPR Panel). The normalised kinetic endpoints following: $k = 0.0002214$ [days⁻¹], $DT_{50} = 3130.7$ [days], $DT_{90} = 10402.9$ [days], kinetic model: **SFO**.

Final conclusion of the assessment:

The data for Flufenacet obtained in the study by [Schocken, Yen and Widmer; 1995], examining the degradation of that compound in natural pelagic (pond) water, were subjected to the kinetic examination performed in line with the provisions of the FOCUS Work Group on the Degradation Kinetics.

That evaluation was first carried out by the Applicant, who, to comply with the provisions of the OECD Test Guideline No. 309, limited the analysed data base to the time points obtained until the DAT 95. The later time points were not included in the evaluation. Additionally, the kinetic analysis was performed only for the non-sterilised samples.

The performed kinetic analysis resulted in the identification of the SFO kinetic model as returning the reliable kinetic fit, with the following set of the kinetic endpoints: $k = 0.0001121$ [days⁻¹], $DT_{50} = 618.25$ [days] and $DT_{90} = 2053.80$ [days].

However, doing that assessment the Applicant did not take into account the fact that in the source study report for the biologically viable (not sterilised) water samples the lag phase was postulated on the basis of the observed formation profile of the degradation products – the two major degradation products: FOE Alcohol and FOE Oxalate, were observed on DAT 60 in the study.

In case the lag phase were taken into account the number of time points for which the degradation was observed was only two, in RMS's opinion too few to obtain the reliable kinetic curve.

Therefore RMS decided to repeat the kinetic assessment using the whole data base obtained for Flufenacet in the study by [Schocken, Yen and Widmer; 1995]. The additional justification for the correctness of such approach was the fact that the microbial viability of the non-sterilised samples determined was comparable to that measured at the beginning of the experiment.

The additional goal of the repeated assessment was to determine the degradation kinetics of Flufenacet in the sterilised samples and, if possible check whether the change of the conditions from the sterile to non-sterile, demonstrated itself somehow, and if yes, then when.

The analysis of the data sets was carried out in two variants:

- assuming no lag-phase;
- assuming the existence of the lag-phase.

The analysis of the data set assuming lag-phase was performed in line of the recommendations of the FOCUS Work Group on the Degradation Kinetics, using the reversed HS kinetic model.

For the non-sterilised samples it was demonstrated that the reliable fit in case the lag-phase was not included was obtained with the SFO kinetic model. Also the full reliable fit was obtained for the analysis assuming the lag-phase, with the k_l value set as a fixed parameter. The comparative analysis indicated that the results of the fitting with and without lag-phase were comparable, in case the lag-phase not being taken into account providing longer DT_{50}/DT_{90} values. RMS therefore decided to consider the SFO fit without lag phase as a good representation of the kinetic behaviour of Flufenacet in biologically viable pelagic (pond) water.

The kinetic analysis of the data obtained for Flufenacet in sterilised samples showed that the approach that assumed the occurrence of the lag-phase did not return reliable kinetic fit. Therefore it may be stated that in the sterilised samples the lag phase did not occur. It was also noticed that there was no break point, therefore it may be stated that either the lack of sterility might resulted from inappropriate handling and processing the samples after their removal from incubation chamber or, if occurred during the incubation, it had minimal impact on the degradation kinetics of Flufenacet in sterilised natural pelagic water.

The analysis resulted in the identification of SFO as the kinetic model adequately characterising the degradation kinetics in sterilised natural pelagic (pond) water.

The kinetic endpoints resulting from that assessment considered reliable by the RMS are presented below in the table B.8.2.2.2._CA-18.

Table B.8.2.2.2._CA-18: The definitive set of the kinetic endpoints obtained for Flufenacet as a result of the data set from the study by [Schocken, Yen and Widmer; 1995], examining the aerobic mineralisation of that compound in natural water.

Type of sample	Experimental conditions - temperature	Determined kinetic endpoints			Kinetic model
		k [days ⁻¹]	DT ₅₀ [days]	DT ₉₀ [days]	
<i>Natural pelagic freshwater (pond), not sterilised</i>	Mean incubation temperature 23.75°C (range 23.1 – 24.4°C)	0.001464	473	1570	SFO
	At standard T = 20°C	0.001044	664	2204.1	SFO
<i>Natural pelagic freshwater (pond), sterilised</i>	Mean incubation temperature 23.75°C (range 23.1 – 24.4°C)	0.000311	2230	7410	SFO
	At standard T = 20°C	0.0002214	3130.7	10402.9	SFO

Summary – Aerobic mineralisation in surface water

The aerobic mineralisation of Flufenacet in surface water was examined in pelagic (pond) freshwater collected from the pond representative for the agricultural area of the use of Flufenacet. The test water had the following characteristic:

- type of water sample: pelagic water (no associated sediment);
- pH: 7.5;
- total alkalinity: 230 mg CaCO₃/L;
- total hardness: 329 mg CaCO₃/L;
- specific conductivity: 500 µmhos/cm;
- [O₂]: 9.6 mg/L;
- Suspended solids: 8.5 mg/L;
- Microbial activity, expressed in number of the colony forming units (CFU): 5.9 E3 CFU/mL.

The examination of the degradation of Flufenacet in water was performed in irradiated test systems, under light regime similar to natural sunlight conditions. The mean temperature of incubation was in range 23.1 – 24.4 (mean estimated by the RMS is 23.75°C), therefore slightly deviating from the assumed T = 25 ± 1°C.

The experiment was performed with Flufenacet radiolabelled in only one position – in fluorophenyl ring, therefore the proposed transformation scheme cannot be considered as complete. In case of the biologically viable samples three degradation products were identified and quantified:

- FOE Alcohol, recorded for the first time on DAT 60, peaking at 4.4% of the applied amount of the parent compound on DAT 368 (end of the study) and that amount was still seemingly increasing;
- FOE Oxalate, recorded for the first time on DAT 60, peaking at 24.0% of the applied amount of the parent compound on DAT 368 (end of the study) and that amount was still increasing;
- FOE Sulfonic acid, recorded for the first time on DAT 278, peaking at 8.6% of the applied amount of the parent compound on DAT 368 (end of the study) and that amount was still increasing;

In sterilised samples only one degradation product was identified – FOE Alcohol, observed for the first time on DAT 278 and formed in amount up to 6.8% of the applied amount of the parent compound (value recorded at the end of the study – on DAT 368).

During that experiment, lasting for 368 days, it was stated that Flufenacet radiolabelled in fluorophenyl moiety, underwent very limited mineralisation – up to 3.0% of the applied dose was fully mineralised in the biologically viable samples. That indicates that Flufenacet cannot be considered ready biodegradable. In the sterilised samples the level of mineralisation was up to 0.8% at the end of incubation period – DAT 368.

The process of degradation of Flufenacet in pelagic water was slow, with DT₅₀ = 473 days and DT₉₀ = 1570 days in non sterilised water, and it followed the SFO kinetic model. When recalculated to the standard

temperature – $T = 20^{\circ}\text{C}$ (using Arrhenius activation energy $E_a = 65.4 \text{ kJ/mol}$) these values were: $DT_{50} = 664$ days and $DT_{90} = 2204.1$ days.

In sterilised water the rate of degradation, also following the SFO kinetics, was much slower, with $DT_{50} = 2230$ days and $DT_{90} = 7410$ days. When recalculated to the standard temperature – $T = 20^{\circ}\text{C}$ (using Arrhenius activation energy $E_a = 65.4 \text{ kJ/mol}$) these values were: $DT_{50} = 3130.7$ days and $DT_{90} = 10402.9$ days.

The kinetic examination of the results for any of the identified and quantified degradation products was not possible due to the fact that all they were still forming at the study end.

The results presented above demonstrated that the process of the degradation of Flufenacet in natural pelagic water was predominantly biologically mediated and that the abiotic degradation processes – hydrolysis and aqueous photolysis (direct and indirect) played only minor role, if any.

The results of the examination of aerobic mineralisation of Flufenacet in surface water, in format recommended for reporting the regulatory endpoints in the EU, are presented below. In that form the values will be inserted into the proposal for the EU List of End Points.

Aerobic mineralisation in surface water (Regulation (EU) N° 283/2013, Annex Part A, point 7.2.2.2 and Regulation (EU) N° 284/2013, Annex Part A, point 9.2.1)

Parent System identifier (indicate fresh, estuarine or marine)	pH water phase	pH sed	t. $^{\circ}\text{C}^{\text{a}}$	DT ₅₀ /DT ₉₀ whole sys. (suspended sediment test)		St. (χ^2)	DT ₅₀ /DT ₉₀ Water (pelagic test)		St. (χ^2)	Method of calculation
				At study temp	Normali- sed to x $^{\circ}\text{C}$		At study temp	Norma lised to 20 $^{\circ}\text{C}^{\text{b}}$		
Pelagic fresh water, biologically viable system	7.5	not appl	23.8	not applicable	not applicable	not appl	473/ 1570	664/ 2204	3.22	SFO
Pelagic fresh water, sterilised system	7.5	not appl	23.8	not applicable	not applicable	not appl	2230/ 7410	3130/ 10403	2.02	SFO

^{a)} Temperature of incubation=temperature that the environmental media was collected or std temperature of 20°C

^{b)} Normalised using a Q10 of 2.58 to the temperature of the environmental media at the point of sampling. (note temp of x should be stated).

Metabolite <i>FOE Alcohol</i> Max in total system 4.4 % after 368 days (biologically viable); 6.8 % after 368 days (sterilised)										
System identifier (indicate fresh, estuarine or marine)	pH water phase	pH sed ^{a)}	t. $^{\circ}\text{C}^{\text{b}}$	DT ₅₀ /DT ₉₀ whole sys. (suspended sediment test)		St. (χ^2)	DT ₅₀ /DT ₉₀ Water (pelagic test)		St. (χ^2)	Method of calculation
				At study temp	Normalise d to x $^{\circ}\text{C}^{\text{c}}$		At study temp	Norma lised to x $^{\circ}\text{C}^{\text{c}}$		
Pelagic fresh water, biologically viable system	7.5	not appl	23.8	not applica- ble	not applicable	not appl	Not deter- mined	Not deter- mined	----	Not determined
Pelagic fresh water, sterilised system	7.5	not appl	23.8	not applica- ble	not applicable	not appl	Not deter- mined	Not deter- mined	----	Not determined

Metabolite <i>FOE Oxalate</i> Max in total system 24.0 % after 368 days (biologically viable); not detected in sterilised samples										
System identifier (indicate fresh, estuarine or marine)	pH water phase	pH sed ^{a)}	t. $^{\circ}\text{C}^{\text{b}}$	DT ₅₀ /DT ₉₀ whole sys. (suspended sediment test)		St. (χ^2)	DT ₅₀ /DT ₉₀ Water (pelagic test)		St. (χ^2)	Method of calculation
				At study temp	Normalise d to x $^{\circ}\text{C}^{\text{c}}$		At study temp	Norma lised to x $^{\circ}\text{C}^{\text{c}}$		
Pelagic fresh water, biologically viable system	7.5	not appl	23.8	not applica- ble	not applicable	not appl	Not deter- mined	Not deter- mined	----	Not determined

Metabolite <i>FOE Sulfonic acid</i>										
Max in total system 8.6 % after 368 days (<i>biologically viable</i>); not detected in sterilised samples										
System identifier (indicate fresh, estuarine or marine)	pH water phase	pH sed ^{a)}	t. °C ^{b)}	DT ₅₀ /DT ₉₀ whole sys. (suspended sediment test)		St. (χ ²)	DT ₅₀ /DT ₉₀ Water (pelagic test)		St. (χ ²)	Method of calculation
				At study temp	Normalise d to x °C ^{c)}		At study temp	Norma lised to x °C ^{c)}		
Pelagic fresh water, biologically viable system	7.5	not appl	23.8	not applica- ble	not applicable	not appl	Not deter- mined	Not deter- mined	----	Not determined

Mineralisation and non extractable residues (for parent dosed experiments)					
System identifier (indicate fresh, estuarine or marine)	pH water phase	pH sed	Mineralisation x % after n d. (end of the study).	Non-extractable residues. max x % after n d (suspended sediment test)	Non-extractable residues. max x % after n d (end of the study) (suspended sediment test)
Pelagic fresh water, biologically viable system	7.5	----	3.0% after 368 days	not applicable	not applicable
Pelagic fresh water, sterilised system	7.5	----	0.8% after 368 days	not applicable	not applicable

B.8.2.2.3. – Water/sediment study

In order to cover that data requirement the Applicant submitted three study reports. Two of them examined the transformation pattern of Flufenacet radiolabelled in two different positions – in phenyl ring (first study) and in C2 position of Thiadiazole moiety (second study) in aerobic water/sediment systems. Both had already been evaluated for the purpose of the previous authorisation of Flufenacet in the EU. The third study, newly submitted, presented the results of the kinetic evaluation of the data obtained in the two studies referred to above.

RMS examining the data set stated that the examination of the fate and behaviour of Flufenacet in aerobic aquatic systems was performed for only two of the three possible radiolabelling positions – phenyl ring and C2 position in thiadiazole moiety. Not covered was the would-be transformation pathway for thiadiazole moiety radiolabelled in C5 position and, as a result there is no information about formation of two degradation products identified in soil as major – FOE 5043 Trifluoroethanesulfonic acid and Trifluoroacetic acid. The lack of the data for that third radiolabelling position may be considered as a data gap.

The Applicant also submitted the study examining fate and behaviour of Flufenacet in anaerobic water/sediment system. That study, also submitted and evaluated for the purpose of the previous authorisation of Flufenacet in the EU, will be evaluated under this point after the evaluation of the aerobic water/sediment studies.

Study 1:

Report: Kelley I., Wood S., McKinney M., (1995): “Degradability and Fate of [Phenyl-UL-¹⁴C]FOE 5043 in Two Sediment/Water Systems.”; Bayer Corporation (formerly Miles Inc), Agriculture Division, Research and Development Department, 17745 S. Metcalf, Stilwell, Kansas 66085, USA (performing laboratory) for Bayer Corporation, Agriculture Division, P. O. Box 4913, Kansas City, Missouri 64120, USA; study No. F3042405; Report No. MR106928; 1 November 1995; study reference number: M-002213-01-1;

Guidelines: The study was performed to comply with the following Guidelines:

- BBA Guidelines for the Official Testing of Plant Protectants Part IV, 5-1 (1990): Degradability and Fate of Plant Protectants in the Water/Sediment System;
- US. EPA Guidelines for Pesticide Registration, Subdivision N, Section 162-4, Aerobic Aquatic Metabolism.

GLP: Yes;

RMS comments: The study had been evaluated for the previous authorisation of Flufenacet in the EU, by its inclusion into the Annex I of the Directive 91/414/EEC. Its summary can be found under the point B.7.4.3.2.1., in section B.7 of the Annex B to the Monograph prepared by the RMS – France, for Flufenacet. For the purpose of the current assessment the study was evaluated for its compliance with OECD Guideline 308 – Aerobic and Anaerobic Transformation in Aquatic Sediment Systems. The study was found acceptable and is summarised below. It shall be indicated however that in its part aimed on the kinetic evaluation of the results the study did not comply with the provisions of the current Guidelines, namely FOCUS Kinetics Guidance document. That assessment was performed separately and presented in the study report summarised further down this Renewal Assessment Report as **Study 3**.

Summary:

The aim of the study was to examine the fate and degradation rate of Flufenacet in two aerobic water/sediment systems.

The test compound used in the experiment was ¹⁴C-Flufenacet radiolabelled uniformly in fluorophenyl ring, as shown below on figure B.8.2.2.3._CA-1. It had a specific activity 66.5 mCi/mmol and radiochemical purity of 98.9%. It was used to prepare the application solutions with which the test systems were treated. It was delivered to the test facility as vial C-584, probably in form of solution in not specified organic solvent.

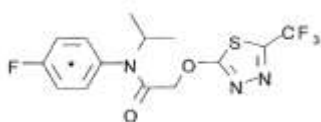


Figure B.8.2.2.3._CA-1: The structural formula of the test compound - [Phenyl-UL-¹⁴C]Flufenacet used in the experiment; radiolabelling position is indicated by an asterisk (copied from the study report).

Additionally, in the experiment the non-radiolabelled Flufenacet was used. That compound, delivered as vial K-597) had a declared chemical purity of 99.6%.

Other radiolabelled compounds used in the experiment were: FOE Methylsulfoxide (specific activity 21.0 mCi/mmole), FOE Methylsulfone (specific activity 21.0 mCi/mmole), FOE Thioglycolate sulfoxide (specific activity 21.0 mCi/mmole), FOE Sulfonic acid (specific activity 21.0 mCi/mmole), FOE Oxalate (specific activity 18.4 mCi/mmole), FOE Methylsulfide (specific activity 21.0 mCi/mmole), FOE Amine acetate (specific activity 115.8 mCi/mmole) and FOE Alcohol (specific activity 115.8 mCi/mmole). All these compounds were radiolabelled uniformly in the fluorophenyl ring. Their structural formulas were presented in the introductory part of this document (point B.8.0.), in the table B.8.0_CA-1. They were used as the reference compounds in the chromatographic analysis.

The examination of the fate and behaviour of Flufenacet in water/sediment systems was carried out using two freshwater sediments and water associated with them. The test matrices – sediment and associated water, were sampled from the ponds located in Kansas, USA, in areas representative for the intended use of Flufenacet.

One of the ponds, from which the test matrices were sampled, was located in Nelson Environmental Study Area near Lawrence, Kansas. It was positioned near the hilltop and was surrounded by the grassland. The test systems containing that set of the test matrices in the experiment bore the codename NESA.

The second sampling pond was located at Bayer Research Park in Stilwell, Kansas and was positioned in a valley surrounded by woods. The test systems containing that set of the test matrices were codenamed in the experiment BRP.

During the sampling several parameters of the pond water were determined. These are presented below in the table B.8.2.2.3._CA-1. In the original study report the depths were expressed in inches. For clarity the RMS recalculated them into standard, SI-related units (cm).

Table B.8.2.2.3._CA-1: The parameters of the test systems recorded on the sampling site.

Parameter		Test system	
		NESA	BRP
Location		Lawrence, KS, USA	Stilwell, KS, USA
Sampling depth [cm]		21.6	25.4
Temperature [°C]	On the surface	20	20
	5 cm above the sediment	19	19
Dissolved oxygen [ppm]	Near the surface	10.8	7.9
	5 cm above the sediment	9.2	7.9
pH		8.7	8.2
Conductivity [μMhos]		162	220
Redox potential [mV]		~365	409

The samples of sediment and associated water were taken to the test facility, where they were stored overnight at T = 4°C and the next day processed. The processing of the test matrices consisted on sieving the sediments through 2-mm sieve to remove larger skeletal elements and passing water through a 0.2-mm sieve to remove larger plant parts.

The subsamples of so prepared test matrices were taken for characterisation. Its results – the physicochemical and biological parameters of sediment and associated water for each test system, are presented below in the table B.8.2.2.3._CA-2.

Table B.8.2.2.3._CA-2: The physicochemical and biological parameters of water and sediment phases of each test system.

Matrix	Parameter	Test system	
		NESA	BRP
Water	<i>pH</i>	7.5	7.3
	<i>Conductivity [mmhos]</i>	0.17	0.24
	<i>Total dissolved solids [ppm]</i>	82	120
	<i>Turbidity [NTU]</i>	0.77	0.69
	<i>Ca content [ppm]</i>	5	11
	<i>Mg content [ppm]</i>	6	4
	<i>Hardness [mg equivalents CaCO₃/L]</i>	38	47
	<i>Redox potential [mV]</i>	259	296
	<i>total N [mg/L]</i>	13	13
	<i>total P [mg/L]</i>	0.04	0.04
	<i>Dissolved O₂ [ppm]</i>	9.2	8.5
Sediment	<i>Textural class (USDA)</i>	Silty clay loam	Silty clay loam
	<i>Particle size distribution</i>	Sand %	14
		Silt %	51
		Clay %	35
	<i>OC content [%]</i>	0.7	1.4
	<i>pH</i>	7.9	7.8
	<i>CEC [meq/100g]</i>	33.5	25.6
	<i>total N</i>	0.057	0.118
	<i>Microbial activity [mg CO₂/kg sediment •hour]</i>	17	8

The experiment was performed using 500-mL reagent bottles as the test vessels.

The test vessels for NESA system were prepared by weighing into each of them ~173 g of the moist sediment to obtain its 2.4-cm layer. It was carefully covered with 310 mL of the associated water to obtain 6-cm water layer.

The test vessels for BRP system were prepared by weighing into each of them ~173 g of the moist sediment to obtain its 2.5-cm layer. It was carefully covered with 325 mL of the associated water to obtain 6-cm water layer.

The amount of so prepared bottles was such to obtain two replicates for each sampling point, except those marked DAT 120 and DAT 157 (test spares) for which the test bottles were prepared in triplicate.

So prepared test vessels were allowed to equilibrate – until an aerobic/anaerobic gradient was established. During that period in selected bottles the following parameters were measured: pH, redox potential, conductivity and the O₂ content.

After pre-equilibration from each test bottle 10-mL samples of water were taken. The samples representing the given test system – NESA or BRP, were then pooled and sterilised by filtering them through 0.22-µm cellulose acetate filter. So prepared water samples were subsequently used to prepare two application solutions, each specific for the given test system. The preparation of the water samples, as well as that of the application solutions, was carried out using the glassware sterilised by autoclaving. The pre-equilibration was performed in a walk-in environmental chamber, in which the whole experiment was carried out, under the experimental conditions – in the darkness and at the incubation temperature $T = 20 \pm 1^{\circ}\text{C}$.

The application solution used to treat the samples of the test system NESA, further called **Application solution 1**, was prepared in a way described below.

Firstly 0.213 mL of the test compound from vial C-584 (2.562 mg using the declared in the study report concentration 12.028 mg/mL) was transferred to the 5-mL centrifuge tube. The solvent was evaporated and the residue redissolved in 1 mL of CH₃CN. So prepared solution was then added to 330 mL of sterilised water from NESA test system to obtain the **Application solution 1** having a nominal concentration of the test compound of 7.8 mg/L. The concentration of the test compound in so prepared solution was verified by LSC using three 100-µL aliquot samples. The concentration of ¹⁴C-Flufenacet in the solution was determined on the basis of the determination of radioactivity content using the calculated specific radioactivity of ¹⁴C-Flufenacet equal to 0.18 µCi/µg, corresponding to 6.8 kBq/µg. On that basis the concentration of ¹⁴C-Flufenacet in solution was determined to be 349575 dpm/100 µL, what corresponded to 8.7 mg/L. RMS noticed that the measured concentration was by 0.9 mg/L higher than the declared nominal concentration. The radiochemical purity of the **Application solution 1**, determined by radio-HPLC, was 95.3%.

The application solution to treat the samples of the test system BRP, further called **Application solution 2**, was prepared in a way described below.

Firstly 3.32 mL of the test compound from vial C-584 (2.686 mg using the declared in the study report concentration 0.809 mg/mL) was transferred to the 5-mL centrifuge tube. The solvent was evaporated and the

residue redissolved in 1 mL of CH₃CN. So prepared solution was then added to 330 mL of sterilised water from NESA test system to obtain the **Application solution 1** having a nominal concentration of the test compound of 8.1 mg/L. The concentration of the test compound in so prepared solution was verified by LSC using three 100-μL aliquot samples. The concentration of ¹⁴C-Flufenacet in the solution was determined on the basis of the determination of radioactivity content using the calculated specific radioactivity of ¹⁴C-Flufenacet equal to 0.18 μCi/μg, corresponding to 6.8 kBq/μg. On that basis the concentration of ¹⁴C-Flufenacet in solution was determined to be 348238 dpm/100 μL, what corresponded to 8.7 mg/L. RMS noticed that the measured concentration was by 0.6 mg/L higher than the declared nominal concentration. The radiochemical purity of the **Application solution 2**, determined by radio-HPLC, was 98.1%.

RMS's comment:

RMS analysing the description of the preparation of the **Application solution 1** and **Application solution 2** provided in the study report noticed the significant discrepancies in the description. Although taken from the same vial the volumes of the test compound solution and its amount in the solution's volume unit were different. Additionally the radiochemical purities of the so prepared application solutions were different by about 3%. Assuming that the source of the test compound for both application solutions was the same vial – C584 and that the compound was homogenous (what shall be true, taking into account that it was, as indicate the description, delivered as a liquid not a solid) and stable during storage (what was confirmed by the results of the adequate analyses), that puts a questionmark over the procedure of the preparation of the application solutions and subsequent treatment of the individual test systems. Therefore in RMS's opinion, although this is not a factor invalidating the study rendering it unreliable, the Applicant should clarify the problem.

Additionally the application solution with non-radiolabelled Flufenacet was prepared. That was done by weighing 10 mg of the material from the vial K-597 into 500-mL volumetric flask, to which 2 mL of CH₃CN were firstly added (to improve the solubility of the test item) and then the appropriate amount of the sterile, distilled water (flask was filled up to the calibration mark). The so prepared solution was used to treat the control samples set to determine the biomass in the test systems during the experiment.

Another set of control samples – sterile control samples, was treated with the modified **Application solution 1** or **Application solution 2**. The modification consisted on addition to the 40-mL aliquots of the application solutions 1 g of HgCl₂ used as a sterilising agent.

The test vessels were treated at application rate 750 g/ha, assuming 30-cm depth of the water column, corresponding to the theoretical rate 0.25 ppm Flufenacet in the water phase of the individual test vessel. For that purpose to each individual test vessel containing the given water/sediment test system was introduced 10 mL of the adequate **Application solution** containing radiolabelled test substance (**Application solution 1** or **Application solution 2**) was added. The given **Application solution** was introduced to the test vessel by evenly applying it to the water surface using pipette. The verification of the application rate showed that in case of the NESA test system it was 0.28 ppm and for BRP system – 0.27 ppm. These application rates were slightly higher than the assumed application rate of 0.25 ppm.

In the similar way, using the same as above amounts of the adequate **Application solutions** to obtain the target application rate of 0.25 ppm, were treated the control samples for the determination of biomass (using the **Application solution** containing non-radiolabelled Flufenacet) and the so-called sterile control samples (using the appropriate **Application solution** containing HgCl₂ as sterilising agent).

Additionally were prepared the blank control samples for each test systems – the vessels not treated with the test compound, neither radiolabelled nor non-radiolabelled one.

The fortification of all test vessels was performed in such way to minimise the access of light. After treatment the test vessels were connected to the flow-through system, presented below (for each individual test vessel) on figure B.8.2.2.3._CA-2, and incubated for the pre-defined amount of time in the climatic walk-in chamber, in the darkness under the constant temperature $T = 20 \pm 1^{\circ}\text{C}$. The exact maximum incubation time for each type of sample was:

- 120 days for the test vessels (both systems);
- 157 days for the spare samples (both systems) to provide enough material for metabolite profiling;
- 120 days for the control samples for determination of biomass;
- 162 days for the sterile control samples;

The maximum incubation time for the blank control samples was not defined.

The test vessels were aerated with continuous air-flow from a pressurized air tank. The air administered to each test vessel were sterilised and moisturised before reaching it.

The main trap for volatile compound in each flow-through system was filled with 3:7 v/v mixture of monoethanolamine:ethylene glycol. It was followed by the secondary trap, containing the same filling, set to trap the volatiles in case of the oversaturation or overflow of the primary trap.

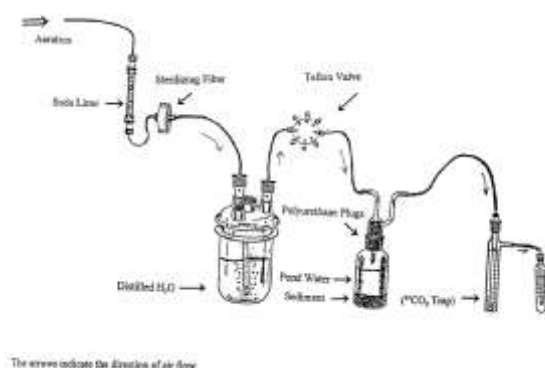


Figure B.8.2.2.3._CA-2: The schematic presentation of the incubation flow-through system used in the experiment (copied from the study report).

At pre-designated sampling points the duplicate test vessels for each water/sediment test system and each type of samples were taken for the analysis. In case of the test samples the sampling points were set at DAT (DAT stands for Days After Treatment): 0, 0.25 (6 hours after treatment), 1, 2, 7, 14, 30, 100 and 120. The DAT 120 samples were taken in triplicate. Additionally triplicate test samples (initially set as spares) were taken for the metabolite profiling analysis.

In case of the control samples for biomass determination the sampling points were set to DAT 0, DAT 43 and DAT 120. Finally the sterile control samples were taken for the analysis on DAT 120 and DAT 162.

After removal from the incubation chamber each test vessel was purged for 1 hour with a gentle stream of N_2 administered at a rate 40-55 mL/min to transfer all volatile compounds remaining in the head space into the traps for volatile compounds. Then the samples were processed in line with the procedure presented below on figure B.8.2.2.3._CA-3.

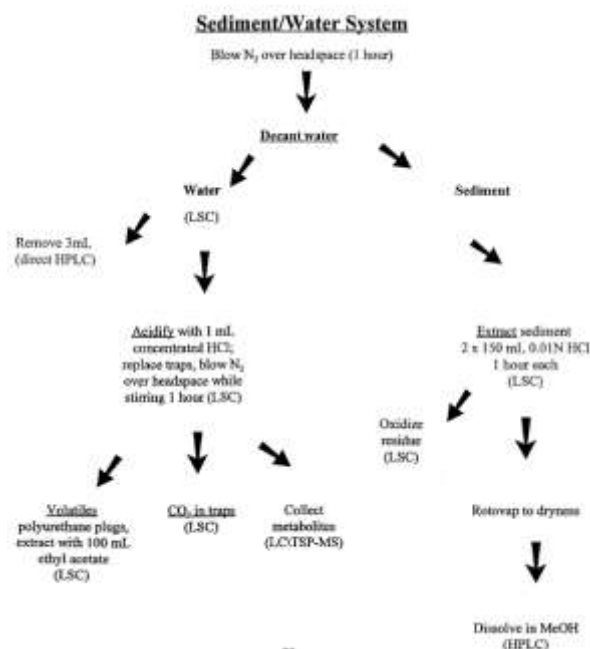


Figure B.8.2.2.3._CA-3: The conceptual scheme of the sample processing procedure (copied from the study report).

The radioactivity in samples was quantified by LSC. The measurements were performed using a Packard Tri-Carb Model 4640 LS counter.

In case of liquid samples the volume of aliquot taken for analysis was 0.1 – 1.0 mL and that of the liquid scintillation cocktail – Ultima Gold, 15 – 20 mL. The detailed parameters were presented for the 0.5-mL aliquots of liquid samples, mixed with 15 mL of Ultima Gold LS cocktail. The minimum sensitivity of LSC analysis for those samples was 1.8 E-4 ppm. When expressed as Lowest Acceptable Gross Count Rate (LAGC) it was 70 cpm, while as Lowest Acceptable Net Count Rate (LANC) – 35 cpm, assuming average background (BCGK) of 35 cpm (LAGC = 2*BCGK and LANC = LAGC – BCGK). The greatest probable error GPE = 8.83%. The counting lasted for 5 minutes.

In case of the solid samples, the amount taken for analysis was 0.1g, pelleted with cellulose. It was oxidised and the formed $^{14}\text{CO}_2$ absorbed in a mixture of 6 mL Carbo-sorb and 15 mL Perma Fluor E⁺. The minimum sensitivity of LSC analysis for those samples was 9.1 E-4 ppm. When expressed as Lowest Acceptable Gross Count Rate (LAGC) it was 70 cpm, while as Lowest Acceptable Net Count Rate (LANC) – 35 cpm, assuming average background (BCGK) of 35 cpm (LAGC = 2*BCGK and LANC = LAGC – BCGK). The greatest probable error GPE = 8.83%. The counting lasted for 5 minutes.

The chromatographic methods used in the study were HPLC, TLC and LC/TPS-MS (Liquid Chromatography/Thermospray – Mass Spectrometry)

The HPLC method was used to analyse pond water and sample extracts for the content of the parent compound and its degradation products.

It was carried out on HP 1090 chromatograph coupled with an UV-detector set to $\lambda = 254$ nm and radioactivity detector (Raytest Ramona). The chromatographic separation was performed in a gradient mode on the Spherisorb 3 μ ODS, 70 • 10 mm, chromatographic column. The mobile phase used in the elution consisted of:

- **Solvent A:** 0.4% CH_3COOH in water;
- **Solvent B:** 0.4% CH_3COOH in CH_3CN ;

The gradient mode used in the analysis was linear from 0% to 100% of **Solvent B** over 60 minutes. The flow rate was 1.0 mL/min. The quantitative analysis was performed by means of the external standards of known concentration and the identification of the fractions by comparing their retention times – R_t , with those of the known standards. The R_t values of the standards are presented in the table B.8.2.2.3._CA-3.

The TLC (Thin-Layer Chromatography) was used as a conformatory method for metabolite identification. The chromatographic separation was performed on pre-coated silica gel plates, 0.25-mm thick, with fluorescent indicator. The TLC plates were developed first in the solvent system $\text{CHCl}_3/\text{CH}_3\text{COOC}_2\text{H}_5$ (3:1 v/v) and then in the solvent system $\text{CH}_3\text{CN}/(\text{CH}_3)_2\text{CHOH}/\text{CH}_3\text{COOH}/\text{H}_2\text{O}$ (20:3:2:1 v/v/v/v). The identification of the bands was performed by means of the comparison of their R_f values with those of the known standards. The R_f values of the standards are presented in the table B.8.2.2.3._CA-3.

Table B.8.2.2.3._CA-3: The R_t (HPLC) and R_f (TLC) values of the standard compounds used as the reference values in identification of the fractions in chromatographic analysis.

Chromatographic fraction	Chromatographic characteristic		Identity of the fraction
	Retention time R_t [min] – HPLC	R_f value – TLC	
Parent	45	0.94	Flufenacet
Metabolite 1	16 – 18	0.54	FOE Sulfonic acid
Metabolite 2	18 – 20	0.36	FOE Oxalate
Metabolite 3	26	0.28	FOE Thioglycolate sulfoxide
Metabolite 4	30	0.62	Foe Methylsulfoxide
Metabolite 5	34	0.85	FOE Methylsulfone
Metabolite 6	38	0.81	FOE Amine acetate
Metabolite 7	40.5 – 42	0.62	FOE Methylsulfide
Metabolite 8	----	0.74	FOE Alcohol

The LC/TPS-MS analysis was performed to conform the identity of Flufenacet and its degradation products. It was carried out using Varian 540 HPLC coupled with Finnigan-MAT 90 thermospray MS detector. The chromatographic separation was performed in a gradient mode on the C18 Novapak, 150 • 3.9 mm, 5 μ , chromatographic column. The mobile phase used in the elution consisted of:

- **Solvent A:** 0.1% CH₃COOH in water;
- **Solvent B:** CH₃OH;

The gradient mode used in the analysis was linear from 0% to 100% of **Solvent B** over 30 minutes. The flow rate was 1.0 mL/min.

The identification was performed by means of the identification of characteristic peaks in the mass spectrum. These are presented, for each compound expected to be present in samples, in the table B.8.2.2.3._CA-4.

Table B.8.2.2.3._CA-4: Identification of the Flufenacet and its degradation products in samples using LC-MS method – the characteristic MS peaks for each compound

Compound	Characteristic MS peak	
	Position m/z	Description
<i>Flufenacet</i>	364	Protonated pseudo-molecular ion $[M + H]^+$
	381	Peak for ammonia adduct $[M + NH_4]^+$
<i>FOE Oxalate</i>	226	Pseudo-molecular ion $[M + H]^+$
	243	Peak for ammonia adduct $[M + NH_4]^+$
<i>FOE Methylsulfide</i>	242	Pseudo-molecular ion $[M + H]^+$
<i>FOE Methylsulfone</i>	274	Protonated molecular ion $[M + H]^+$
	291	Peak for ammonia adduct $[M + NH_4]^+$
<i>FOE Methylsulfoxide</i>	258	Protonated molecular ion $[M + H]^+$
	275	Peak for ammonia adduct $[M + NH_4]^+$
<i>FOE Thioglycolate sulfoxide</i>	302	Protonated molecular ion $[M + H]^+$
<i>FOE Thioglycolate sulfide</i>	286	Pseudo-molecular ion $[M + H]^+$
	308	Sodium adduct $[M + Na]^+$
<i>FOE Alcohol</i>	212	Pseudo-molecular ion $[M + H]^+$
	229	Peak for ammonia adduct $[M + NH_4]^+$

Results and their discussion:

The test vessels containing the given systems were equilibrated in order to establish the stable aerobic/anaerobic gradient. In case of NESA test system the process lasted for 10 days and at its end the following parameters were recorded:

- temperature of the test system: $T = 20^\circ\text{C}$;
- the dissolved O₂ near surface (2 cm below water surface): 5.4 – 7.1 [mg/L];
- pH: 7.1 – 7.3;
- conductivity measured in water phase: 313 – 677 μMHO ;
- redox potential of water phase: 142 – 246 mV;
- redox potential of the sediment phase: -124 – -153 mV.

The equilibration of the vessels containing BRP test systems lasted for 6 days. At its end the following parameters were recorded:

- temperature of the test system: $T = 20^\circ\text{C}$;
- the dissolved O₂ near surface (2 cm below water surface): 5.6 – 7.0 [mg/L];
- pH: 7.0 – 7.3;
- conductivity measured in water phase: 417 – 437 μMHO ;
- redox potential of water phase: 126 – 138 mV;
- redox potential of the sediment phase: -191 – -199 mV.

The results indicate that while the conditions in the water phase were aerobic, in the sediment they were rather anaerobic.

The temperature was constantly monitored and results recorded in 7-days periods. It was demonstrated that it was on the constant level throughout the study – $T = 20 \pm 1^\circ\text{C}$. All samples were incubated without the access of light and during the sampling periods they were additionally protected by covering them with heavy demin cover pulled over the shelves.

The results of the determination of microbial activity in the test systems is presented below in the table B.8.2.2.3._CA-5. On their basis it was stated that for the NESA test system during 120-days lasting incubation in blank systems it dropped by 50% while in those treated with Flufenacet (“cold” material) by 15%. In case of the BRP test systems the decrease in microbial activity over 120-days period of incubation was 37% for the blank

systems and 12% in those treated with Flufenacet (“cold” material). On that basis it was stated that the test systems maintained their biological viability during the experiment.

Table B.8.2.2.3._CA-5: The results of the determination of the microbial viability of the test systems during the incubation period.

Kind of sample	Microbial activity in [mg CO ₂ /kg sediment • hour] obtained for the sediment of the test system:			
	NESA		BRP	
	Blank	Treated with flufenacet	Blank	Treated with flufenacet
<i>Fresh after sampling</i>	17	Not applicable	8	Not applicable
<i>DAT 0, after initial equilibration</i>	13 – 14	Not applicable	9 – 10	Not applicable
<i>DAT 120</i>	8 – 9	12 – 17	4 – 6	7

The analysis of the samples of NESA test system showed that the total recovery of radioactivity was in range 92.9 – 100.9% of the applied.

The level of mineralisation was 3.4% AR after 157 days of incubation. The NER fraction in sediment at the end of the experiment (DAT 157) in that system was 23.2% AR. Additionally at that time point 22.7% AR was the fraction extractable from the sediment while 38.1% AR was in water.

The concentration of Flufenacet in that test system declined steadily from ~100% AR at the beginning of the experiment to 27.7% AR at its end – on DAT 157. The following degradation products were detected in the whole system:

- FOE Oxalate, reaching max. 4.6% AR on DAT 157;
- FOE Sulfonic acid, reaching max. of 1.7% AR on DAT 157;
- FOE Alcohol, reaching max. of 0.7% AR on DAT 120;
- FOE Methylsulfide, reaching max. of 11.4% on DAT 157;
- FOE Methylsulfone, reaching max. of 6.4% AR on DAT 100;
- FOE Methylsulfoxide, reaching max. of 3.2% AR on DAT 157;
- FOE Thioglycolate sulfoxide, reaching max. of 2.0% AR on DAT 157.

Also recorded were eight minor fractions, of which only those having $t_R \approx 6$ min (max 3.5% AR), $t_R \approx 29$ min (max 1.8% AR) and $t_R \approx 43$ min (max 1.1% AR), surpassed 1% AR at any sampling point.

The detailed results of the analysis are presented below in numerical form in the table B.8.2.2.3._CA-6 and additionally on two figures – B.8.2.2.3._CA-4, showing the distribution of radioactivity in the test system, and B.8.2.2.3._CA-5 presenting the results of the profiling of extractable radioactivity in the system. The values reported in the table are the averages of the two replicates. RMS noticed some inconsistencies between the values reported as total for the given compartment and their counterparts representing the sums of the individual constituents. That may be due to the fact that the values reported as representing the mass balance and those that are the sums of the individual components of radioactivity in the given component were determined using different analytical method: those for the mass balance were measured using LSC, while the profiling of radioactivity was performed using chromatographic methods.

The results obtained for the sterilized samples showed that the major constituent of the extractable fraction, accounting for 75.5% AR on DAT 120 and 67.0% AR on DAT 157, was Flufenacet – 86.8% of extracted on DAT 120 and 84.2% of extracted on DAT 157.

On that basis, after comparison with the results obtained for analogous test samples, it was stated that the mechanism of transformation of Flufenacet in NESA water/sediment system was predominantly biologically-mediated. The amount of radioactivity recovered as bound residues was 23.2% AR on DAT 120 and 26.4% AR on DAT 157 what may indicate that the formation of NER fraction contributes to some extent to the dissipation of Flufenacet from the water/sediment system. Finally, the level of mineralization was very low – 0.3% AR on DAT 120 and 0.5% AR on DAT 157 what additionally indicates that the process of the degradation of Flufenacet in NESA water/sediment system is biologically mediated (it shall be indicated that in the study report it was clearly stated that the sterility of the sterilized samples was not checked during the experiment).

Table B.8.2.2.3._CA-6: The numerical results of the examination of transformation of Flufenacet in NESA water/sediment test system.

Radioactivity in the test system		% AR recorded on DAT										
		0	0.25	1	2	7	14	30	60	100	120	157
Extractable, total	Flufenacet	98.4	96.6	100.8	99.5	98.1	91.5	83.4	65.8	47.9	38.8	27.7
	FOE Oxalate	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.3	1.4	4.3	4.6
	FOE Alcohol	0.0	0.0	0.2	0.0	0.2	0.0	0.0	0.0	0.0	0.7	0.6
	FOE Sulfonic acid	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.5	1.7
	FOE Methylsulfide	0.0	0.0	0.0	0.0	0.5	1.0	2.0	6.6	8.6	9.2	11.4
	FOE Methylsulfone	0.0	0.0	0.0	0.0	0.0	0.0	0.3	4.9	6.4	4.7	5.3
	FOE Methylsulf-oxide	0.4	0.3	0.0	0.0	0.1	0.0	0.0	0.0	0.3	2.3	3.2
	FOE Thioglycolate sulfoxide	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.5	1.3	2.0
	Others	1.8	1.7	0.0	0.0	0.1	3.5	0.3	0.6	4.5	4.9	5.3
	Total	100.6	98.6	101.0	99.5	98.8	95.8	86.0	79.3	69.5	67.2	61.6
In water phase	Flufenacet	94.91	86.61	94.66	90.02	85.53	73.02	60.52	45.67	30.71	23.94	15.80
	FOE Oxalate	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.33	1.17	4.26	4.55
	FOE Alcohol	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.10	0.16
	FOE Sulfonic acid	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.52	1.65
	FOE Methylsulfide	0.00	0.00	0.00	0.00	0.00	0.00	0.00	3.36	5.41	6.32	7.95
	FOE Methylsulfone	0.00	0.00	0.00	0.00	0.00	0.00	0.00	4.12	5.06	3.84	4.35
	FOE Methylsulf-oxide	0.37	0.29	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	FOE Thioglycolate sulfoxide	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.47	1.27	2.00
	Others	1.80	1.68	0.00	0.00	0.00	3.42	0.00	0.00	3.62	3.40	2.43
	Total	97.1	88.6	94.7	90.0	85.5	76.4	60.5	54.5	46.4	43.7	38.9
In sediment, extractable	Flufenacet	3.49	9.98	6.11	9.51	12.58	18.44	22.91	20.17	17.22	14.82	11.87
	FOE Oxalate	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.18	0.00	0.00
	FOE Alcohol	0.00	0.00	0.21	0.00	0.16	0.00	0.00	0.00	0.00	0.55	0.39
	FOE Sulfonic acid	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	FOE Methylsulfide	0.00	0.00	0.00	0.00	0.45	0.96	1.97	3.27	3.15	2.90	3.46
	FOE Methylsulfone	0.00	0.00	0.00	0.00	0.00	0.00	0.31	0.76	1.36	0.86	0.93
	FOE Methylsulf-oxide	0.00	0.00	0.00	0.00	0.07	0.00	0.04	0.00	0.34	2.30	3.20
	FOE Thioglycolate sulfoxide	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Others	0.00	0.00	0.00	0.00	0.05	0.05	0.29	0.58	0.88	2.04	2.86
	Total	3.5	10.0	6.3	9.5	13.3	19.4	25.5	24.8	23.1	23.5	22.7
In sediment, NER fraction		0.3	1.0	0.6	1.5	3.3	5.8	10.9	17.5	22.8	25.9	28.5
In sediment, total		3.8	11.0	6.9	11.0	16.6	25.2	36.4	42.3	45.9	49.4	51.2
Volatile compounds	¹⁴ CO ₂	0.0	0.1	0.1	0.1	0.1	0.8	1.1	1.4	1.9	2.6	3.4
	Organic volatiles	0.0	0.0	0.0	0.0	0.1	0.1	0.1	0.2	0.2	0.2	0.2
	Sum	0.0	0.1	0.1	0.1	0.1	0.9	1.2	1.6	2.1	2.8	3.6
Total radioactivity recovered		100.9	99.9	100.6	100.1	98.3	98.1	98.9	96.0	93.9	96.5	92.9

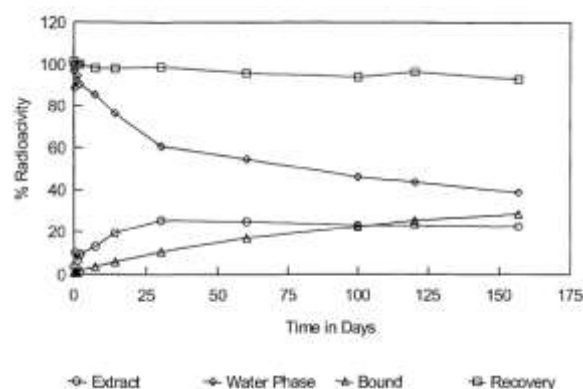


Figure B.8.2.2.3_CA-4: The distribution of radioactivity in NESA test system in function of time (copied from the study report).

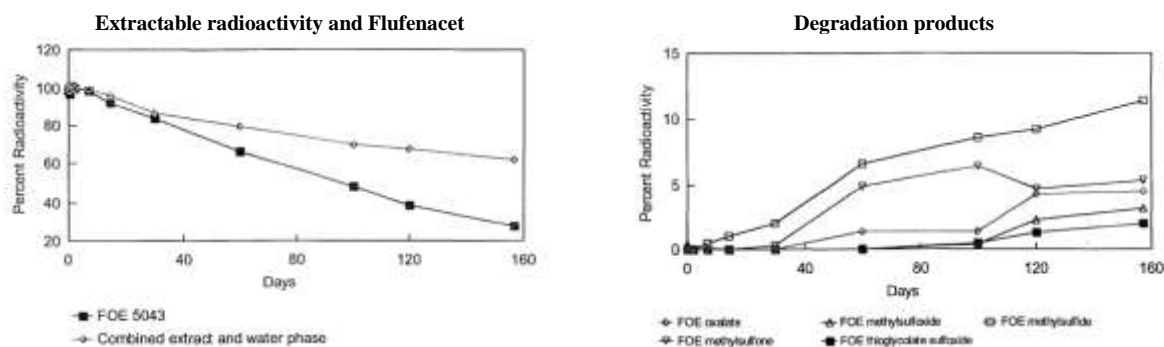


Figure B.8.2.2.3_CA-5: The results of the profiling of extractable radioactivity in NESA test system in function of time (copied from the study report).

The results obtained for Flufenacet were subjected to the kinetic analysis in order to derive the kinetic endpoints – DT_{50} and DT_{90} values for the dissipation/degradation of Flufenacet in the whole system and water phase.

The kinetic analysis was carried out using the approach developed by Timme and Frehse. As that approach is no longer considered valid in the EU for the purpose of the deriving the regulatory endpoints, RMS decided not to present the results of that analysis in the summary. The analysis of the same data, performed in line with the recommendation of FOCUS workgroup of the degradation kinetics, are presented in the **Study 3**.

The results obtained for the identified degradation products were not subjected to the kinetic analysis due to the fact that their levels were too low and some of them were still forming at the end of the study.

The analysis of the samples of BRP test system showed that the total recovery of radioactivity was in range 93.4 – 100.6% of the applied.

The level of mineralisation was 1.5% AR after 157 days of incubation. The NER fraction in sediment at the end of the experiment (DAT 157) in that system was 46.4% AR. Additionally at that time point 24.9.7% AR was the fraction extractable from the sediment while 21.9% AR was in water.

The concentration of Flufenacet in that test system declined steadily from ~100% AR at the beginning of the experiment to 22.3% AR at its end – on DAT 157. The following degradation products were detected in the whole system:

- FOE Oxalate, reaching max. 5.4% AR on DAT 157;
- FOE Sulfonic acid, reaching max. of 3.2% AR on DAT 157;
- FOE Alcohol, reaching max. of 1.3% AR on DAT 157;
- FOE Methylsulfide, reaching max. of 4.5% on DAT 157;
- FOE Methylsulfone, reaching max. of 7.2% AR on DAT 120;
- FOE Methylsulfoxide, reaching max. of 2.2% AR on DAT 120;
- FOE Thioglycolate sulfoxide, reaching max. of 1.9% AR on DAT 60.

Also recorded were eight minor fractions, none of them surpassing 1.5% AR at any sampling point.

The detailed results of the analysis are presented below in numerical form in the table B.8.2.2.3._CA-7 and additionally on two figures – B.8.2.2.3._CA-6, showing the distribution of radioactivity in the test system, and B.8.2.2.3._CA-7 presenting the results of the profiling of radioactivity in water and sediment extracts. RMS noticed some inconsistencies between the values reported as total for the given compartment and their counterparts representing the sums of the individual constituents. That may be due to the fact that the values reported as representing the mass balance and those that are the sums of the individual components of radioactivity in the given compartment were determined using different analytical method: those for the mass balance were measured using LSC, while the profiling of radioactivity was performed using chromatographic methods.

The results obtained for the sterilized samples showed that the major constituent of the extractable fraction, accounting for 67.5% AR on DAT 120 and 59.0% AR on DAT 157, was Flufenacet – 100% of extracted on DAT 120 and 94.9% of extracted on DAT 157.

On that basis, after comparison with the results obtained for analogous test samples, it was stated that the mechanism of transformation of Flufenacet in BRP water/sediment system was predominantly biologically-mediated. The amount of radioactivity recovered as bound residues was 28.2% AR on DAT 120 and 37.4% AR on DAT 157 what may indicate that the formation of NER fraction contributes to some extent to the dissipation of Flufenacet from the water/sediment system. Finally, the level of mineralization was very low – 0.1% AR on both DAT 120 and DAT 157 what additionally indicates that the process of the degradation of Flufenacet in BRP water/sediment system is biologically mediated (it shall be indicated that in the study report it was clearly stated that the sterility of the sterilized samples was not checked during the experiment).

Table B.8.2.2.3._CA-7: The numerical results of the examination of transformation of Flufenacet in BRP water/sediment test system.

Radioactivity in the test system		% AR recorded on DAT										
		0	0.25	1	2	7	14	30	60	100	120	157
Extractable, total	Flufenacet	95.5	99.8	100.2	98.0	95.4	92.0	84.1	60.9	52.6	39.1	22.3
	FOE Oxalate	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.3	2.0	0.0	5.4
	FOE Alcohol	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.7	1.3
	FOE Sulfonic acid	0.5	0.0	0.0	0.0	0.0	0.0	0.0	1.7	0.0	0.1	3.2
	FOE Methylsulfide	0.0	0.0	0.0	0.0	0.7	0.5	0.3	1.3	2.4	3.0	4.5
	FOE Methylsulfone	0.0	0.0	0.0	0.0	0.0	0.0	0.2	1.7	5.3	7.2	3.8
	FOE Methylsulf-oxide	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.0	0.0	2.2	1.7
	FOE Thioglycolate sulfoxide	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.9	0.0	0.0	1.4
	Others	1.0	0.0	0.0	0.0	0.0		0.3	0.4	0.5	2.1	3.6
	Total	96.9	99.8	100.2	98.0	96.1	92.7	84.9	70.3	62.7	54.5	47.2
In water phase	Flufenacet	95.02	90.73	91.02	88.33	74.52	65.15	49.88	28.05	24.77	18.24	7.53
	FOE Oxalate	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.32	1.98	0.00	4.83
	FOE Alcohol	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	FOE Sulfonic acid	0.49	0.00	0.00	0.00	0.00	0.00	0.00	1.73	0.00	0.00	2.95
	FOE Methylsulfide	0.00	0.00	0.00	0.00	0.54	0.51	0.00	0.80	1.20	2.67	1.88
	FOE Methylsulfone	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.68	4.27	6.50	2.92
	FOE Methylsulf-oxide	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.04	0.00	0.00	0.48
	FOE Thioglycolate sulfoxide	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.89	0.00	0.00	1.38
	Others	1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.35
	Total	96.5	90.7	91.0	88.3	75.1	65.7	49.9	36.5	32.2	27.4	22.3
In sediment, extractable	Flufenacet	0.51	9.06	9.16	9.72	20.86	26.84	34.17	32.83	27.80	20.89	14.75
	FOE Oxalate	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.59
	FOE Alcohol	0.00	0.00	0.02	0.00	0.00	0.17	0.00	0.00	0.00	0.74	1.30
	FOE Sulfonic acid	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.09	0.28
	FOE Methylsulfide	0.00	0.00	0.00	0.00	0.14	0.00	0.34	0.53	1.19	0.29	2.65
	FOE Methylsulfone	0.00	0.00	0.00	0.00	0.00	0.00	0.21	0.00	1.01	0.68	0.90
	FOE Methylsulf-oxide	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.18	1.22
	FOE Thioglycolate sulfoxide	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Others	0.00	0.00	0.00	0.00	0.00	0.00	0.28	0.39	0.53	2.25	3.17
	Total	0.5	9.1	9.2	9.7	21.0	27.0	35.0	33.8	30.5	27.1	24.9
In sediment, NER fraction		0.2	0.4	0.4	0.6	3.1	5.9	14.1	23.7	32.4	40.8	46.4
In sediment, total		0.7	9.5	9.6	10.3	24.1	32.9	49.1	57.5	62.9	67.9	70.3
Volatile compounds	¹⁴ CO ₂	0.0	0.0	0.0	0.0	0.0	0.1	0.2	0.5	0.4	0.5	1.5
	Organic volatiles	0.0	0.0	0.0	0.0	0.1	0.1	0.1	0.1	0.1	0.1	0.2
	Sum	0.0	0.0	0.0	0.0	0.1	0.2	0.3	0.6	0.5	0.6	1.7
Total radioactivity recovered		96.2	99.6	100.6	98.2	99.0	98.4	98.6	93.4	95.8	95.1	94.9

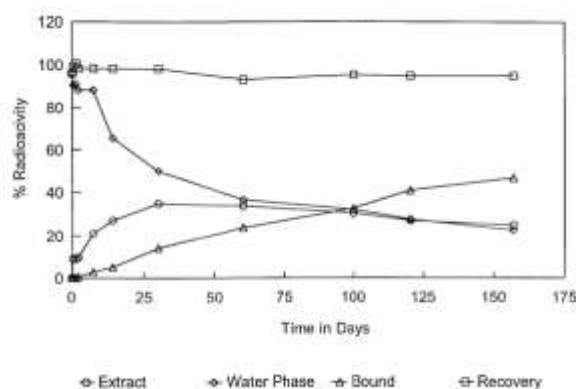


Figure B.8.2.2.3_CA-6: The distribution of radioactivity in BRP test system in function of time (copied from the study report).

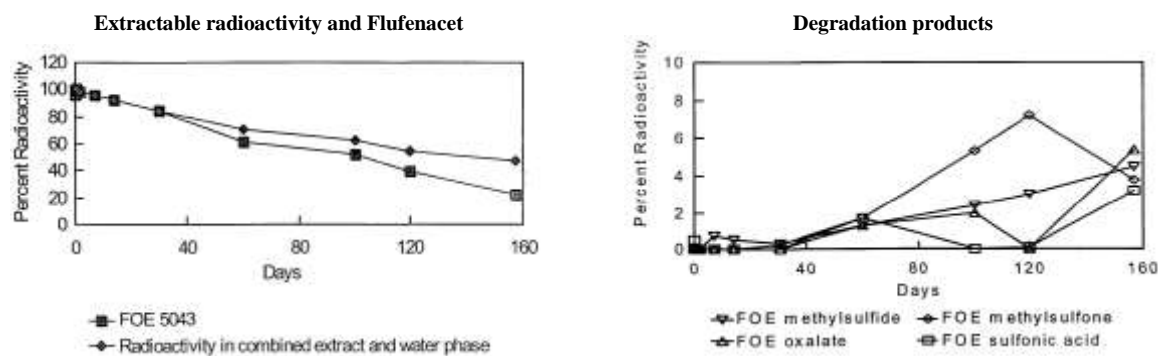


Figure B.8.2.2.3_CA-7: The results of the profiling of extractable radioactivity in BRP test system in function of time (copied from the study report).

The results obtained for Flufenacet were subjected to the kinetic analysis in order to derive the kinetic endpoints – DT_{50} and DT_{90} values for the dissipation/degradation of Flufenacet in the whole system and water phase.

The kinetic analysis was carried out using the approach developed by Timme and Frehse. As that approach is no longer considered valid in the EU for the purpose of the deriving the regulatory endpoints, RMS decided not to present the results of that analysis in the summary. The analysis of the same data, performed in line with the recommendation of FOCUS workgroup of the degradation kinetics, are presented in the *Study 3*.

The results obtained for the identified degradation products were not subjected to the kinetic analysis in this study report. Such analysis was performed by the Applicant in the *Study 3* for the identified major degradation product – FOE Methylsulfide. In RMS's opinion however it cannot be considered fully reliable (that concerns in particular the kinetic endpoints representing degradation) because of the lack of decline in one test system – NESA and only one data point representing the decline phase in the second test system – BRP. As for the other identified degradation products the kinetic analysis of the data obtained for them was not carried out due to the fact that their levels were too low and some of them were still forming at the end of the study.

Conclusions of the study:

The examination of the transformation of Flufenacet in aerobic water/sediment system showed that that compound quite quickly degraded in that environment, forming several degradation products. The mechanism of dissipation from the water phase was mixed – the compound partly degraded in that phase, but also quite significant migration to the sediment phase, where it was degraded, was observed. The degradation products, the same as identified in other studies examining the transformation of Flufenacet in the environment, were detected. One new degradation product was identified – FOE Methylsulfide, the metabolite specific only for the aquatic

environment. The degradation products were found predominantly in water phase, but their presence in the sediment phase as well may indicate that they could be formed also, if not predominantly, in sediment and from there released to the water phase.

The data for Flufenacet was kinetically examined, but that assessment was performed not in line with the current requirements, so its results were not reported. The data were kinetically re-examined, in line with the current recommendations, in a separate study.

The kinetic analysis of the data for the degradation products could not be carried out because, even when sufficient amount of data points was available, the metabolite was either still forming or its decline was in its initial phase.

On the basis of the results of the metabolite profiling the transformation scheme of Flufenacet in water/sediment system, determined for the part of the molecule containing the fluorophenyl ring was proposed. It is shown below on figure B.8.2.2.3._CA-8. The FOE Cysteine conjugate presented on the scheme in brackets is an hypotesized intermediate, postulated on the basis of the analysis of the structural formulae of the identified degradation products, in particular that of FOE Thioglycolate sulfoxide.

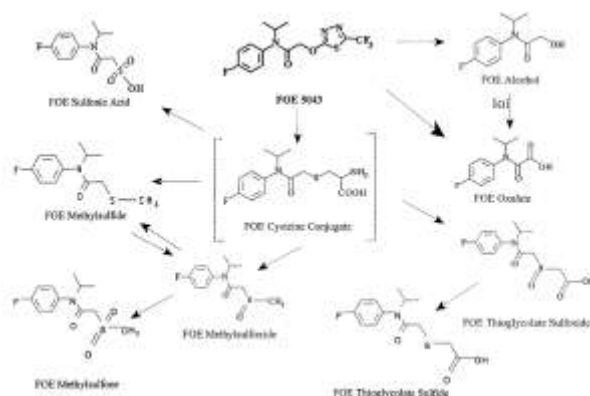


Figure B.8.2.2.3. CA-8: The postulated transformation pathway of Flufenacet in water/sediment system, determined for the part of the molecule containing the fluorophenyl ring (copied from the study report).

Study 2:

Report: Halarnkar P. P., Irwin D. W., (1997): “Degradability and Fate of [Thiadiazole-2-¹⁴C]FOE 5043 in Two Water/Sediment Systems.”; Bayer Corporation, Agriculture Division, Environmental Research, 17745 S. Metcalf, Stilwell, Kansas 66085, USA (performing laboratory) for Bayer Corporation, Agriculture Division, Research and Development Department, P. O. Box 4913, Kansas City, Missouri 64120, USA; study No. F3042406; Report No. 107822; 6 October 1997; study reference number: M-004595-01-1;

Guidelines: The study was performed to comply with the following Guidelines:

- Society of environmental Toxicology and Chemistry (SETAC-Europe) Procedures for Assessing the Environmental Fate and Ecotoxicity of Pesticides, March 1995;
- US. EPA Guidelines for Pesticide Registration, Subdivision N, Section 162-4, Aerobic Aquatic Metabolism.

GLP: Yes;

RMS comments: The study had been evaluated for the previous authorisation of Flufenacet in the EU, by its inclusion into the Annex I of the Directive 91/414/EEC. Its summary can be found in the Addenda to the Monograph for Flufenacet, e. g. Addendum to the Volume 3, Annex B issued in January 2003, under the the point B.7.4.3.2.2. These documents were prepared by the then-RMS – France, for Flufenacet. For the purpose of the current assessment the study was evaluated for its compliance with OECD Guideline 308 – Aerobic and Anaerobic Transformation in Aquatic Sediment Systems. The study was found acceptable and is summarised below. It shall be indicated however that in its part aimed on the kinetic evaluation of the results the study did not comply with the provisions of the current Guidelines, namely FOCUS Kinetics Guidance document. That assessment was performed separately and presented in the study report summarised further down this Renewal Assessment Report as *Study 3*.

Summary:

The aim of the study was to examine the fate and degradation rate of Flufenacet in two aerobic water/sediment systems.

The test compound used in the experiment was ¹⁴C-Flufenacet radiolabelled in C-2 position in the thiadiazole moiety, as shown below on figure B.8.2.2.3._CA-9. It had a specific activity 18.47 mCi/mmol. It was delivered to the test facility as vial C-573A, probably in form of solution in a not specified organic solvent.

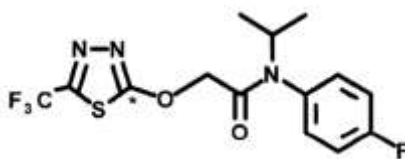


Figure B.8.2.2.3._CA-9: The structural formula of the test compound - [Thiadiazole-2-¹⁴C]Flufenacet used in the experiment; radiolabelling position is indicated by an asterisk (copied from the study report).

The test substance was used to prepare the application solution, which in turn was used to treat the test systems. The application solution was prepared by transferring the appropriate amount of the test compound into a vessel. The solvent was evaporated under the gentle stream of N₂ and the residue redissolved in the appropriate amount of CH₃CN to obtain the solution having a radiochemical purity of 98.8%.

The examination of the fate and behaviour of Flufenacet in water/sediment systems was carried out using two freshwater sediments and water associated with them. The test matrices – sediment and associated water, were sampled from the ponds located in Kansas, USA, in areas representative for the intended use of Flufenacet.

One of the ponds, from which the test matrices were sampled, was located in Nelson Environmental Study Area near Lawrence, Kansas. It was positioned near the hilltop and was surrounded by the grassland. The test systems containing that set of the test matrices in the experiment bore the codename NESA.

The second sampling pond was located at Bayer Research Park in Stilwell, Kansas and was positioned in a valley surrounded by woods. The test systems containing that set of the test matrices were codenamed in the experiment BRP.

During the sampling several parameters of the pond water were determined. These are presented below in the table B.8.2.2.3._CA-8.

Table B.8.2.2.3._CA-8: The parameters of the sampled water recorded on the sampling site.

Parameter	Test system	
	NESA	BRP
<i>Location</i>	Lawrence, KS, USA	Stilwell, KS, USA
<i>Temperature [°C]</i>	12	15
<i>Dissolved oxygen [ppm]</i>	5.6	10.0
<i>pH</i>	8.8	7.6
<i>Redox potential [mV]</i>	150	158

The samples of sediment and associated water were taken to the test facility, where they were stored overnight at $T = 4^{\circ}\text{C}$ and the next day processed. The processing of the test matrices consisted on sieving the sediments through 2-mm sieve to remove larger skeletal elements and passing water through a 0.2-mm sieve to remove larger plant parts.

The subsamples of so prepared test matrices were taken for characterisation. Its results – the physicochemical and biological parameters of sediment and associated water for each test system, are presented below in the table B.8.2.2.3._CA-9.

Table B.8.2.2.3._CA-9: The physicochemical and biological parameters of water and sediment phases of each test system.

Matrix	Parameter	Test system	
		NESA	BRP
Water	<i>pH</i>	7.2	6.9
	<i>Conductivity [mmhos]</i>	0.32	0.48
	<i>Total dissolved solids [ppm]</i>	220	300
	<i>Turbidity [NTU]</i>	15.6	2.96
	<i>Ca content [ppm]</i>	30	71
	<i>Mg content [ppm]</i>	9	5
	<i>Hardness [mg equivalents CaCO_3/L]</i>	114	197
	<i>Redox potential [mV]</i>	379.9	308.1
	<i>total N [ppm]</i>	8	10
	<i>total P [ppm]</i>	2	2
	<i>OC content [ppm]</i>	331	415
	<i>Dissolved O_2 [ppm]</i>	8.0	8.5
Sediment	<i>Textural class (USDA)</i>	Silty Clay	Silty clay loam
	<i>Particle size distribution</i>	Sand %	3.6
		Silt %	56.0
		Clay %	40.4
	<i>OM content [%]</i>	0.65	2.66
	<i>OC content [%] (recalculated by RMS)</i>	0.38	1.54
	<i>pH (measured in H_2O)</i>	7.8	7.8
	<i>CEC [meq/100g]</i>	22.00	13.02
	<i>Bulk density [g/cm^3]</i>	1.37	1.19
	<i>Moisture content at $\frac{1}{3}$ bar [%]</i>	39.41	37.57
	<i>Microbial activity [mg C/100 g sediment]</i>	1.18	21.41

Analysing the properties of each test system RMS noticed that the sediment in NESA test system displayed very low OC content – below the lower limit of 0.5% recommended for the sediments with low OC content. That however had probably no significant impact on the results of the study, therefore the stated deviation is acceptable.

The experiment was performed using 500-mL reagent bottles as the test vessels. To each of them 75-g (d.w.) aliquot of the given sediment was weighed. Next, it was carefully covered with 300 mL of the associated water. The so prepared test bottles were closed and attached to the flow-through system, presented below (for each individual test vessel) on figure B.8.2.2.3._CA-10. They were then preincubated for 7 days before being treated with the test compound, in the climatic walk-in chamber, in the darkness under the constant temperature $T = 20 \pm 1^\circ\text{C}$.

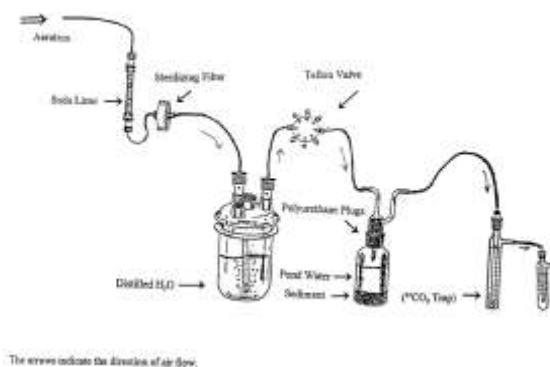


Figure B.8.2.2.3._CA-10: The schematic presentation of the incubation flow-through system used in the experiment (copied from the study report).

After pre-equilibration 25 test vessels containing NESAs water/sediment system and another 25 test vessels with BRP water/sediment system were treated with the application solution of ^{14}C -Flufenacet at application rate 0.250 ppm in water, what corresponded to a field application rate of 750 g/ha, assuming 30-cm depth of the water column. That was done by adding 438 μL of the application solution, containing 75 μg of ^{14}C -Flufenacet onto the water surface in each test vessel. After treatment the test vessels were re-attached to their flow-through systems in the incubation chamber and incubated there for up to 156 days.

Additionally, for each test system 5 test vessels were treated with the non-radiolabelled Flufenacet at application rate 75 μg /test vessels for biomass control. 5-7 vessels containing the same test systems were incubated alongside the treated vessels as blank controls.

The test vessels were aerated with continuous air-flow from a pressurized air tank. The air administered to each test vessel were sterilised and moisturised before reaching it.

The main trap for volatile compound in each flow-through system was filled with 3:7 v/v mixture of monoethanolamine:ethylene glycol. It was followed by the secondary trap, containing the same filling, set to trap the volatiles in case of the oversaturation or overflow of the primary trap.

At pre-designated sampling points the duplicate test vessels for each water/sediment test system and each type of samples were taken for the analysis. In case of the test samples the sampling points were set at DAT (DAT stands for Days After Treatment): 0, 7, 14, 28, 55, 100 and 156.

In case of the control samples for biomass determination the sampling points were set to DAT 0, DAT 65 and DAT 156.

After removal from the incubation chamber each test vessel was purged for 15 – 20 minutes with a gentle stream of N_2 administered at a rate 40 mL/min to transfer all volatile compounds remaining in the head space into the traps for volatile compounds. Then the samples were processed in line with the procedure presented below on figure B.8.2.2.3._CA-11.

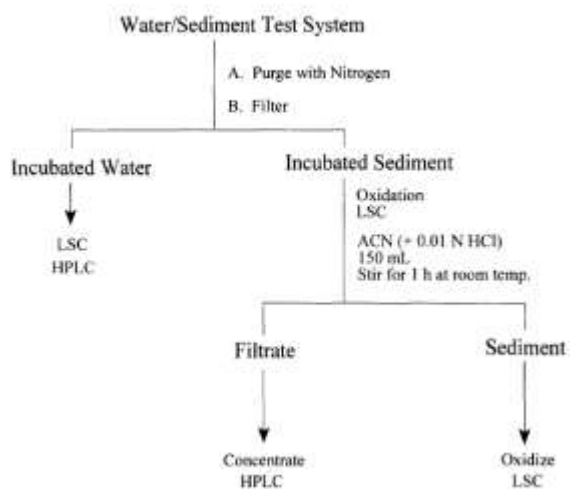


Figure B.8.2.2.3._CA-11: The conceptual scheme of the sample processing procedure (copied from the study report).

The radioactivity in samples was quantified by LSC. The measurements were performed using a Packard Tri-Carb Model 4640 LS counter.

The average volume of analysed sample was 0.5-mL and it was mixed with 10 mL of Ultima Gold LS cocktail and 2 mL of water. The minimum sensitivity of LSC analysis for those samples was 6.0 E-4 ppm. When expressed as Lowest Acceptable Gross Count Rate (LAGC) it was 64 cpm, while as Lowest Acceptable Net Count Rate (LANC) – 32 cpm, assuming average background (BCGK) of 32 cpm (LAGC = 2*BCGK and LANC = LAGC – BCGK). The greatest probable error GPE = 9.2%. The counting lasted for 5 minutes.

In case of the solid samples, the amount taken for analysis was 0.2 g. It was oxidised and the formed $^{14}\text{CO}_2$ absorbed in a mixture of 6 mL Carbo-sorb and 15 mL Perma Fluor E⁺. The minimum sensitivity of LSC analysis for those samples was 1.6 E-3 ppm. When expressed as Lowest Acceptable Gross Count Rate (LAGC) it was 64 cpm, while as Lowest Acceptable Net Count Rate (LANC) – 32 cpm, assuming average background (BCGK) of 32 cpm (LAGC = 2*BCGK and LANC = LAGC – BCGK). The greatest probable error GPE = 9.2%. The counting lasted for 5 minutes.

The chromatographic methods used in the study were HPLC and LC-MS/ESI.

The HPLC method was used to analyse pond water and sample extracts for the content of the parent compound and its degradation products.

It was carried out on HP 1090 chromatograph coupled with an UV-detector set to $\lambda = 254$ nm and radioactivity detector (Raytest Ramona). The chromatographic separation was performed in a gradient mode on the RP ODS chromatographic column (Phenomenex, Econex-sil, 10 μ , 250 • 4.6 mm), preceded by an RP-18, 30 • 4.6 mm, guard column. The mobile phase used in the elution consisted of:

- **Solvent A:** 0.4% CH_3COOH in water;
- **Solvent B:** 0.4% CH_3COOH in CH_3CN ;

The gradient mode used in the analysis is presented below in the table B.8.2.2.3._CA-10. The flow rate was 1.0 mL/min.

Table B.8.2.2.3._CA-10: The HPLC gradient mode used in the study.

Time [min]	Solvent ratio	
	<i>Solvent A – Water + 0.4% CH_3COOH</i>	<i>Solvent B – Acetonitrile + 0.4% CH_3COOH</i>
0	80	20
50	0	100
60	0	100

The quantitative analysis was performed by means of the external standards of known concentration and the identification of the fractions by comparing their retention times – R_t , with those of the known standards. They were following:

- for Flufenacet the $R_t = 32.2$ min;
- for FOE-Thiadone the $R_t = 16.3$ min.

The LC-MS/ESI analysis was performed on the CONSTAMETRIC 3500/3200 HPLC coupled with TSQ 700 triple quadrupole mass spectrometer. The chromatographic separation was performed in a gradient mode on the Zorbax ODS, 150 • 4.6 mm chromatographic column. The mobile phase used in the elution consisted of:

- **Solvent A:** 0.1% HCOOH in water;
- **Solvent B:** CH₃OH;

The gradient mode used in the analysis is presented below in the table B.8.2.2.3._CA-11. The flow rate was 0.8 mL/min.

Table B.8.2.2.3._CA-11: The HPLC gradient mode used in the study.

Time [min]	Solvent ratio	
	<i>Solvent A – Water + 0.1% HCOOH</i>	<i>Solvent B – CH₃OH</i>
0	95	5
1	95	5
15	0	100
22	0	100
23	95	5
30	95	5

The identification was performed by means of the identification of characteristic peaks in the mass spectrum, which were following:

- for Flufenacet m/z 364 [amu] - Protonated [M + 1] molecular ion;
- for FOE-Thiadone m/z 169 – deprotonated [M-1] molecular ion.

Additionally, at each sampling point the content of the dissolved oxygen, pH and the redox potential was determined in the collected samples.

Results and their discussion:

The results of the measurements of pH, dissolved O₂ and redox potential in samples are presented below in the table B.8.2.2.3._CA-12. On their basis it was stated that the aerobic conditions were maintained in the test systems throughout the study duration. The temperature was maintained at the constant level throughout the study – $T = 20 \pm 1^\circ\text{C}$. All samples were incubated without the access of light and during the sampling periods they were additionally protected.

Table B.8.2.2.3._CA-12: The results of the monitoring of pH, redox potential and O₂ content in incubated samples during the experiment.

Sampling time point	Replicate	Results obtained in NESA test system			Results obtained in BRP test system		
		pH	Redox potential [mV]	Dissolved O ₂ [mg/L]	pH	Redox potential [mV]	Dissolved O ₂ [mg/L]
0	1	7.4	171	3.2	7.3	155	3.1
	2	7.4	177	3.1	7.3	148	2.7
	3	7.4	175	3.3	7.4	151	3.0
7	1	7.2	114	2.7	6.9	131	1.8
	2	7.7	169	0.3	6.9	130	0.3
14	1	7.6	181	2.3	6.9	139	3.2
	2	7.5	196	2.4	7.1	138	3.5
28	1	7.9	125	3.0	7.9	125	2.9
	2	7.7	123	3.0	8.0	127	3.4
55	1	7.9	94	0.8	7.9	84	2.3
	2	7.8	62	1.1	8.0	97	4.1
100	1	7.6	151	3.8	7.1	121	3.1
	2	7.0	135	2.7	7.2	120	0.9
156	1	5.8	223	1.5	6.7	219	2.2
	2	6.3	203	3.7	6.8	220	1.3

The results of the determination of microbial activity in the test systems are presented below in the table B.8.2.2.3._CA-13. On their basis it was stated that the test systems maintained their biological viability during the experiment.

Table B.8.2.2.3._CA-13: The results of the determination of the microbial viability of the test systems during the incubation period.

Sampling time point	Microbial biomass in [mg C/100 g sediment] obtained for the sediment of the test system:			
	NESA		BRP	
	Blank	Treated with flufenacet	Blank	Treated with flufenacet
DAT 0	1.18	Not applicable	21.41	Not applicable
DAT 65	6.83	7.19	16.41	18.97
DAT 156	5.15	6.97	17.29	25.77

The analysis of the samples of NESA test system showed that the total recovery of radioactivity was in range 89.6 – 99.0% of the applied.

The level of mineralisation was 15.3% AR after 156 days of incubation. The NER fraction in sediment at the end of the experiment (DAT 156) in that system was 2.2% AR. Its maximum level was 3.3% AR recorded on DAT 55.

The concentration of Flufenacet in that test system declined steadily from 94.2% AR at the beginning of the experiment to 0.6 – 0.9% AR at its end. One degradation product was identified – FOE-Thiadone, reaching maximum of 84.3% AR on DAT 55.

The detailed results of the analysis are presented below in numerical form in the table B.8.2.2.3._CA-14. The values reported in the table are the averages of the two replicates. Additionally RMS recalculated the concentrations of Flufenacet and FOE Thiadone in water and sediment extracts to express them in % AR as in the study report they were presented as % in the fraction.

Table B.8.2.2.3._CA-14: The numerical results of the examination of transformation of Flufenacet in NESA water/sediment test system.

Radioactivity in the test system		% AR recorded on DAT						
		0	7	14	28	55	100	156
<i>Extractable, total</i>	Flufenacet	94.2	87.9	65.2	42.1	5.0	0.6	0.9
	FOE Thiadone	0.0	0.6	18.8	51.3	84.3	81.7	68.7
	Others	1.4	1.7	8.4	1.0	0.4	6.5	2.5
	Total	95.6	90.2	92.4	94.4	89.7	88.8	72.1
<i>In water phase</i>	Flufenacet	83.9	75.2	55.2	36.9	3.1	0.0	0.0
	FOE Thiadone	0.0	0.5	18.4	50.2	81.8	80.0	65.5
	Others	1.0	1.9	8.2	1.0	0.2	6.1	2.4
	Total	84.9	77.5	82.2	88.0	85.0	86.1	68.0
<i>In sediment, extractable</i>	Flufenacet	10.4	12.4	10.1	5.1	2.0	0.6	1.0
	FOE Thiadone	0.02	0.3	0.3	1.2	2.4	1.7	3.0
	Others	0.4	0.1	0.1	0.1	0.3	0.4	0.1
	Total	10.8	12.8	10.5	6.4	4.7	2.7	4.1
<i>In sediment, NER fraction</i>		2.2	2.9	3.2	2.8	3.3	2.0	2.2
<i>In sediment, total</i>		13.0	15.7	13.7	9.2	8.0	4.7	6.3
<i>Volatile compounds</i>	¹⁴ CO ₂	0.0	0.0	0.0	0.5	6.0	5.1	15.3
	Organic volatiles	0.0	0.0	0.0	0.1	0.0	0.0	0.0
	Sum	0.0	0.0	0.0	0.6	6.0	5.1	15.3
Total radioactivity recovered		97.9	93.2	95.9	97.8	99.0	95.9	89.6

The results obtained for Flufenacet were subjected to the kinetic analysis in order to derive the kinetic endpoints – DT₅₀ and DT₉₀ values for the dissipation/degradation of Flufenacet in the whole system and water phase.

The kinetic analysis was carried out using the approach developed by Timme and Frehse. As that approach is no longer considered valid in the EU for the purpose of the deriving the regulatory endpoints, RMS decided not to present the results of that analysis in the summary. The analysis of the same data, performed in line with the recommendation of FOCUS workgroup of the degradation kinetics, are presented in the *Study 3*.

The results obtained for the identified degradation products were not subjected to the kinetic analysis, neither performed by the Applicant nor by the RMS. That was due to the fact that the decline phase consisted only of the two data points, in RMS's opinion too few to obtain the reliable kinetic endpoints.

The analysis of the samples of BRP test system showed that the total recovery of radioactivity was in range 82.7 – 100.5% of the applied.

The level of mineralisation was 15.0% AR after 156 days of incubation. The NER fraction in sediment at the end of the experiment (DAT 156) in that system was 7.5% AR. Its maximum level was 9.6% AR recorded on DAT 100.

The concentration of Flufenacet in that test system declined steadily from 96.3% AR at the beginning of the experiment to 3.3% AR at its end – on DAT 156. One degradation product was identified – FOE-Thiadone, reaching maximum of 63.8% AR on DAT 100.

The detailed results of the analysis are presented below in numerical form in the table B.8.2.2.3._CA-15. The values reported in the table are the averages of the two replicates. Additionally RMS recalculated the concentrations of Flufenacet and FOE Thiadone in water and sediment extracts to express them in % AR as in the study report they were presented as % in the fraction.

Table B.8.2.2.3._CA-15: The numerical results of the examination of transformation of Flufenacet in BRP water/sediment test system.

Radioactivity in the test system		% AR recorded on DAT						
		0	7	14	28	55	100	156
<i>Extractable, total</i>	Flufenacet	96.3	91.8	75.6	65.4	41.0	11.1	3.3
	FOE Thiadone	0.2	0.6	12.7	22.6	44.0	63.8	54.2
	Others	1.3	1.1	2.9	1.0	0.7	2.6	2.8
	Total	97.8	93.5	90.8	89.0	87.6	77.5	60.3
<i>In water phase</i>	Flufenacet	83.2	69.9	49.7	46.8	25.1	4.0	0.9
	FOE Thiadone	0.0	0.1	8.9	20.0	41.4	60.0	52.2
	Others	1.3	0.7	2.7	0.4	0.3	2.5	2.7
	Total	84.5	70.7	61.3	67.2	66.8	66.5	55.8
<i>In sediment, extractable</i>	Flufenacet	12.2	21.8	26.1	18.7	15.9	7.1	2.3
	FOE Thiadone	0.1	0.7	3.5	2.5	2.5	3.8	1.9
	Others	0.1	0.4	0.3	0.6	0.4	0.2	0.1
	Total	12.4	22.9	29.9	21.8	18.8	11.1	4.4
<i>In sediment, NER fraction</i>		2.7	5.1	5.9	8.3	8.1	9.6	7.5
<i>In sediment, total</i>		15.1	28.0	35.8	30.1	26.9	20.7	11.9
<i>Volatile compounds</i>	¹⁴ CO ₂	0.0	0.0	0.0	0.5	3.8	5.1	15.0
	Organic volatiles	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Sum	0.0	0.0	0.0	0.5	3.8	5.1	15.0
Total radioactivity recovered		100.5	98.7	97.1	97.8	97.5	92.3	82.7

The results obtained for Flufenacet were subjected to the kinetic analysis in order to derive the kinetic endpoints – DT₅₀ and DT₉₀ values for the dissipation/degradation of Flufenacet in the whole system and water phase.

The kinetic analysis was carried out using the approach developed by Timme and Frehse. As that approach is no longer considered valid in the EU for the purpose of the deriving the regulatory endpoints, RMS decided not to present the results of that analysis in the summary. The analysis of the same data, performed in line with the recommendation of FOCUS workgroup of the degradation kinetics, are presented in the *Study 3*.

The results obtained for the identified major degradation product – FOE Thiadone were not subjected to the kinetic analysis performed by the Applicant. RMS however is of the opinion that that analysis, and the kinetic endpoints in particular, is of the limited reliability because of too few data points representing the decline phase – one or two after maximum was reached, depending on the test system.

Conclusions of the study:

The examination of the transformation of Flufenacet in aerobic water/sediment system showed that that compound quite quickly degraded in that environment, forming one degradation degradation product – FOE Thiadone – the same as identified in other studies with Flufenacet radiolabelled in that position. The mechanism of dissipation from the water phase was mixed – the compound partly degraded in that phase, but also quite significant migration to the sediment phase, where it was degraded, was observed.

FOE Thiadone was found predominantly in water phase, but its presence in the sediment phase as well may indicate that it was possibly formed also, if not predominantly, in sediment and from there released to the water phase.

The data for Flufenacet was kinetically examined, but that assessment was performed not in line with the current requirements, so its results were not reported. The data were kinetically re-examined, in line with the current recommendations, in a separate study.

The kinetic analysis of the data for the identified degradation product – FOE Thiadone, could not be carried out because of the too few data points at the decline phase (one or two, depending on the test system).

On the basis of the results of the metabolite profiling the transformation scheme of Flufenacet in water/sediment system, determined for the part of the molecule containing the thiadiazole moiety was proposed. It is shown below on figure B.8.2.2.3._CA-12. It shall be indicated that the proposed transformation pathway may not fully cover all processes occurring within the thiadiazole moiety. That is due to the fact that the thiadiazole ring contains two possible radiolabelling positions – C2, examined in this study does, and C5, which was not covered by this study.

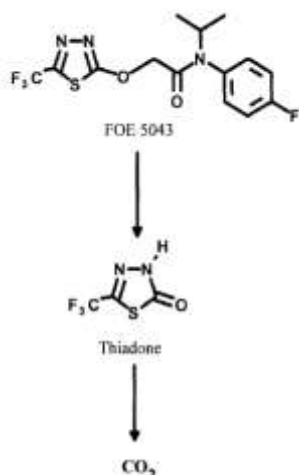


Figure B.8.2.2.3._CA-12: The postulated transformation pathway of Flufenacet in water/sediment system, determined for the part of the molecule containing the thiadiazole moiety (copied from the study report).

RMS, further analysing the proposed metabolic pathway, also in light of the results obtained in other studies aimed on the elucidation of the transformation pattern of Flufenacet within the thiadiazole moiety, came to the conclusions presented below.

It may be assumed, with high probability, that radiolabelling at C5 position would lead to the identification of at least one other major degradation product – TFA (Trifluoroacetic acid). That compound, as indicated by the results of the study on the degradation of Flufenacet at C5 in the thiadiazole ring, could be formed either directly from Flufenacet or from FOE Thiadone as its immediate precursor. That second option seems to be more probable in light of the results of this study – FOE Thiadone was observed in amounts well above 50% AR, up to ~85% AR. Therefore, on the analysis of the available results it may be anticipated that were the fate and behaviour in water/sediment system of [Thiadiazole-5-¹⁴C]Flufenacet examined using the same test systems, for the same study duration up to 50% AR could be observed in form of TFA. It cannot be excluded that for the study lasting longer than 156 days the amount of TFA formed in the test system could be even higher, up to 100% of the applied amount of the parent compound.

Also, taking into consideration the results of the transformation in water/sediment systems obtained for Flufenacet radiolabelled in phenyl ring, it cannot be excluded the formation of another, possibly major degradation product – TFESA.

However, all that theoretical analysis needs to be confirmed by the experimental data, hence in RMS's opinion the lack of the examination of the fate and behavior of [Thiadiazole-5-¹⁴C]Flufenacet (or FOE-Thiadone radiolabelled in the same position) should be considered as a potential data gap.

Study 3:

Report: Reinken G., Maassen K., (2014): “Kinetic Evaluation of Degradation and Dissipation Behaviour of Flufenacet and its Degradation Products in Water/Sediment Systems According to FOCUS Kineitics Using the KinGUI 2 Tool. Flufenacet (FOE 5043); FOE Methylsulfide; FOE-thiadone.”; Bayer CropScience AG, Environmental Safety, Alfred-Nobel-Strasse 50, 40789 Monheim, Germany; Study report No. En-Sa-13-0973; 17. 02. 2014; study reference number: M-477845-01-1.

Guidelines: The study was performed to comply with the following Guidelines:

- FOCUS (2006): “Guidance Document on Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration.”; Report of the Work Group on Degradation Kinetics, EC Document Reference SANCO/10058/2005, version 2.0, 434 pp.;
- FOCUS (2011): “Generic Guidance for Estimating Persistence and Degradation Kinetics from Environmental Fate Studies in EU Registration, version 1.0, 436 pp.

GLP: No, not required – modelling study;

RMS comments: This is a newly submitted study, evaluated for the purpose of the current assessment. RMS evaluated it for its compliance with the Guidelines listed as the reference Guidelines. The analysis was performed in line with the recommendations given by FOCUS Work Group on Degradation Kinetics. In case of the parent compound – Flufenacet, it was performed on the Level P-I for the whole system and for each compartment individually. That analysis was verified and was found acceptable by the RMS.

Due to the fact that the results of the kinetic analysis performed at Level P-I individually for each compartment were subsequently used as supporting information in the decision making process aimed on the determination of the appropriate kinetic endpoints to be used as input data in SW modelling, RMS decided to repeat the analysis at the Level P-II in order to verify the correctness of the Applicant’s proposal.

The results of the additional kinetic examination of the data performed by the RMS will be presented immediately below the presentation of the results of the kinetic analysis performed by the Applicant.

The kinetic analysis of the data for the two identified major degradation products – FOE Methylsulfide and FOE Thiadone, were performed at the Level M-I and for the whole system only. The fitting was performed for parent compound – Flufenacet, and for the given degradation product. The results of that analysis will be presented further down the summary, below the whole set of the results of the analysis for the parent compound performed by the Applicant and RMS.

The study, after the thorough examination, was found acceptable and is summarised below.

Summary:

The aim of the study was to perform the kinetic analysis of the data obtained for Flufenacet and its two major aquatic degradation products – FOE Methylsulfide and FOE Thiadone, in water/sediment systems examined in two different studies – by [Kelley et al; 1995] and by [Halarankar and Irwin; 1997], to obtain the kinetic endpoints representing persistence and those suitable for modelling exposure assessment.

The assessment was carried out for Flufenacet at the Level P-I and was aimed on the determination of the persistence endpoints as well as those suitable for SW modelling. The kinetic analysis of the data for the degradation products was performed at the Level M-I and was aimed on the determination of the kinetic endpoints for them.

The brief characteristic of the water/sediment test systems used in the source studies is presented below in the table B.8.2.2.3._CA-16.

Table B.8.2.2.3._CA-16: The brief characteristic of the water/sediment test systems used in data-source studies.

Compartment	Parameter	Study by [Kelley et al.; 1995]		Study by [Halarnkar and Irwin; 1997]	
		Test system: NESAs	Test system: BRP	Test system: NESAs	Test system: BRP
Water	pH	7.5	7.3	7.2	6.9
	Conductivity [mmhos]	0.17	0.24	0.32	0.48
	Redox potential [mV]	259	296	15.6	308.1
	Total dissolved solids [ppm]	82	120	220	300
	Dissolved O ₂ [ppm]	9.2	8.5	8.0	8.5
Sediment	Textural class (USDA)	Silty clay loam	Silty clay loam	Silty clay	Silty clay loam
	pH	7.9	7.8	7.8	7.8
	OC [%]	0.7	1.4	0.38	1.54
	CEC [meq/100g]	33.5	25.6	39.41	37.57

The non-processed input data used in the kinetic analysis are presented below, separately for each test system, in tables B.8.2.2.3._CA-17 – B.8.2.2.3._CA-20.

Table B.8.2.2.3._CA-17: The non-processed data obtained in the study by [Kelley et al.; 1995] in NESAs water/sediment system, used as input in kinetic analysis.

Time Point – DAT ¹⁾ [days]	Concentration of Flufenacet, expressed as [% AR], in:			Concentration of FOE Methylsulfide, expressed as [% AR], in:			Total AR recovered [%]
	Whole system	Water phase	Sediment phase	Whole system	Water phase	Sediment phase	
0	98.4	94.91	3.49	0.00	0.00	0.00	100.9
0.25	96.6	86.61	9.98	0.00	0.00	0.00	99.9
1	100.8	94.66	6.11	0.00	0.00	0.00	100.6
2	99.5	90.02	9.51	0.00	0.00	0.00	100.1
7	98.1	85.53	12.58	0.5	0.00	0.45	98.3
14	91.5	73.02	18.44	1.0	0.00	0.96	98.1
30	83.4	60.52	22.91	2.0	0.00	1.97	98.9
60	65.8	45.67	20.17	6.6	3.36	3.27	96.0
100	47.9	30.71	17.22	8.6	5.41	3.15	93.9
120	38.8	23.94	14.82	9.2	6.32	2.9	96.5
157	27.7	15.80	11.87	11.4	7.95	3.46	92.9

Footnotes to the table:

1) DAT stands for “Days After Treatment”;

Table B.8.2.2.3._CA-18: The non-processed data obtained in the study by [Kelley et al.; 1995] in BRP water/sediment system, used as input in kinetic analysis.

Time Point – DAT ¹⁾ [days]	Concentration of Flufenacet, expressed as [% AR], in:			Concentration of FOE Methylsulfide, expressed as [% AR], in:			Total AR recovered [%]
	Whole system	Water phase	Sediment phase	Whole system	Water phase	Sediment phase	
0	95.5	95.02	0.51	0.00	0.00	0.00	96.20
0.25	99.8	90.73	9.06	0.00	0.00	0.00	99.60
1	100.2	91.02	9.16	0.00	0.00	0.00	100.60
2	98.0	88.33	9.72	0.00	0.00	0.00	98.20
7	95.4	74.52	20.86	0.7	0.54	0.14	99.00
14	92.0	65.15	26.84	0.5	0.51	0.00	98.40
30	84.1	49.88	34.17	0.3	0.00	0.34	98.60
60	60.9	28.05	32.83	1.3	0.80	0.53	93.40
100	52.6	24.77	27.80	2.4	1.20	1.19	95.80
120	39.1	18.24	20.89	3.0	2.67	0.29	95.10
157	22.3	7.53	14.75	4.5	1.88	2.65	94.90

Footnotes to the table:

1) DAT stands for “Days After Treatment”;

Table B.8.2.2.3._CA-19: The non-processed data obtained in the study by [Halarnkar and Irwin; 1997] in NESAs water/sediment system, used as input in kinetic analysis.

Time Point – DAT ¹⁾ [days]	Concentration of Flufenacet, expressed as [% AR], in:			Concentration of FOE Thiadone, expressed as [% AR], in:			Total AR recovered [%]
	Whole system	Water phase	Sediment phase	Whole system	Water phase	Sediment phase	
0	94.2	83.88	10.42	0	0.00	0.02	97.9
7	87.9	75.18	12.42	0.6	0.47	0.29	93.2
14	65.2	55.16	10.06	18.8	18.41	0.35	95.9
28	42.1	36.87	5.10	51.3	50.16	1.18	97.8
55	5.0	3.06	1.96	84.3	81.77	2.45	99.0
100	0.6	0.00	0.60	81.7	79.99	1.73	95.9
156	0.9	0.00	0.95	68.7	65.66	3.05	89.6

Footnotes to the table:

1) DAT stands for “Days After Treatment”;

Table B.8.2.2.3._CA-20: The non-processed data obtained in the study by [Halarnkar and Irwin; 1997] in BRP water/sediment system, used as input in kinetic analysis.

Time Point – DAT ¹⁾ [days]	Concentration of Flufenacet, expressed as [% AR], in:			Concentration of FOE Thiadone, expressed as [% AR], in:			Total AR recovered [%]
	Whole system	Water phase	Sediment phase	Whole system	Water phase	Sediment phase	
0	96.3	84.12	12.21	0.2	0.00	0.15	100.5
7	91.8	69.92	21.78	0.6	0.14	0.66	98.7
14	75.6	49.71	26.10	12.7	8.89	3.53	97.1
28	65.4	46.84	18.68	22.6	19.96	2.46	97.8
55	41.0	25.05	15.94	44.0	41.42	2.50	97.5
100	11.1	3.99	7.13	63.8	59.98	3.80	92.3
156	3.3	0.89	2.35	54.2	52.23	1.92	82.7

Footnotes to the table:

1) DAT stands for “Days After Treatment”;

The data presented in the above tables were subjected to a multistep evaluation procedure performed in line with the recommendations of FOCUS Kinetics Guidelines [FOCUS; 2006].

For the parent compound it was performed at the Level P-I and consisted of the following steps:

- **Step 1:** Processing of the raw input data;
- **Step 2:** Kinetic evaluation of the processed data, separately for each compartment, using following, 1st - order, kinetic models: SFO, FOMC, DFOP and HS, and KinGUI 2 as a modelling tool. That step consisted of the three sub-steps:
 - **Sub-step 1:** kinetic evaluation of the data for the whole system;
 - **Sub-step 2:** kinetic evaluation of the data for the water phase alone;
 - **Sub-step 3:** kinetic evaluation of the data for the sediment phase alone using the top-down approach and the data set limited to the time points after the maximum was reached;
- **Step 3:** Evaluation of the results of kinetic examination of the data;
- **Step 4:** Reporting of the obtained results, in particular kinetic parameters recommended for modelling.

The raw input data for Flufenacet, presented in tables B.8.2.2.3._CA-17 – B.8.2.2.3._CA-20, were processed following the recommendations given by FOCUS. In general terms it looked as follows:

- The total AR recovery recorded in DAT-0 samples was used as concentration of Flufenacet at that time point, but the M_0 value was allowed to be estimated by the model;
- Values between LOD and LOQ were set to measured values;
- All single values <LOD or the non-detects (n. d.) were set to ½LOD. The same procedure was applied to the first appearances. However, when the values <LOD/n.d. appeared consecutively for second and next times, the kinetic curve was cut off until the appearance of the first value >LOQ;
- Sampling times for sediment phases were shifted, starting with the time point DAT 0 at the day of the maximum measured concentration of Flufenacet.
- For the whole system the pre-processed values in water and sediment compartments were summed up and used as the input.

The processed values used as input data for the kinetic examination are presented below in two separate tables – in the table B.8.2.2.3._CA-21 for the results from the study by [Kelley et al.; 1995] and in the table B.8.2.2.3._CA-22 for those obtained in the study by [Halarnkar and Irwin; 1997]. In case of the values <LOD they were set to NaN (“Not a Number” – KinGUI default when numbers are not available).

Table B.8.2.2.3._CA-21: The processed residue data for Flufenacet from the study by [Kelley et al.; 1995].

Water/sediment test system	The values for the compartment:					
	Whole system		Water phase		Sediment phase	
	Time point - DAT	Concentration of Flufenacet – [% AR]	Time point - DAT	Concentration of Flufenacet – [% AR]	Time point – Days after maximum	Concentration of Flufenacet – [% AR]
NESA	0	100.90	0	100.9	----	----
	0.25	96.59	0.25	86.61	----	----
	1	100.77	1	94.66	----	----
	2	99.53	2	90.02	----	----
	7	98.11	7	85.53	----	----
	14	91.46	14	73.02	----	----
	30	83.43	30	60.52	0	22.91
	60	65.84	60	45.67	30	20.17
	100	47.93	100	30.71	70	17.22
	120	38.76	120	23.94	90	14.82
BRP	157	27.67	157	15.80	127	11.87
	0	96.20	0	96.20	----	----
	0.25	99.79	0.25	90.73	----	----
	1	100.18	1	91.02	----	----
	2	98.05	2	88.33	----	----
	7	95.38	7	74.52	----	----
	14	91.99	14	65.15	----	----
	30	84.05	30	49.88	0	34.17
	60	60.88	60	28.05	30	32.83
	100	52.57	100	24.77	70	27.80
	120	39.13	120	18.24	90	20.89
	157	22.28	157	7.53	127	14.75

Table B.8.2.2.3._CA-22: The processed residue data for Flufenacet from the study by [Halarnkar and Irwin; 1997].

Water/sediment test system	The values for the compartment:					
	Whole system		Water phase		Sediment phase	
	Time point - DAT	Concentration of Flufenacet – [% AR]	Time point - DAT	Concentration of Flufenacet – [% AR]	Time point – Days after maximum	Concentration of Flufenacet – [% AR]
NESA	0	97.90	0	97.90	----	----
	7	87.59	7	75.18	0	12.42
	14	65.22	14	55.16	7	10.06
	28	41.97	28	36.87	21	5.10
	55	5.02	55	3.06	48	1.96
	100	0.65	100	0.05	93	0.60
BRP	156	0.95	156	NaN	149	0.95
	0	100.50	0	100.50	----	----
	7	91.70	7	69.92	0	26.10
	14	75.82	14	49.71	7	18.68
	28	65.52	28	46.84	21	15.94
	55	40.99	55	25.05	48	7.13
	100	11.12	100	3.99	93	2.35
	156	3.25	156	0.89	149	

The processed data were kinetically examined using KinGUI ver. 2 modelling tool, developed by Bayer. The optimisation was performed using IRLS (Iteratively Reweighed Nonlinear Least Squares) algorithm. The fitting procedure was a two-stage one. At first stage – **Step 1**, the performance of the two kinetic models – SFO and FOMC, was examined. In case the SFO returned visually and statistically better results than FOMC, the fitting exercise was stopped at that stage. In case however FOMC returned better fit The Applicant passed to the second stage – **Step 2**. At this stage two additional bi-phasic models – DFOP and HS, were tested.

It shall be indicated that the analysis at both stages was performed in order to derive the persistence endpoints, while the determination of the modelling endpoints focused rather on the results of **Step-1** analysis.

The obtained results of the kinetic analysis of the data were evaluated by the Applicant. That was done by means of a detailed statistical analysis, comprising the following components:

- visual assessment of the fit;
- χ^2 -error statistics;
- t-test significance;
- correlation analysis.

Characterising the whole procedure the Applicant stated at the beginning that it is generally preferred to select the simplest kinetic model with a high goodness of fit. That principle was followed when the assessment of the results obtained at the **Step 1** of kinetic analysis of the data was carried out.

Characterising the adopted approach to the visual assessment of the fit, considered to be the first step in the evaluation, the Applicant stated that it focused on the following features:

- the conformity of the fitted decline curve with measured residue concentrations;
- the distribution of the residuals, which should be random and not systematic;
- level of residuals, which should be as small as possible – in such case even if their distribution is rather systematic, the fit may be still qualified as acceptable.

Based on these criteria the fit could be classified as:

- **good fit**, when the conformity of the kinetic curve and measured residues was good, levels of residuals were low, they were randomly scattered and no obvious systematic deviation in residual plot was visible;
- **acceptable fit**, when the conformity of the kinetic curve and measured residues was acceptable, levels of residuals were medium and they were more-or-less randomly scattered, and the absolute level of residuals was low;
- **poor fit**, when the fitted decline curve significantly deviated from the measured residues and did not match the observed pattern, the level of residuals was high and they were clearly not randomly scattered around zero line.

Characterising the next component of the assessment – χ^2 -error statistics, the Applicant indicated that 15% threshold value was not considered to be an absolute cut-off criterion. It was therefore indicated that in some cases, even though χ^2 -error > 15%, the fit may be acceptable, in particular for the deradation products.

Finally, characterising the t-test, the Applicant stated that the t-test probability of 0.05 was sufficiently small and should be used as acceptability criterion, in case however of degradation products, or the results of field dissipation studies the $prob > t$ value of 0.10 or even higher may be still acceptable.

On that basis the following multistep assessment procedure was followed:

- **Step 1:** bearing in mind the aim of the kinetic evaluation of the data – determination of the kinetic parameters used in as persistence and modelling endpoints, two kinetic models were tested – SFO and FOMC for passing the acceptance criteria (visually acceptable, χ^2 -error not exceeding, or not significantly exceeding, 15%, $prob. > t$ value in t-test less than 0.05 for parent and 0.10 for the degradation products), it was considered acceptable;
- **Step 2:** in case the SFO model passed the acceptance criteria and returned statistically and visually better fit than FOMC, it was considered the appropriate fit and the fitting procedure was terminated there;
- **Step 3:** if at the **Step-2** FOMC model was identified as returning better fit than SFO two additional bi-phasic models were introduced; these were DFOP and, possibly HS; they were then assessed for passing the acceptance criteria (visually acceptable, χ^2 -error not exceeding, or not significantly exceeding, 15%, $prob. > t$ value in t-test less than 0.05). The model with smaller error was indicated as the most appropriate;
- **Step 4:** if none of the bi-phasic model returned significantly improved and fully reliable fit, SFO model was selected if visually acceptable. That was done in order to avoid of an over-parameterised model based on a marginally better fit.

Analysing the proposed assessment procedure RMS stated that it complied with the procedure for determination of the kinetic endpoints for modelling, presented in FOCUS Kinetics Guidance Document [FOCUS; 2006].

The results of the kinetic examination of the data and their evaluation are provided below, individually for each test system.

- 1) The kinetic evaluation of the data obtained in the test system NESA treated with [Phenyl-U-¹⁴C]Flufenacet (study by [Kelley et al.; 1995]):

The results of the fitting are presented below, individually for each compartment.

a) Whole system:

The kinetic analysis of the whole-system data for Flufenacet was carried out using two kinetic models – SFO and FOMC. Its graphical results are presented on figure B.8.2.2.3._CA-13 and the numerical results in the table B.8.2.2.3._CA-23. Additionally, in the table B.8.2.2.3._CA-24 are provided the kinetic endpoints returned by the modelling tool for each kinetic model.

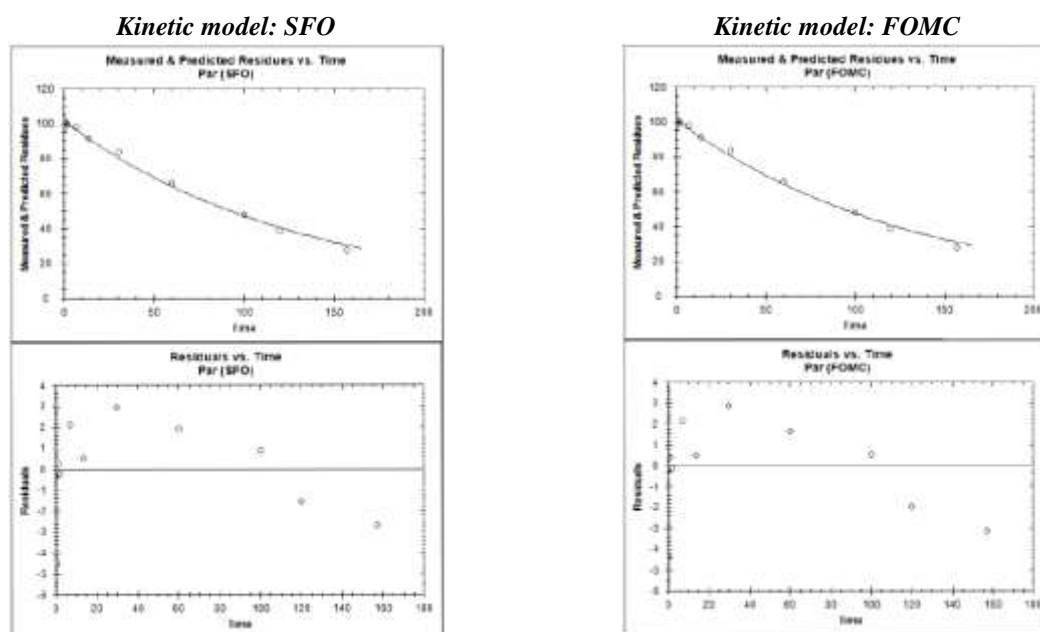


Figure B.8.2.2.3._CA-13: The graphical results of the kinetic analysis (copied from the study report).

Table B.8.2.2.3._CA-23: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	Visual assessment ¹⁾
				Lower	Upper			
SFO	M ₀	101.30	0.979	99.39	103.23	1.87 E-15	2.185	Good fit
	k	0.00767	2.72 E-4	0.00714	0.008	2.13 E-10		
FOMC	M ₀	101.15	1.065	99.07	103.20	8.42 E-14	2.306	Good fit
	α	331.79	329.80	-314.61	978.20	0.172		
	β	43732.09	43494.68	-41515.92	128980.10	0.172		

Footnotes to the table:

- 1) Visual assessment of the kinetic curve as proposed by the Applicant.

Table B.8.2.2.3._CA-24: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested	
		SFO	FOMC
Flufenacet	DT ₅₀ [days]	90.34	91.46
	DT ₉₀ [days]	300.10	304.60

Evaluation:

The Applicant stated that the SFO model returned visually and statistically better fit, therefore it was selected as adequately representing the kinetic behaviour of Flufenacet in the whole water/sediment system. RMS analysing the result noticed that FOMC fit cannot be considered acceptable, because it returned the kinetic parameters that were not reliable – for both α and β the CI passed through zero. Therefore RMS confirms the correctness of the decision made by the Applicant.

The definitive set of the kinetic endpoints determined for this experiment, representing the persistence of Flufenacet in the whole water/sediment system and suitable to derive the input values for modelling, is following: the rate of degradation $k = 0.00767$ [days⁻¹], $DT_{50} = 90.34$ days, $DT_{90} = 300.10$ [days], kinetic model: **SFO**.

b) Water phase:

The kinetic analysis of the data for Flufenacet in the water phase was carried out using two kinetic models – SFO and FOMC. Its graphical results are presented on figure B.8.2.2.3._CA-14 and the numerical results in the table B.8.2.2.3._CA-25. Additionally, in the table B.8.2.2.3._CA-26 are provided the kinetic endpoints returned by the modelling tool for each kinetic model.

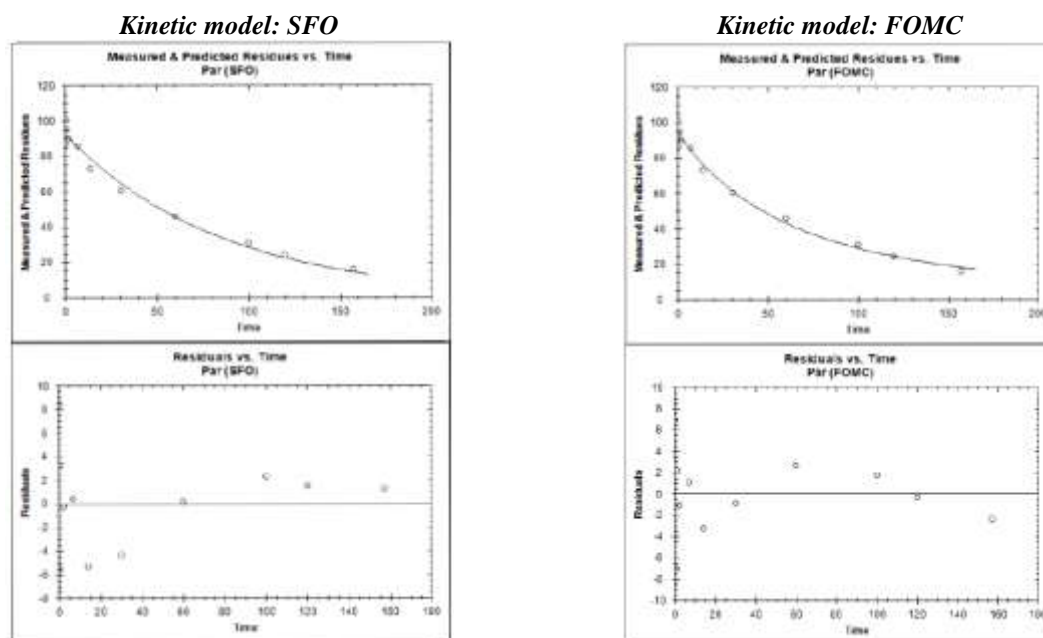


Figure B.8.2.2.3._CA-14: The graphical results of the kinetic analysis (copied from the study report).

Table B.8.2.2.3._CA-25: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	Visual assessment ¹⁾
				Lower	Upper			
SFO	M_0	92.45	1.925	88.68	96.23	1.84 E-12	4.936	Good fit
	k	0.0118	0.000868	0.0101	0.014	1.31 E-7		
FOMC	M_0	93.96	2.351	89.36	98.57	8.44 E-11	4.519	Good fit
	α	2.179	1.599	-0.954	5.313	0.105		
	β	139.359	131.199	-117.787	396.504	0.160		

Footnotes to the table:

1) Visual assessment of the kinetic curve as proposed by the Applicant.

Table B.8.2.2.3._CA-26: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested	
		SFO	FOMC
Flufenacet	DT ₅₀ [days]	58.72	52.18
	DT ₉₀ [days]	195.10	261.50

Evaluation:

The Applicant stated that the SFO model returned visually and statistically better fit, therefore it was selected as adequately representing the kinetic behaviour of Flufenacet in the water phase of the test system. RMS analysing the result noticed that FOMC fit cannot be considered acceptable, because it returned the kinetic parameters that were not reliable – for both α and β the CI passed through zero. Therefore RMS confirms the correctness of the decision made by the Applicant.

The definitive set of the kinetic endpoints determined for this experiment, representing the persistence of Flufenacet in the water phase, is following: the rate of degradation $k = 0.0118 \text{ [days}^{-1}\text{]}$, DT₅₀ = **58.72 days**, DT₉₀ = **195.10 [days]**, kinetic model: **SFO**. The Applicant also proposed to consider them as reliable modelling endpoints. RMS however noticed that the dissipation of Flufenacet from the water phase comprised both degradation of that compound and its migration to the sediment phase. The experiments on abiotic degradation of Flufenacet in water – aqueous hydrolysis and photolysis, showed that these processes contributed only to the limited extent to the degradation of Flufenacet in water, the only really relevant process being indirect photolysis. Also the biologically-mediated degradation in that compartment was demonstrated to be slow. On that basis it shall be indicated that without further verification the Applicant's proposal with regard to the suitability of the derived kinetic endpoints for modelling cannot be accepted. That verification was performed by the RMS and its results are presented further down this summary.

c) Sediment:

The kinetic analysis of the data for Flufenacet in the sediment phase was carried out using two kinetic models – SFO and FOMC. Its graphical results are presented on figure B.8.2.2.3._CA-15 and the numerical results in the table B.8.2.2.3._CA-27. Additionally, in the table B.8.2.2.3._CA-28 are provided the kinetic endpoints returned by the modelling tool for each kinetic model.

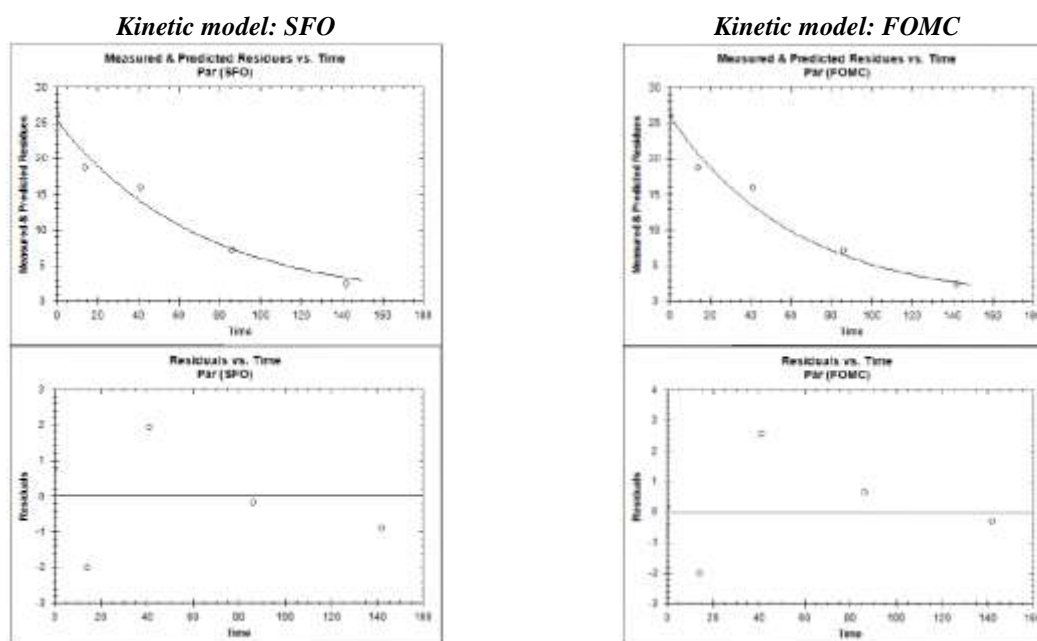


Figure B.8.2.2.3._CA-15: The graphical results of the kinetic analysis (copied from the study report).

Table B.8.2.2.3._CA-27: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	Visual assessment ¹⁾
				Lower	Upper			
SFO	M ₀	23.23	0.491	22.27	24.19	1.04 E-4	2.079	Good fit
	k	0.00493	0.000343	0.00426	0.006	0.000366		
FOMC	M ₀	23.66	0.585	22.51	24.80	0.000305	2.925	Poor fit
	α	371.30	811.200	-1219.00	1961.28	0.3460		
	β	6921.00	151300.00	-227400.00	365801.00	0.3461		

Footnotes to the table:

1) Visual assessment of the kinetic curve as proposed by the Applicant.

Table B.8.2.2.3._CA-28: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested	
		SFO	FOMC
Flufenacet	DT ₅₀ [days]	140.50	129.30
	DT ₉₀ [days]	466.80	430.50

Evaluation:

The Applicant stated that the SFO model returned visually and statistically better fit, therefore it was selected as adequately representing the kinetic behaviour of Flufenacet in sediment phase of the test system. RMS analysing the result noticed that FOMC fit cannot be considered acceptable, because it returned the kinetic parameters that were not reliable – for both α and β the CI passed through zero. Therefore RMS conforms the correctness of the decision made by the Applicant.

The definitive set of the kinetic endpoints determined for this experiment, representing the persistence of Flufenacet in the water phase, is following: the rate of degradation $k = 0.00493$ [days⁻¹], DT₅₀ = 140.50 days, DT₉₀ = 466.80 [days], kinetic model: SFO. The Applicant also proposed to consider them as reliable modelling endpoints. RMS however is of the opinion that that proposal may require further verification. That verification was performed by the RMS and its results are presented further down this summary.

Conclusions:

The kinetic analysis performed at the Level P-I of the data obtained for Flufenacet, radiolabelled in fluorophenyl ring, in the NESA water sediment system resulted in the following set of the kinetic endpoints:

- for the whole system: the rate of degradation $k = 0.00767$ [days⁻¹], DT₅₀ = 90.34 days, DT₉₀ = 300.10 [days], kinetic model: SFO; the kinetic endpoints represent the persistence of Flufenacet in that compartment and are suitable to derive the input values for SW modelling;
- for the water phase: the rate of degradation $k = 0.0118$ [days⁻¹], DT₅₀ = 58.72 days, DT₉₀ = 195.10 [days], kinetic model: SFO; the kinetic endpoints represent the persistence of Flufenacet in that compartment;
- for the sediment phase: the rate of degradation $k = 0.00493$ [days⁻¹], DT₅₀ = 140.50 days, DT₉₀ = 466.80 [days], kinetic model: SFO; the kinetic endpoints represent the persistence of Flufenacet in that compartment.

- 2) The kinetic evaluation of the data obtained in the test system **BRP** treated with [Phenyl-U-¹⁴C]Flufenacet (study by [Kelley et al.; 1995]):

The results of the fitting are presented below, individually for each compartment.

- a) Whole system:

The kinetic analysis of the whole-system data for Flufenacet was carried out using two kinetic models – SFO and FOMC. Its graphical results are presented on figure B.8.2.2.3._CA-16 and the numerical results in the table B.8.2.2.3._CA-29. Additionally, in the table B.8.2.2.3._CA-30 are provided the kinetic endpoints returned by the modelling tool for each kinetic model.

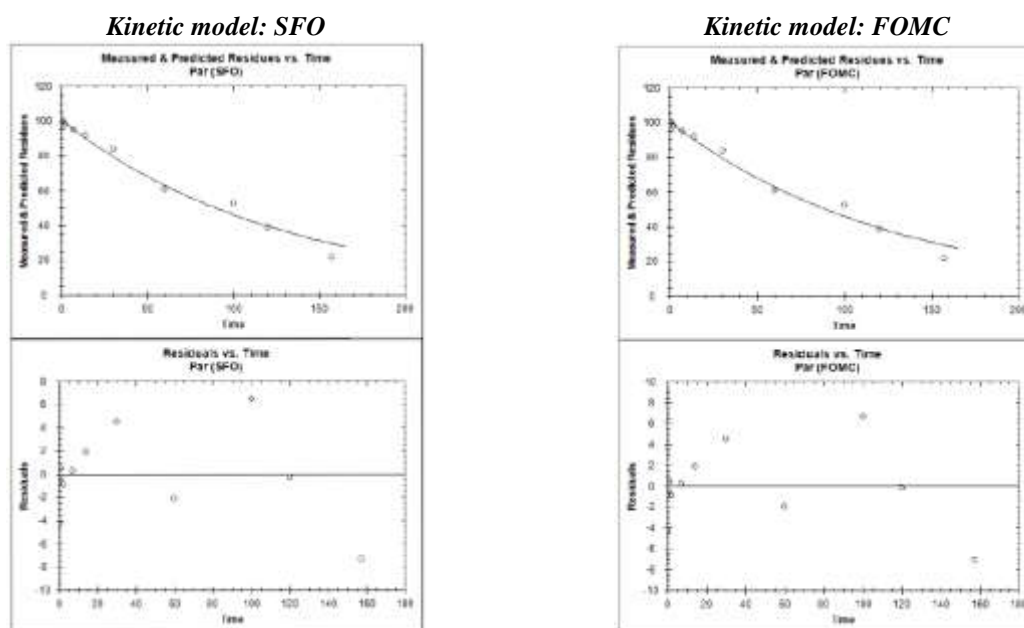


Figure B.8.2.2.3._CA-13: The graphical results of the kinetic analysis (copied from the study report).

Table B.8.2.2.3._CA-29: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	Visual assessment ¹⁾
				Lower	Upper			
SFO	M ₀	100.40	1.663	97.17	103.69	2.36 E-13	3.804	Good
	k	0.00779	0.000470	0.00687	0.009	2.38 E-8		
FOMC	M ₀	100.50	1.234	98.10	102.90	2.87 E-13	3.983	Good
	α	282.50	857.30	-1398.00	1962.70	0.375		
	β	36020.00	109500.00	-178500.00	250553.30	0.375		

Footnotes to the table:

- 1) Visual assessment of the kinetic curve as proposed by the Applicant.

Table B.8.2.2.3._CA-30: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested	
		SFO	FOMC
Flufenacet	DT ₅₀ [days]	89.00	88.48
	DT ₉₀ [days]	295.70	294.80

Evaluation:

The Applicant stated that the SFO model returned visually and statistically better fit, therefore it was selected as adequately representing the kinetic behaviour of Flufenacet in the whole water/sediment system. RMS analysing the result noticed that FOMC fit cannot be considered acceptable, because it returned the kinetic parameters that were not reliable – for both α and β the CI passed through zero. Therefore RMS confirms the correctness of the decision made by the Applicant.

The definitive set of the kinetic endpoints determined for this experiment, representing the persistence of Flufenacet in the whole water/sediment system and suitable to derive the input values for modelling, is following: the rate of degradation $k = 0.00779$ [days⁻¹], $DT_{50} = 89.00$ days, $DT_{90} = 295.70$ [days], kinetic model: **SFO**.

b) Water phase:

The kinetic analysis of the data for Flufenacet in the water phase was carried out using all four models – SFO, FOMC, DFOP and HS. Its graphical results are presented on figure B.8.2.2.3._CA-17 and the numerical results in the table B.8.2.2.3._CA-31. Additionally, in the table B.8.2.2.3._CA-32 are provided the kinetic endpoints returned by the modelling tool for each kinetic model.

Table B.8.2.2.3._CA-31: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Statistical evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	Visual assessment ¹⁾
				Lower	Upper			
SFO	M_0	89.99	2.510	85.07	94.91	2.53 E-11	6.808	Good
	k	0.01695	0.00182	0.01338	0.021	3.26 E-6		
FOMC	M_0	93.31	1.848	89.69	96.94	1.31 E-11	4.041	Good
	α	1.3394	0.3571	0.6396	2.039	0.00281		
	β	46.0745	18.8187	9.1905	82.959	0.02002		
DFOP	M_0	93.77	1.863	90.12	97.42	1.60 E-10	3.854	Good
	k_1	0.0741	0.0423	-0.00889	0.157	0.06179		
	k_2	0.0110	0.00247	0.00616	0.016	0.00148		
	g	0.3394	0.149	0.0472	0.632	0.02845		
HS	M_0	94.04	2.099	89.93	98.16	3.60 E-10	4.339	Poor
	k_1	0.03322	0.00788	0.0178	0.049	0.00198		
	k_2	0.01331	0.00144	0.0105	0.016	1.77 E-5		
	t_b	10.78	4.484	1.99	19.57	0.02358		

Footnotes to the table:

1) Visual assessment of the kinetic curve as proposed by the Applicant.

Table B.8.2.2.3._CA-32: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested			
		SFO	FOMC	DFOP	HS
Flufenacet	DT_{50} [days]	40.89	31.23	31.50	35.94
	DT_{90} [days]	135.80	211.00	171.60	156.80

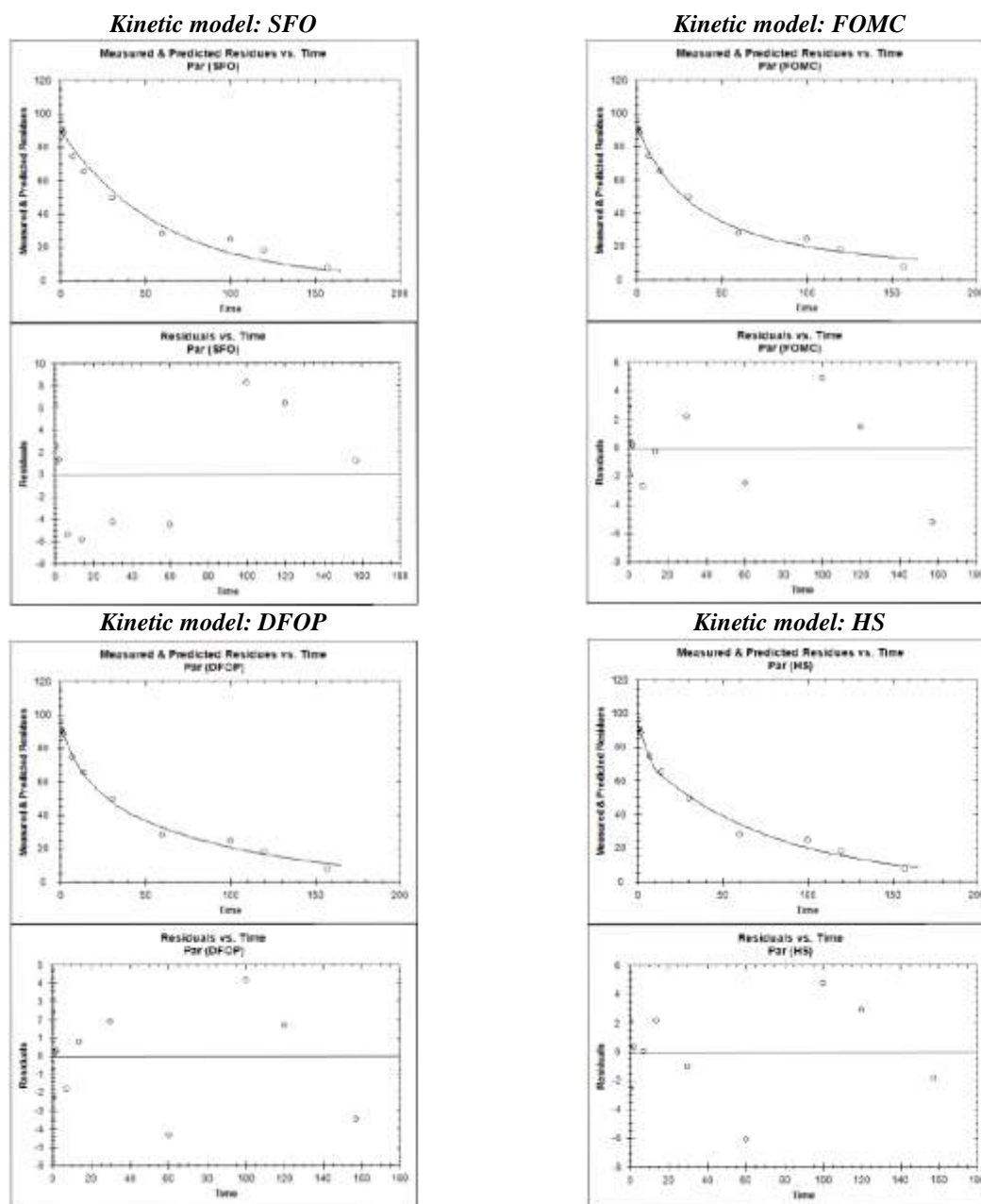


Figure B.8.2.2.3_CA-17: The graphical results of the kinetic analysis (copied from the study report).

Evaluation:

The Applicant stated when the data were fitted using the SFO and FOMC models, FOMC returned statistically better results – the χ^2 error was lower. It shall be indicated that both models tested returned reliable kinetic parameters. As a result, two additional bi-phasic models were tested – DFOP and HS. They both returned statistically better fits, that with the lowest χ^2 error being DFOP. However, the kinetic parameters returned by DFOP model were not fully reliable – the rate constant k_1 did not pass the acceptability criterion of the t-test. In case of the remaining kinetic fits the determined kinetic parameters were fully reliable. Therefore, although the Applicant indicated it as returning the best fit because of the lowest value of the χ^2 error, it cannot be considered such.

The analysis of the results performed by the RMS showed that of the three, the best in statistical terms was FOMC fit with χ^2 error being the lowest – 4.041. The Applicant indicated that the FOMC cannot be used in case

the final concentration is >10% of the initial. RMS checked that and stated that at the last time point – DAT 157, the concentration of Flufenacet in water phase was 7.53% AR. Therefore the FOMC fit shall be considered as returning the best fit.

The definitive set of the kinetic endpoints determined for this experiment, representing the persistence of Flufenacet in the water phase is following: parameters of the kinetic curve – $\alpha = 1.339$, $\beta = 46.0745$, **DT₅₀ = 31.23 days**, **DT₉₀ = 211.00 [days]**, kinetic model: **FOMC**. These parameters represent solely the dissipation of Flufenacet from the water phase.

c) Sediment:

The kinetic analysis of the data for Flufenacet in the sediment phase was carried out using two kinetic models – SFO and FOMC. Its graphical results are presented on figure B.8.2.2.3._CA-18 and the numerical results in the table B.8.2.2.3._CA-33. Additionally, in the table B.8.2.2.3._CA-34 are provided the kinetic endpoints returned by the modelling tool for each kinetic model.

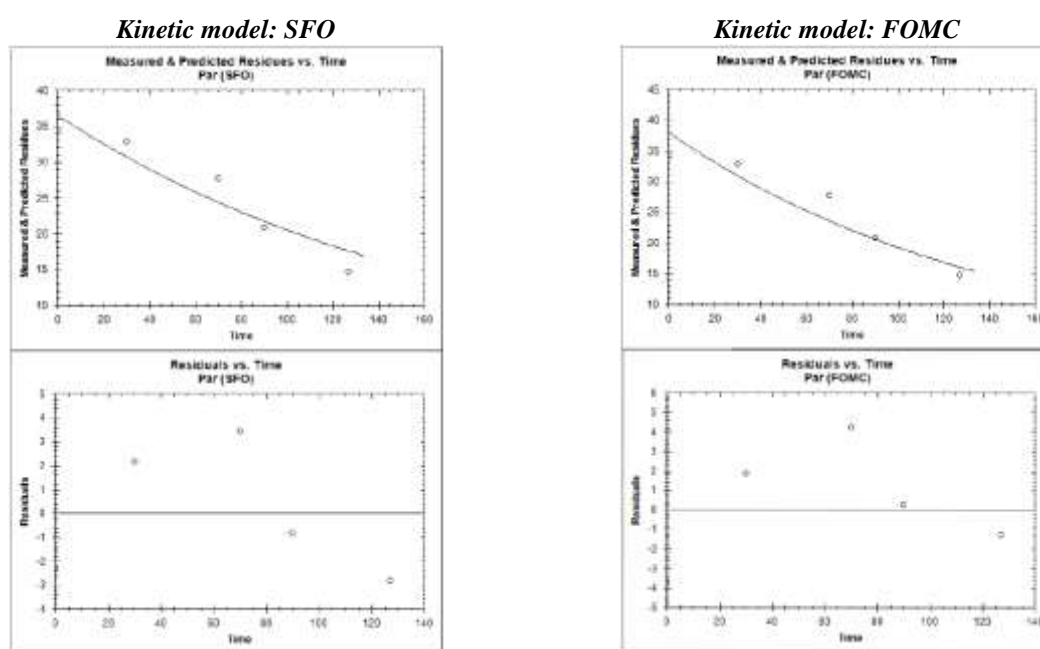


Figure B.8.2.2.3._CA-18: The graphical results of the kinetic analysis (copied from the study report).

Table B.8.2.2.3._CA-33: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	Visual assessment ¹⁾
				Lower	Upper			
SFO	M ₀	36.45	2.666	31.22	41.67	0.000423	7.534	Not given (RMS: intermediate)
	k	0.00575	0.00122	0.00336	0.008	0.009191		
FOMC	M ₀	37.94	2.630	32.79	43.09	0.00238	9.553	Not given (RMS: intermediate)
	α	354.24	839.61	-1291.36	1999.84	0.3571		
	β	52143.93	123698.30	-190300.00	294588.00	0.3572		

Footnotes to the table:

1) Visual assessment of the kinetic curve as proposed by the Applicant.

Table B.8.2.2.3._CA-34: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested	
		SFO	FOMC
Flufenacet	DT ₅₀ [days]	120.50	102.10
	DT ₉₀ [days]	400.20	340.00

Evaluation:

The Applicant stated that the SFO model returned visually and statistically better fit, therefore it was selected as adequately representing the kinetic behaviour of Flufenacet in sediment phase of the test system. RMS analysing the result noticed that FOMC fit cannot be considered acceptable, because it returned the kinetic parameters that were not reliable – for both α and β the CI passed through zero. Therefore RMS confirms the correctness of the decision made by the Applicant.

The definitive set of the kinetic endpoints determined for this experiment, representing the persistence of Flufenacet in the water phase, is following: the rate of degradation $k = 0.005754$ [days⁻¹], $DT_{50} = 120.50$ days, $DT_{90} = 400.20$ [days], kinetic model: **SFO**. The Applicant also proposed to consider them as reliable modelling endpoints. RMS however is of the opinion that that proposal may require further verification. That verification was performed by the RMS and its results are presented further down this summary.

Conclusions:

The kinetic analysis performed at the Level P-I of the data obtained for Flufenacet, radiolabelled in fluorophenyl ring, in the BRP water sediment system resulted in the following set of the kinetic endpoints:

- for the whole system: the rate of degradation $k = 0.00779$ [days⁻¹], $DT_{50} = 89.00$ days, $DT_{90} = 295.70$ [days], kinetic model: **SFO**; the kinetic endpoints represent the persistence of Flufenacet in that compartment and are suitable to derive the input values for SW modelling;
- for the water phase: parameters of the kinetic curve – $\alpha = 1.339$, $\beta = 46.0745$, $DT_{50} = 31.23$ days, $DT_{90} = 211.00$ [days], kinetic model: **FOMC**; the kinetic endpoints represent the persistence of Flufenacet in that compartment;
- for the sediment phase: the rate of degradation $k = 0.005754$ [days⁻¹], $DT_{50} = 120.50$ days, $DT_{90} = 400.20$ [days], kinetic model: **SFO**; the kinetic endpoints represent the persistence of Flufenacet in that compartment.

- 3) The kinetic evaluation of the data obtained in the test system NESA treated with [Thiadiazole-2-¹⁴C]Flufenacet (study by [Halarnkar and Irwin; 1997]):

The results of the fitting are presented below, individually for each compartment.

a) Whole system:

The kinetic analysis of the whole-system data for Flufenacet was carried out using two kinetic models – SFO and FOMC. Its graphical results are presented on figure B.8.2.2.3._CA-19 and the numerical results in the table B.8.2.2.3._CA-35. Additionally, in the table B.8.2.2.3._CA-36 are provided the kinetic endpoints returned by the modelling tool for each kinetic model.

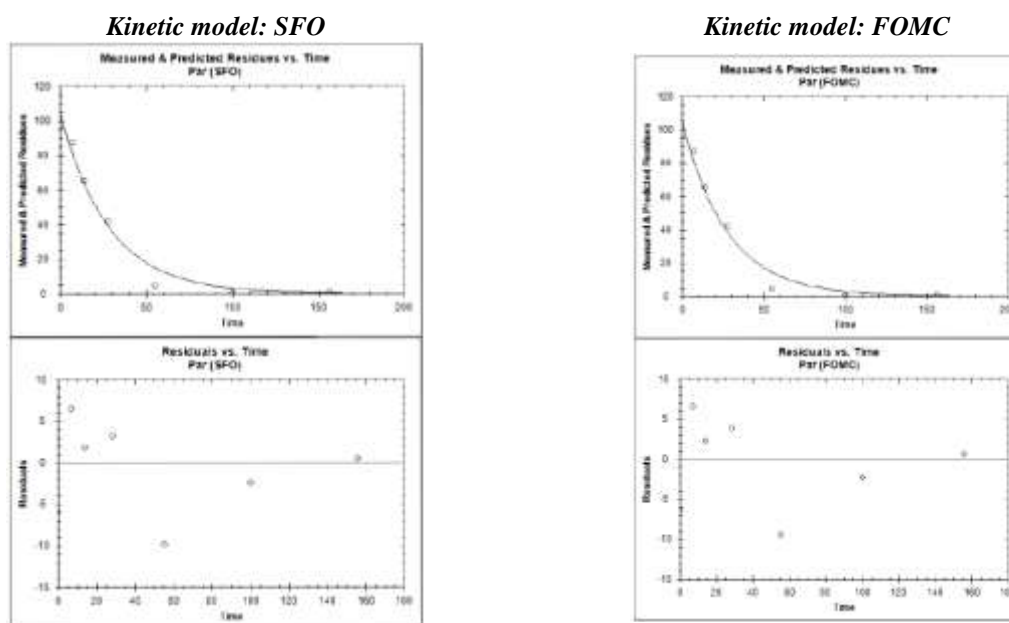


Figure B.8.2.2.3._CA-19: The graphical results of the kinetic analysis (copied from the study report).

Table B.8.2.2.3._CA-35: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	Visual assessment ¹⁾
				Lower	Upper			
SFO	M ₀	103.80	5.138	93.74	113.88	2.75 E-6	9.836	Good
	k	0.03525	0.00408	0.02726	0.043	0.000171		
FOMC	M ₀	104.30	4.097	96.26	112.30	7.07 E-6	10.67	Good
	α	853.00	3829.00	-6652.00	8357.50	0.417		
	β	23710.00	106600.00	-185200.00	232598.50	0.417		

Footnotes to the table:

- 1) Visual assessment of the kinetic curve as proposed by the Applicant.

Table B.8.2.2.3._CA-36: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested	
		SFO	FOMC
Flufenacet	DT ₅₀ [days]	19.67	19.28
	DT ₉₀ [days]	65.33	64.09

Evaluation:

The Applicant stated that the SFO model returned visually and statistically better fit, therefore it was selected as adequately representing the kinetic behaviour of Flufenacet in the whole water/sediment system. RMS analysing the result noticed that FOMC fit cannot be considered acceptable, because it returned the kinetic parameters that were not reliable – for both α and β the CI passed through zero. Therefore RMS confirms the correctness of the decision made by the Applicant.

The definitive set of the kinetic endpoints determined for this experiment, representing the persistence of Flufenacet in the whole water/sediment system and suitable to derive the input values for modelling, is following: the rate of degradation $k = 0.03525$ [days⁻¹], $DT_{50} = 19.67$ days, $DT_{90} = 65.33$ [days], kinetic model: SFO.

b) Water phase:

The kinetic analysis of the data for Flufenacet in the water phase was carried out using two kinetic models – SFO and FOMC. Its graphical results are presented on figure B.8.2.2.3._CA-20 and the numerical results in the table B.8.2.2.3._CA-37. Additionally, in the table B.8.2.2.3._CA-38 are provided the kinetic endpoints returned by the modelling tool for each kinetic model.

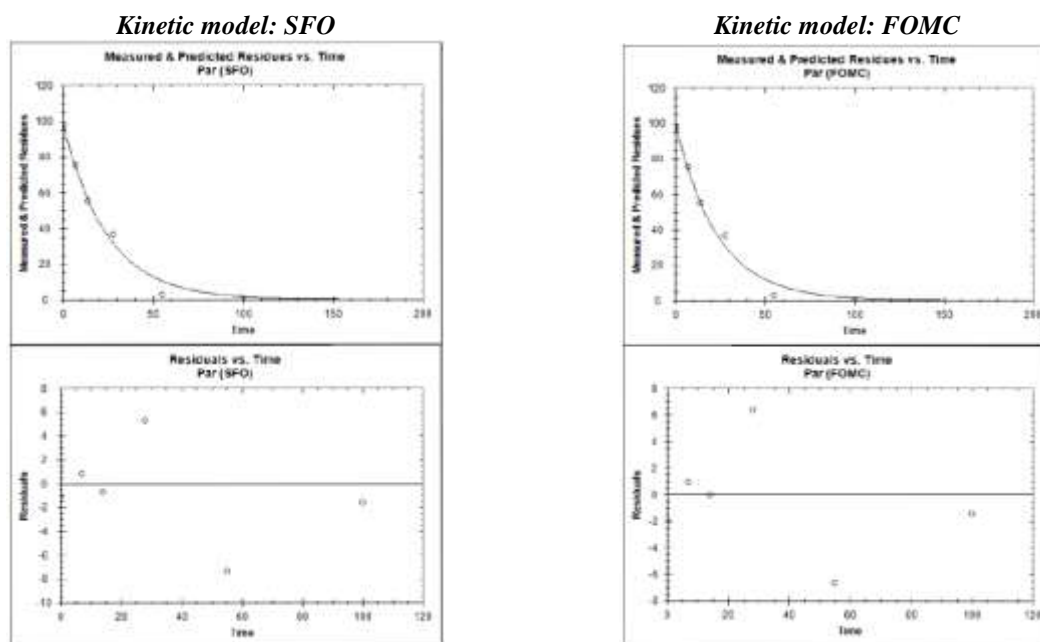


Figure B.8.2.2.3._CA-20: The graphical results of the kinetic analysis (copied from the study report).

Table B.8.2.2.3._CA-37: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	Visual assessment ¹⁾
				Lower	Upper			
SFO	M_0	98.98	4.047	91.04	106.91	8.29 E-6	6.823	Good fit
	k	0.04083	0.003883	0.03321	0.048	0.000231		
FOMC	M_0	99.88	3.887	92.26	107.50	6.45 E-5	7.673	Good fit
	α	1272.00	9015.00	-16400.00	18941.80	0.448		
	β	29990.00	212700.00	-386800.00	446782.70	0.448		

Footnotes to the table:

1) Visual assessment of the kinetic curve as proposed by the Applicant.

Table B.8.2.2.3._CA-38: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested	
		SFO	FOMC
Flufenacet	DT ₅₀ [days]	16.98	16.34
	DT ₉₀ [days]	56.40	54.33

Evaluation:

The Applicant stated that the SFO model returned visually and statistically better fit, therefore it was selected as adequately representing the kinetic behaviour of Flufenacet in the water phase of the test system. RMS analysing the result noticed that FOMC fit cannot be considered acceptable, because it returned the kinetic parameters that were not reliable – for both α and β the CI passed through zero. Therefore RMS confirms the correctness of the decision made by the Applicant.

The definitive set of the kinetic endpoints determined for this experiment, representing the persistence of Flufenacet in the water phase, is following: the rate of degradation $k = 0.04083 \text{ [days}^{-1}\text{]}$, DT₅₀ = 16.98 days, DT₉₀ = 56.40 [days], kinetic model: SFO. The Applicant also proposed to consider them as reliable modelling endpoints. RMS however noticed that the dissipation of Flufenacet from the water phase comprised both degradation of that compound and its migration to the sediment phase. The experiments on abiotic degradation of Flufenacet in water – aqueous hydrolysis and photolysis, showed these processes contributed only to the limited extent to the degradation of Flufenacet in water, the only really relevant process being indirect photolysis. Also the biologically-mediated degradation in that compartment was demonstrated to be slow. On that basis it shall be indicated that without further verification the Applicant's proposal with regard to the suitability of the derived kinetic endpoints for modelling cannot be accepted. That verification was performed by the RMS and its results are presented further down this summary.

c) Sediment:

The kinetic analysis of the data for Flufenacet in the sediment phase was carried out using two kinetic models – SFO and FOMC. Its graphical results are presented on figure B.8.2.2.3._CA-21 and the numerical results in the table B.8.2.2.3._CA-39. Additionally, in the table B.8.2.2.3._CA-40 are provided the kinetic endpoints returned by the modelling tool for each kinetic model.

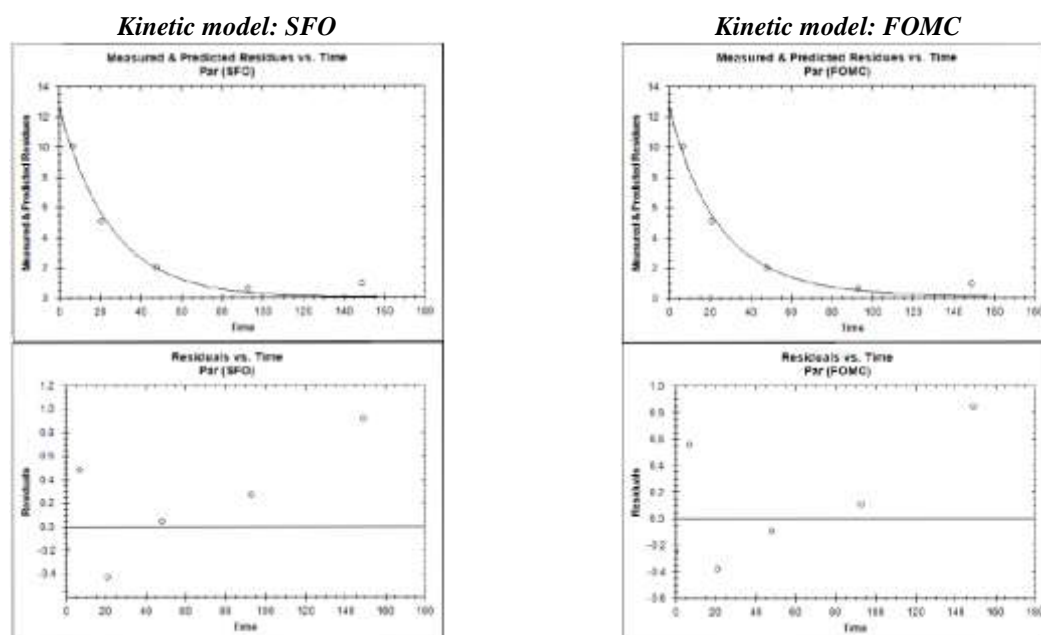


Figure B.8.2.2.3._CA-21: The graphical results of the kinetic analysis (copied from the study report).

Table B.8.2.2.3._CA-33: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	Visual assessment ¹⁾
				Lower	Upper			
SFO	M ₀	12.61	0.516	11.60	13.63	8.3 E-6	7.312	Good
	k	0.03929	0.004253	0.03095	0.048	0.000382		
FOMC	M ₀	12.67	0.571	11.55	13.79	0.0010	7.726	Good
	α	9.590	1.094	7.446	11.73	0.001564		
	β	230.119	0.9171	228.322	231.92	6.98 E-8		

Footnotes to the table:

1) Visual assessment of the kinetic curve as proposed by the Applicant.

Table B.8.2.2.3._CA-34: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested	
		SFO	FOMC
Flufenacet	DT ₅₀ [days]	17.64	17.25
	DT ₉₀ [days]	58.61	62.45

Evaluation:

The Applicant stated that the SFO model returned visually and statistically better fit, therefore it was selected as adequately representing the kinetic behaviour of Flufenacet in sediment phase of the test system. RMS analysing the results stated that both fits returned fully reliable parameters and very similar kinetic curves, therefore the factor indicating the prevalence of SFO over FOMC is the level of the χ^2 error, slightly lower in case of SFO fit (7.312 for SFO and 7.726 for FOMC). Using that criterion, in line with the recommendations of FOCUS, RMS is of the opinion that the decision made by the Applicant is correct.

The definitive set of the kinetic endpoints determined for this experiment, representing the persistence of Flufenacet in the water phase, is following: the rate of degradation $k = 0.03929$ [days⁻¹], DT₅₀ = 17.64 days, DT₉₀ = 58.61 days, kinetic model: SFO. The Applicant also proposed to consider them as reliable modelling endpoints. RMS however is of the opinion that that proposal may require further verification. That verification was performed by the RMS and its results are presented further down this summary.

Conclusions:

The kinetic analysis performed at the Level P-I of the data obtained for Flufenacet, radiolabelled at C2 in the thiadiazole ring, in the NESA water sediment system resulted in the following set of the kinetic endpoints:

- for the whole system: the rate of degradation $k = 0.03525$ [days⁻¹], DT₅₀ = 19.67 days, DT₉₀ = 65.33 [days], kinetic model: SFO; the kinetic endpoints represent the persistence of Flufenacet in that compartment and are suitable to derive the input values for SW modelling;
- for the water phase: the rate of degradation $k = 0.04083$ [days⁻¹], DT₅₀ = 16.98 days, DT₉₀ = 56.40 [days], kinetic model: SFO; the kinetic endpoints represent the persistence of Flufenacet in that compartment;
- for the sediment phase: the rate of degradation $k = 0.03929$ [days⁻¹], DT₅₀ = 17.64 days, DT₉₀ = 58.61 [days], kinetic model: SFO; the kinetic endpoints represent the persistence of Flufenacet in that compartment.

- 4) The kinetic evaluation of the data obtained in the test system **BRP** treated with [Thiadiazole-2-¹⁴C]Flufenacet (study by [Halarnkar and Irwin; 1997]):

The results of the fitting are presented below, individually for each compartment.

a) Whole system:

The kinetic analysis of the whole-system data for Flufenacet was carried out using two kinetic models – SFO and FOMC. Its graphical results are presented on figure B.8.2.2.3._CA-22 and the numerical results in the table B.8.2.2.3._CA-41. Additionally, in the table B.8.2.2.3._CA-42 are provided the kinetic endpoints returned by the modelling tool for each kinetic model.

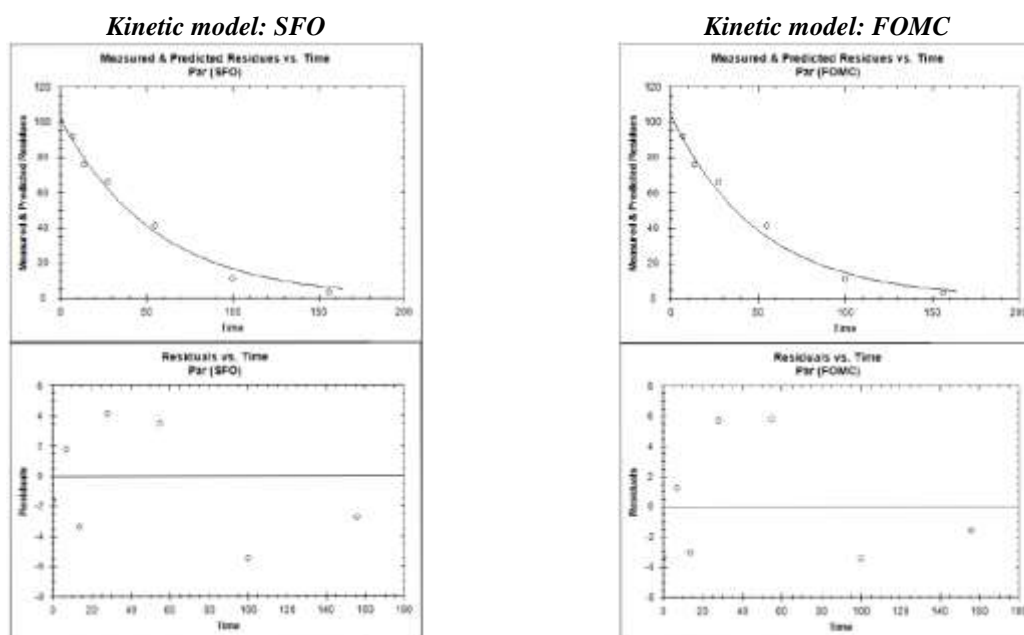


Figure B.8.2.2.3._CA-22: The graphical results of the kinetic analysis (copied from the study report).

Table B.8.2.2.3._CA-41: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	Visual assessment ¹⁾
				Lower	Upper			
SFO	M ₀	102.10	2.916	96.43	107.86	1.78 E-7	4.933	Good
	k	0.01819	0.001368	0.01551	0.021	2.15 E-5		
FOMC	M ₀	103.90	3.133	97.73	110.00	2.47 E-6	5.894	Good
	α	1685.00	3272.00	-4727.00	8097.30	0.317		
	β	85590.00	166200.00	-240200.00	411424.00	0.317		

Footnotes to the table:

- 1) Visual assessment of the kinetic curve as proposed by the Applicant.

Table B.8.2.2.3._CA-42: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested	
		SFO	FOMC
Flufenacet	DT ₅₀ [days]	38.11	35.22
	DT ₉₀ [days]	126.60	117.00

Evaluation:

The Applicant stated that the SFO model returned visually and statistically better fit, therefore it was selected as adequately representing the kinetic behaviour of Flufenacet in the whole water/sediment system. RMS analysing the result noticed that FOMC fit cannot be considered acceptable, because it returned the kinetic parameters that were not reliable – for both α and β the CI passed through zero. Therefore RMS confirms the correctness of the decision made by the Applicant.

The definitive set of the kinetic endpoints determined for this experiment, representing the persistence of Flufenacet in the whole water/sediment system and suitable to derive the input values for modelling, is following: the rate of degradation $k = 0.01819$ [days⁻¹], $DT_{50} = 38.11$ days, $DT_{90} = 126.60$ [days], kinetic model: **SFO**.

b) Water phase:

The kinetic analysis of the data for Flufenacet in the water phase was carried out using all four models – SFO, FOMC, DFOP and HS. Its graphical results are presented on figure B.8.2.2.3._CA-23 and the numerical results in the table B.8.2.2.3._CA-43. Additionally, in the table B.8.2.2.3._CA-44 are provided the kinetic endpoints returned by the modelling tool for each kinetic model.

Table B.8.2.2.3._CA-43: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Statistical evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	Visual assessment ¹⁾
				Lower	Upper			
SFO	M_0	92.25	6.597	79.32	105.18	1.68 E-5	12.50	Good
	k	0.02908	0.00556	0.01818	0.04	0.00169		
FOMC	M_0	97.55	8.075	81.72	113.38	0.000135	11.76	Good
	α	1.927	1.668	-1.342	5.196	0.1561		
	β	43.560	53.812	-61.909	149.030	0.2318		
DFOP	M_0	100.64	6.036	88.80	112.47	0.000235	8.669	Good
	k_1	0.2671	0.2536	-0.2299	0.7640	0.1848		
	k_2	0.02121	0.004594	0.01221	0.030	0.00956		
	g	0.2616	0.1166	0.03295	0.490	0.05536		
HS	M_0	100.50	6.324	88.10	112.90	0.000276	9.104	Poor
	k_1	0.1003	0.2346	-0.3595	0.560	0.3489		
	k_2	0.02239	0.004825	0.01294	0.032	0.00943		
	t_b	3.216	9.449	-15.304	21.736	0.3780		

Footnotes to the table:

1) Visual assessment of the kinetic curve as proposed by the Applicant.

Table B.8.2.2.3._CA-44: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested			
		SFO	FOMC	DFOP	HS
Flufenacet	DT_{50} [days]	23.84	18.86	18.55	19.76
	DT_{90} [days]	79.20	100.30	94.25	91.63

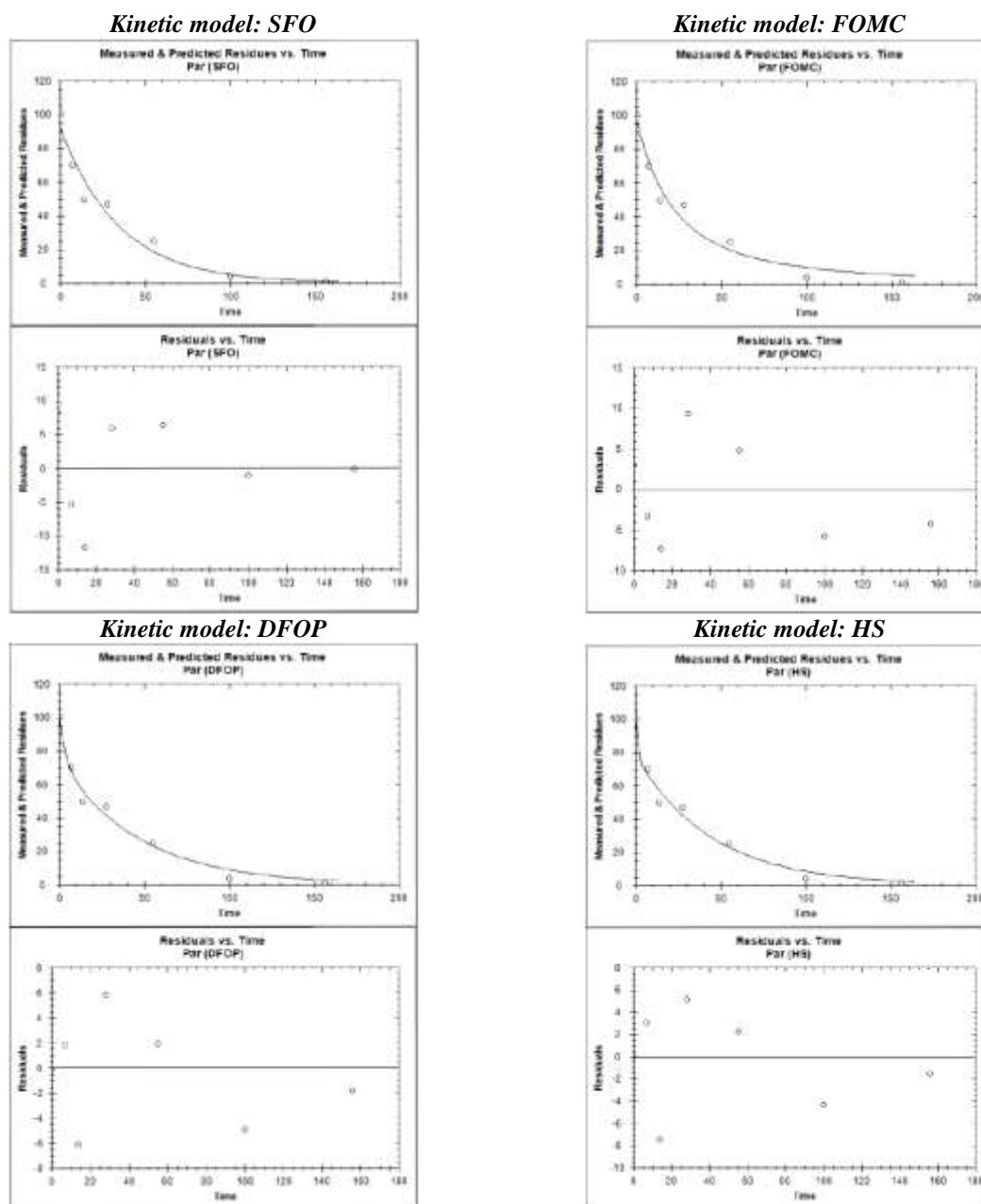


Figure B.8.2.2.3_CA-23: The graphical results of the kinetic analysis (copied from the study report).

Evaluation:

The Applicant stated when the data were fitted using the SFO and FOMC models, FOMC returned statistically better results – the χ^2 error was lower. For that reason the Applicant tested two additional bi-phasic models – DFOP and HS. RMS analysing the results of the fitting noticed that although all bi-phasic models returned statistically better fits than SFO none of them can be considered acceptable because of the lack of reliability of the kinetic parameters. In case of FOMC fit for both α and β the CI passed through zero. DFOP cannot be considered acceptable because of the lack of reliability of k_1 and g – they did not pass the acceptability criterion of the t-test. Similar problem was observed for HS fit in which of k_1 and t_b did not pass the acceptability criterion of the t-test.

Therefore the fit adequately characterising the persistence of Flufenacet in the water phase in that experiment is SFO. The Applicant proposed to consider as such the DFOP displaying the good visual fit and the lowest χ^2 error, but that fit cannot be taken into account because the lack of reliability of the kinetic parameters.

The definitive set of the kinetic endpoints determined for this experiment, representing the persistence of Flufenacet in the water phase is following: the rate of degradation $k = 0.02908 \text{ [days}^{-1}\text{]}$, $DT_{50} = 23.84 \text{ days}$, $DT_{90} = 79.20 \text{ [days]}$, kinetic model: **SFO**. These parameters represent solely the dissipation of Flufenacet from the water phase.

c) Sediment:

The kinetic analysis of the data for Flufenacet in the sediment phase was carried out using two kinetic models – SFO and FOMC. Its graphical results are presented on figure B.8.2.2.3._CA-24 and the numerical results in the table B.8.2.2.3._CA-45. Additionally, in the table B.8.2.2.3._CA-46 are provided the kinetic endpoints returned by the modelling tool for each kinetic model.

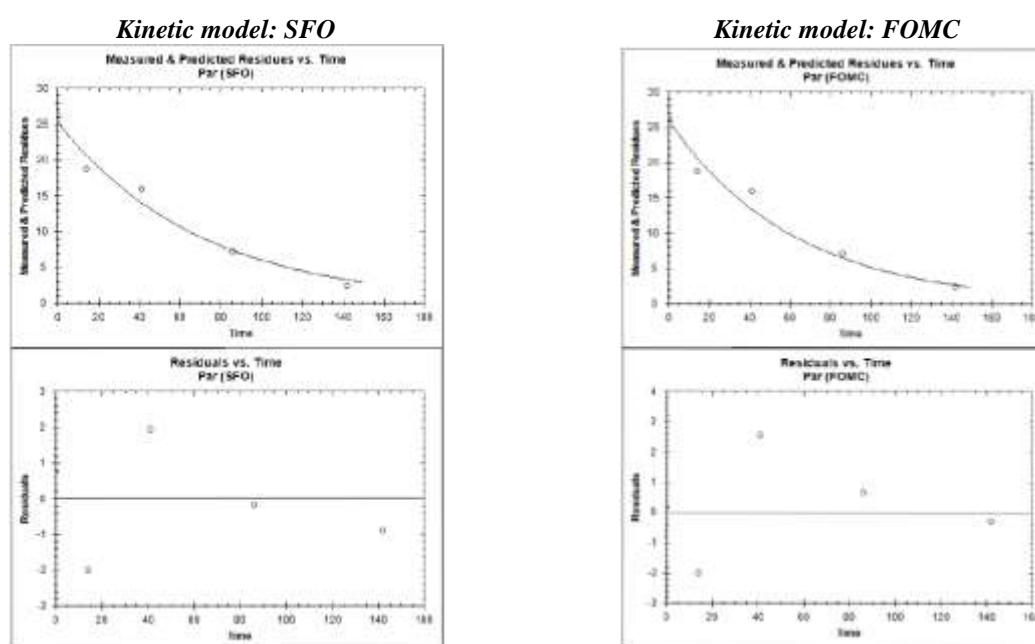


Figure B.8.2.2.3._CA-24: The graphical results of the kinetic analysis (copied from the study report).

Table B.8.2.2.3._CA-45: The numerical results of the kinetic analysis.

Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
		Value	Error	Confidence intervals		Prob. > t	χ^2 % error	Visual assessment ¹⁾
				Lower	Upper			
SFO	M_0	25.35	1.445	22.52	28.18	0.000202	7.738	Good
	k	0.01447	0.002028	0.01049	0.018	0.002835		
FOMC	M_0	25.94	1.677	22.66	29.23	0.00208	9.698	Good
	α	304.90	1069.00	-1790.00	2399.51	0.4011		
	β	18870.00	66290.00	-111100.00	148797.30	0.4014		

Footnotes to the table:

1) Visual assessment of the kinetic curve as proposed by the Applicant.

Table B.8.2.2.3._CA-46: The kinetic endpoints obtained as a result of the fitting.

Compound	Kinetic endpoint	Kinetic model tested	
		SFO	FOMC
Flufenacet	DT_{50} [days]	47.91	42.94
	DT_{90} [days]	159.10	143.00

Evaluation:

The Applicant stated that the SFO model returned visually and statistically better fit, therefore it was selected as adequately representing the kinetic behaviour of Flufenacet in sediment phase of the test system. RMS analysing the result noticed that FOMC fit cannot be considered acceptable, because it returned the kinetic parameters that were not reliable – for both α and β the CI passed through zero. Therefore RMS confirms the correctness of the decision made by the Applicant.

The definitive set of the kinetic endpoints determined for this experiment, representing the persistence of Flufenacet in the water phase, is following: the rate of degradation $k = 0.01447$ [days⁻¹], $DT_{50} = 47.91$ days, $DT_{90} = 159.10$ [days], kinetic model: **SFO**. The Applicant also proposed to consider them as reliable modelling endpoints. RMS however is of the opinion that that proposal may require further verification. That verification was performed by the RMS and its results are presented further down this summary.

Conclusions:

The kinetic analysis performed at the Level P-I of the data obtained for Flufenacet radiolabelled in fluorophenyl ring in the BRP water sediment system resulted in the following set of the kinetic endpoints:

- for the whole system: the rate of degradation $k = 0.01819$ [days⁻¹], $DT_{50} = 38.11$ days, $DT_{90} = 126.60$ [days], kinetic model: **SFO**; the kinetic endpoints represent the persistence of Flufenacet and are suitable to derive the input values for SW modelling;
- for the water phase: the rate of degradation $k = 0.02908$ [days⁻¹], $DT_{50} = 23.84$ days, $DT_{90} = 79.20$ [days], kinetic model: **SFO**; the kinetic endpoints represent the persistence of Flufenacet;
- for the sediment phase: the rate of degradation $k = 0.01447$ [days⁻¹], $DT_{50} = 47.91$ days, $DT_{90} = 159.10$ [days], kinetic model: **SFO**; the kinetic endpoints represent the persistence of Flufenacet.

The Applicant indicated that the persistence endpoints determined for Flufenacet in water and sediment phases of each test system may also be considered the modelling endpoints.

As subsequently the Applicant proposed to consider for SW model exposure assessment the geomean whole system DT_{50} values as representing the degradation of Flufenacet in water phase, attributing the default value $DT_{50} = 1000$ days to degradation in sediment phase, RMS performed the additional kinetic analysis of the data for Flufenacet in water and sediment phases in line with the principles of the Level P-II analysis. The aim of that additional kinetic analysis was to check whether dissipation from the water phase can be attributed wholly to degradation, or it is a mixed process in which migration to the sediment phase plays an important role. It is presented below.

Additional kinetic analysis of the data for Flufenacet performed by the RMS

The aim of the kinetic analysis was to determine, by means of the kinetic examination of the data, which processes are responsible for the dissipation of Flufenacet from the water phase in water/sediment studies. The analysis was carried out in a way characterised as Level P-II analysis in the FOCUS Kinetics Guidance Document – the results for water phase and sediment phase were kinetically examined in one fitting exercise.

The not-processed input data used in that analysis were presented in this summary, in the tables B.8.2.2.3._CA-17 – B.8.2.2.3._CA-20. For the purpose of the fitting they were processed in line with the procedure outlined on pp. 1231 – 1233. For completeness the non-processed and processed data used as the input in the kinetic analysis are presented below in the table B.8.2.2.3._CA-47. As the concentrations in sediment in the fitting corresponded to the “A 1” compartment, RMS set the DAT-0 concentration to zero. The concentration in water phase was adjusted to the whole-system concentration on DAT 0. These values are:

- for NESA test system in the study by [Kelley et al.; 1995]: 98.4% AR;
- for BRP test system in the study by [Kelley et al.; 1995]: 95.5% AR;
- for NESA test system in the study by [Halarnkar and Irwin; 1997]: 94.2% AR;
- for BRP test system in the study by [Halarnkar and Irwin; 1997]: 96.3% AR;

Table B.8.2.2.3._CA-47: The not processed and pre-processed data obtained in the studies examining degradation in water/sediment systems, used as input in kinetic analysis.

Study	Test system/test compound	Concentrations of Flufenacet – the not processed data			Concentrations of Flufenacet in [% AR] – the pre-processed data		
		Time Point – DAT ¹⁾ [days]	Concentration [% AR] in:		Time Point – DAT ¹⁾ [days]	Concentration [% AR] in:	
			Water phase	Sediment		Water phase	Sediment
[Kelley et al.; 1995]	NESA	0	94.91	3.49	0	98.4	0.00
		0.25	86.61	9.98	0.25	86.61	9.98
		1	94.66	6.11	1	94.66	6.11
		2	90.02	9.51	2	90.02	9.51
		7	85.53	12.58	7	85.53	12.58
		14	73.02	18.44	14	73.02	18.44
		30	60.52	22.91	30	60.52	22.91
		60	45.67	20.17	60	45.67	20.17
		100	30.71	17.22	100	30.71	17.22
		120	23.94	14.82	120	23.94	14.82
[Kelley et al.; 1995]	BRP	157	15.80	11.87	157	15.80	11.87
		0	95.02	0.51	0	95.5	0.00
		0.25	90.73	9.06	0.25	90.73	9.06
		1	91.02	9.16	1	91.02	9.16
		2	88.33	9.72	2	88.33	9.72
		7	74.52	20.86	7	74.52	20.86
		14	65.15	26.84	14	65.15	26.84
		30	49.88	34.17	30	49.88	34.17
		60	28.05	32.83	60	28.05	32.83
		100	24.77	27.80	100	24.77	27.80
[Halarnkar and Irwin; 1997]	NESA	120	18.24	20.89	120	18.24	20.89
		157	7.53	14.75	157	7.53	14.75
		0	83.88	10.42	0	94.2	0.00
		7	75.18	12.42	7	75.18	12.42
		14	55.16	10.06	14	55.16	10.06
		28	36.87	5.10	28	36.87	5.10
[Halarnkar and Irwin; 1997]	BRP	55	3.06	1.96	55	3.06	1.96
		100	0.00	0.60	100	0.00	0.60
		156	0.00	0.95	156	0.00	0.95
		0	84.12	12.21	0	96.3	0.00
		7	69.92	21.78	7	69.92	21.78
		14	49.71	26.10	14	49.71	26.10
		28	46.84	18.68	28	46.84	18.68
[Halarnkar and Irwin; 1997]	BRP	55	25.05	15.94	55	25.05	15.94
		100	3.99	7.13	100	3.99	7.13
		156	0.89	2.35	156	0.89	2.35

Footnotes to the table:

1) DAT stands for “Days After Treatment”;

The pre-processed data presented in the tables above were subjected to the kinetic analysis in line with the recommendations of FOCUS Kinetics Guideline [FOCUS; 2006] for the fitting of the data at the Level P-II. The kinetic analysis was performed using CAKE ver. 3.1 modelling tool, developed by Tessella. The optimisation was performed using IRLS (Iteratively Reweighed Nonlinear Least Squares) algorithm. The settings of the optimiser were the defaults of the tool:

- maximum iterations: 100,
- maximum reweighing: 10,
- SANN maximum iterations: 10000,
- convergence tolerance: 1 E-5,
- error variance tolerance: 1 E-5,
- extra solver: yes, if required.

The whole analysis consisted of the following steps:

- **Step 1:** Processing of the raw input data, presented above;
- **Step 2:** Kinetic evaluation of the processed data for water and sediment phases kinetically fitted together, the using CAKE ver. 3.1 modelling tool; for water phase, representing in the fitting the “Parent” compartment, three kinetic models – SFO, FOMC and DFOP, were used, while for the sediment,

representing in the fitting the “A1” compartment, only SFO model was tested; the conceptual scheme used in the fitting (copied as a screenshot from the modelling tool) is presented below on figure B.8.2.2.3_CA-25;

- **Step 3:** Evaluation of the results of kinetic examination of the data;
- **Step 4:** Reporting of the obtained results.

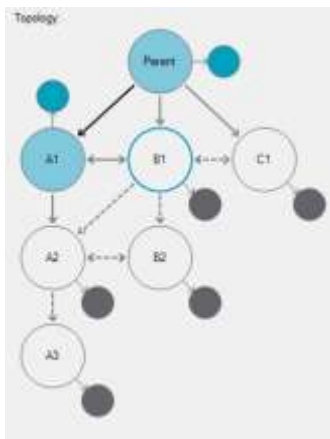


Figure B.8.2.2.3_CA-25: The conceptual scheme used in the kinetic analysis of the data for Flufenacet obtained in the water/sediment studies, performed by the RMS.

The obtained results of the kinetic analysis of the data were evaluated by means of a detailed statistical analysis, comprising the following components:

- visual assessment of the fit;
- χ^2 -error statistics;
- t-test significance;
- correlation analysis.

It followed the principles outlined on pages 1231-1233.

The results of the kinetic examination of the data and their evaluation are provided below, individually for each test system.

- 1) The results of the kinetic analysis of the data for Flufenacet at the Level P-II obtained for NESA test system treated with [Phenyl- $U-^{14}C$]Flufenacet (study by [Kelley et al.; 1995]):

The kinetic analysis was performed for the results obtained in water and sediment compartments fitted together, as shown on figure B.8.2.2.3_CA-25. For the results obtained in water phase, defined in the fitting as “parent” compartment, the fitting was performed using three kinetic models – SFO, FOMC and DFOP. The results obtained in the sediment phase were kinetically analysed using solely SFO kinetic model, due to the fact that in the conceptual model within the tool they were defined as the compartment “A1”. The results of the fitting are presented below, individually for each combination of the kinetic models.

a) Fitting using the SFO as kinetic model for water phase:

The results of the fitting are presented below in graphical form on the figure B.8.2.2.3._CA-26 and in the numerical form in the table B.8.2.2.3._CA-48.

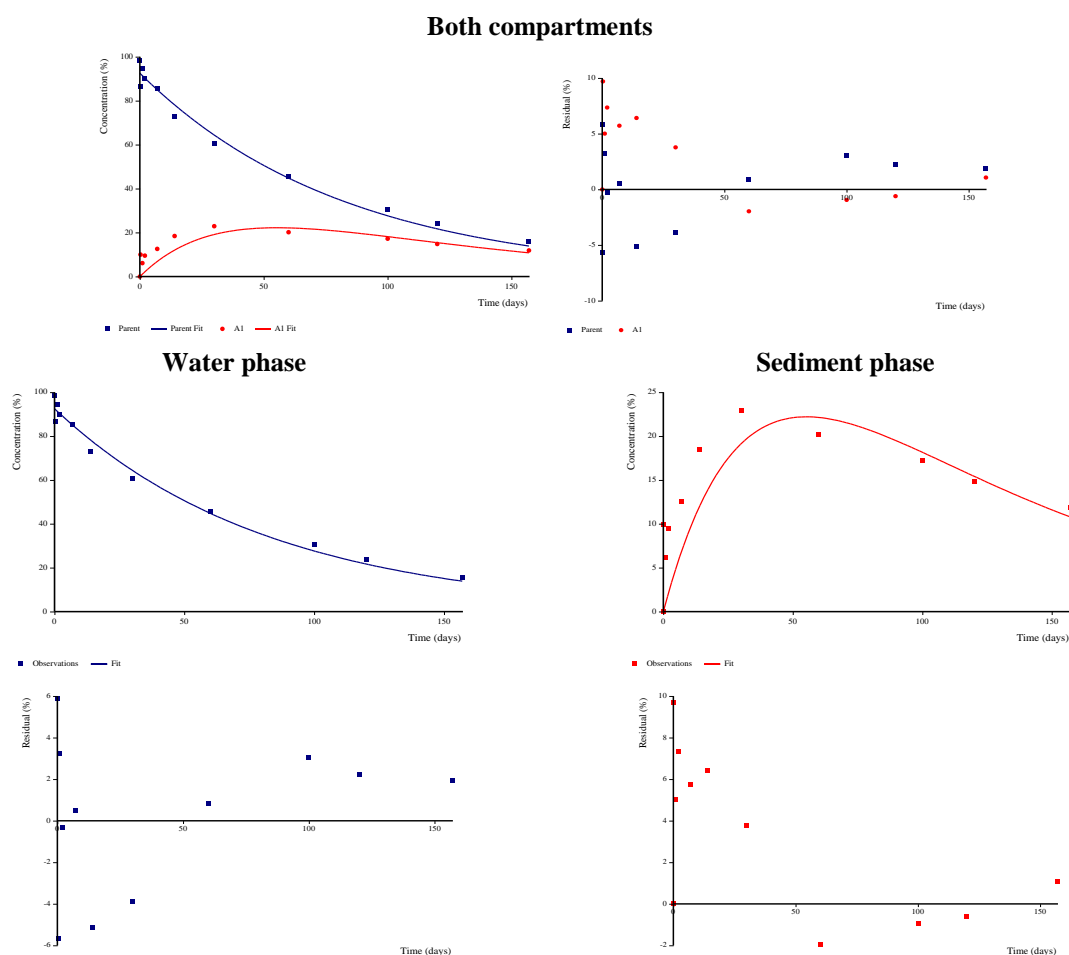


Figure B.8.2.2.3._CA-26: The graphical results of the kinetic fitting of the data for Flufenacet in water and sediment phases obtained in NESA system, study by [Kelley et al.; 1995], using SFO model for water phase.

Table B.8.2.2.3._CA-48: The numerical results of the kinetic fitting of the data for Flufenacet in water and sediment phases obtained in NESA system, study by [Kelley et al.; 1995], using SFO model for water phase.

Compartment	Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
			Value	Error	Confidence intervals		Prob. > t	χ^2 % error	Visual assessment; R
					Lower	Upper			
Water phase	SFO	M_0	92.53	1.767	89.46	95.6	----	4.44	Good fit; R = 0.986
		k	0.01208	7.91 E-4	0.01071	0.01346	1.16 E-11		
Sediment phase	SFO	M_0	0.00	----	----	----	----	28.9	Acceptable fit; R = 0.780
		k	0.02581	9.72 E-3	8.90 E-3	0.04272	8.33 E-3		
		ff	1.00	0.311	0.4586	1.541	----		

b) Fitting using the FOMC as kinetic model for water phase:

The results of the fitting are presented below in graphical form on the figure B.8.2.2.3._CA-27 and in the numerical form in the table B.8.2.2.3._CA-49.

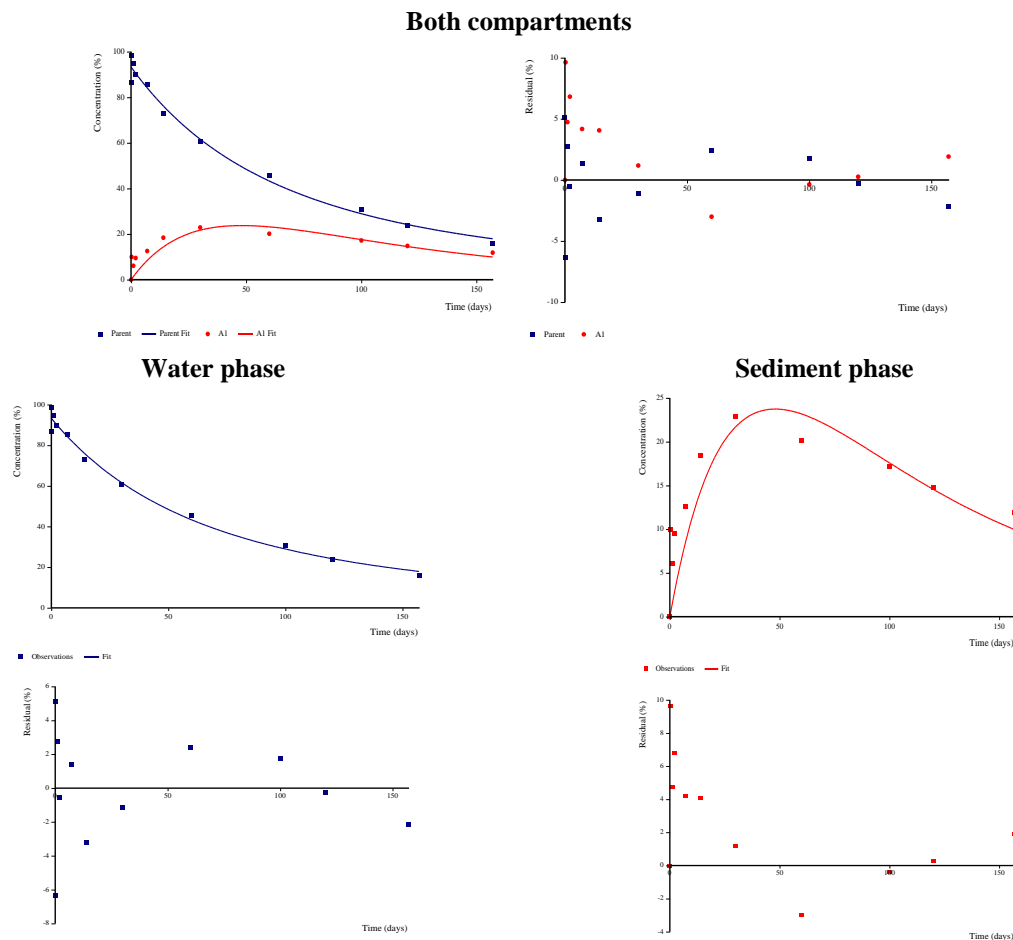


Figure B.8.2.2.3._CA-27: The graphical results of the kinetic fitting of the data for Flufenacet in water and sediment phases obtained in NESA system, study by [Kelley et al.; 1995], using FOMC model for water phase.

Table B.8.2.2.3._CA-49: The numerical results of the kinetic fitting of the data for Flufenacet in water and sediment phases obtained in NESA system, study by [Kelley et al.; 1995], using FOMC model for water phase.

Compartment	Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
			Value	Error	Confidence intervals		Prob. > t	χ^2 % error	Visual assessment; R
					Lower	Upper			
Water phase	FOMC	M_0	93.31	1.778	90.21	96.41	----	3.98	Good fit; R = 0.9891
		α	2.404	1.474	-0.1689	4.978	----		
		β	159.4	121.8	-53.23	372.1	----		
Sediment phase	SFO	M_0	0.00	----	----	----	----	25.6	Acceptable fit; R = 0.8402
		k	0.02419	8.508 E-3	9.34 E-3	3.905 E-2	5.868 E-3		
		ff	0.9998	0.2801	0.5108	1.489	----		

c) Fitting using the DFOP as kinetic model for water phase:

The results of the fitting are presented below in graphical form on the figure B.8.2.2.3._CA-28 and in the numerical form in the table B.8.2.2.3._CA-50.

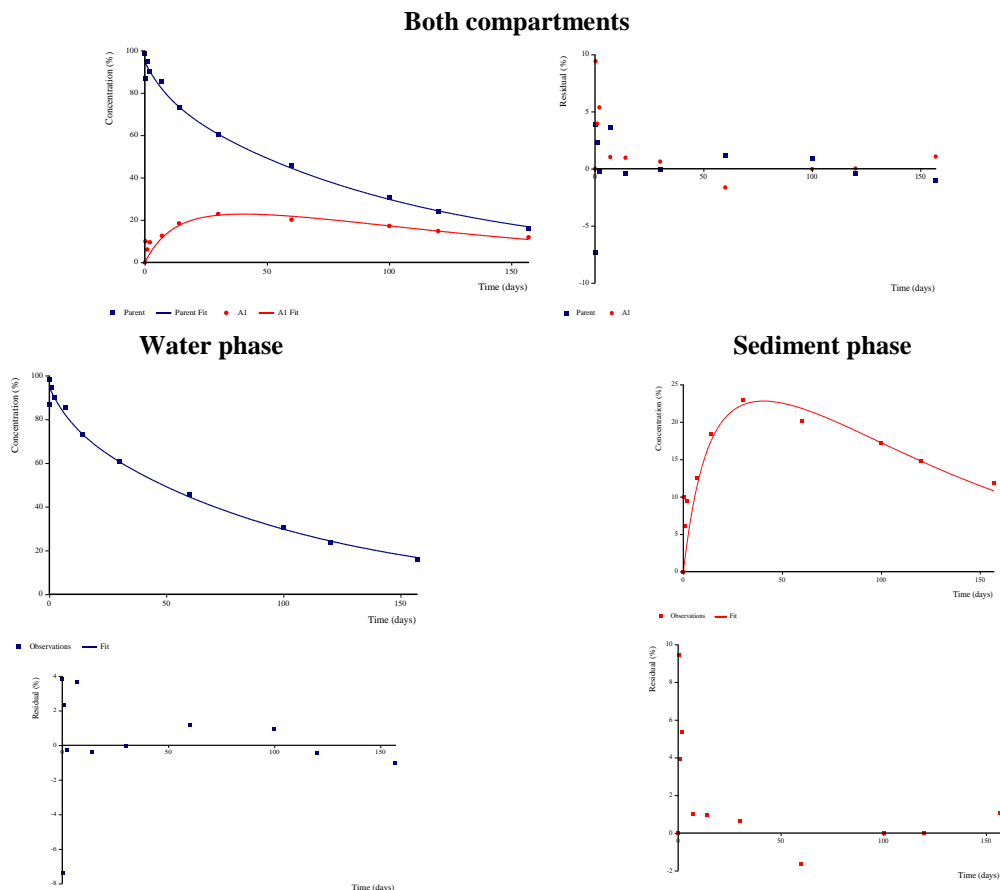


Figure B.8.2.2.3._CA-28: The graphical results of the kinetic fitting of the data for Flufenacet in water and sediment phases obtained in NESA system, study by [Kelley et al.; 1995], using DFOP model for water phase.

Table B.8.2.2.3._CA-50: The numerical results of the kinetic fitting of the data for Flufenacet in water and sediment phases obtained in NESA system, study by [Kelley et al.; 1995], using DFOP model for water phase.

Compartment	Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
			Value	Error	Confidence intervals		Prob. > t	χ^2 % error	Visual assessment; R
					Lower	Upper			
Water phase	DFOP	M_0	94.54	2.008	91.02	98.05	----	3.98	Good fit; $R = 0.990$
		k_1	0.1089	0.09423	-0.05628	0.2741	0.1329		
		k_2	0.01002	1.266 E-3	7.801 E-3	0.01224	4.89 E-7		
		g	0.1421	0.0821	-1.83 E-3	0.286	----		
Sediment phase	SFO	M_0	0.00	----	---	----	----	20.9	Good fit; $R = 0.876$
		k	0.02452	7.35 E-3	0.01164	0.03741	2.256 E-3		
		ff	1.00	0.2408	0.5779	1.422	----		

Evaluation of the fits:

Of the three tested options DFOP-SFO returned the best fits for both phases in visual and statistical terms. The improvement was observed already for the combination FOMC-SFO, what may indicate that the dissipation of Flufenacet from water phase may follow bi-phasic pattern. While the kinetic fit for the water phase was visually and statistically acceptable for all three kinetic models used, it was not possible to obtain the fully acceptable fit, mainly in statistical terms, for any of the options tested. The lowest χ^2 error for the fit representing the kinetic behaviour of Flufenacet in sediment phase, also the best visually, was obtained in combination with DFOP for water phase. It shall be indicated that none of the bi-phasic models tested for water phase returned reliable kinetic parameters. Therefore SFO-SFO fit shall be regarded as appropriate description of kinetic behaviour of Flufenacet in water and sediment compartments. For the water phase the kinetic model identified as returning the best fit is the same as indicated by the Applicant in the kinetic examination carried out at the Level P-I.

The kinetic endpoints obtained for each tested combination are presented below in the table B.8.2.2.3._CA-51.

Table B.8.2.2.3._CA-51: The kinetic endpoints obtained in the fitting for each combination of the kinetic models.

Compartment	Kinetic endpoint	Kinetic model tested for water phase:		
		<i>SFO</i>	<i>FOMC</i>	<i>DFOP</i>
<i>Water phase</i>	DT ₅₀ [days]	57.4	53.3	54.0
	DT ₉₀ [days]	191	256	215
<i>Sediment phase (SFO model used only)</i>	DT ₅₀ [days]	26.9	28.7	28.3
	DT ₉₀ [days]	89.2	95.2	93.9
	Kinetic formation fraction <i>ff</i>	1.00	0.9998	1.00

Analysing the values of the kinetic formation fractions – *ff*, representing here the flow from water to the sediment phase, RMS noticed that for all three combinations of the kinetic models tested they were very close or equal to 1. That may indicate that the dominant mechanism of dissipation of Flufenacet from water phase is its migration to sediment. Therefore the kinetic parameters determined for Flufenacet in water phase in that test system should be regarded as persistence endpoints not to be used in modelling.

The comparison of the results obtained for Flufenacet in water phase by RMS and the Applicant showed, that they were very similar. For that reason RMS decided to keep as reliable the values determined by the Applicant.

The kinetic endpoints determined in this fitting exercise for the sediment phase lacked the reliability due to the rather poor fitting. For that reason RMS decided to consider the values determined by the Applicant as reliable kinetic characteristic of the persistence of Flufenacet in sediment phase.

Finally, in RMS's opinion the results of this fitting, and in particular that of *ff* (representing the flow from water to sediment compartment), clearly indicate that the whole system DT₅₀ value is more appropriate for SW modelling at higher tiers as representing the degradation in the sediment phase. Therefore the appropriate value for SW modelling at higher tiers as representing the degradation in water will be DT₅₀ = 1000 days (FOCUS default).

- 2) The results of the kinetic analysis of the data for Flufenacet at the Level P-II obtained for BRP test system treated with [Phenyl-U-¹⁴C]Flufenacet (study by [Kelley et al.; 1995]):

The kinetic analysis was performed for the results obtained in water and sediment compartments fitted together, as shown on figure B.8.2.2.3._CA-25. For the results obtained in water phase, defined in the fitting as “parent” compartment, the fitting was performed using three kinetic models – SFO, FOMC and DFOP. The results obtained in the sediment phase were kinetically analysed using solely SFO kinetic model, due to the fact that in the conceptual model within the tool they were defined as the compartment “A1”. The results of the fitting are presented below, individually for each combination of the kinetic models.

a) Fitting using the SFO as kinetic model for water phase:

The results of the fitting are presented below in graphical form on the figure B.8.2.2.3._CA-29 and in the numerical form in the table B.8.2.2.3._CA-52.

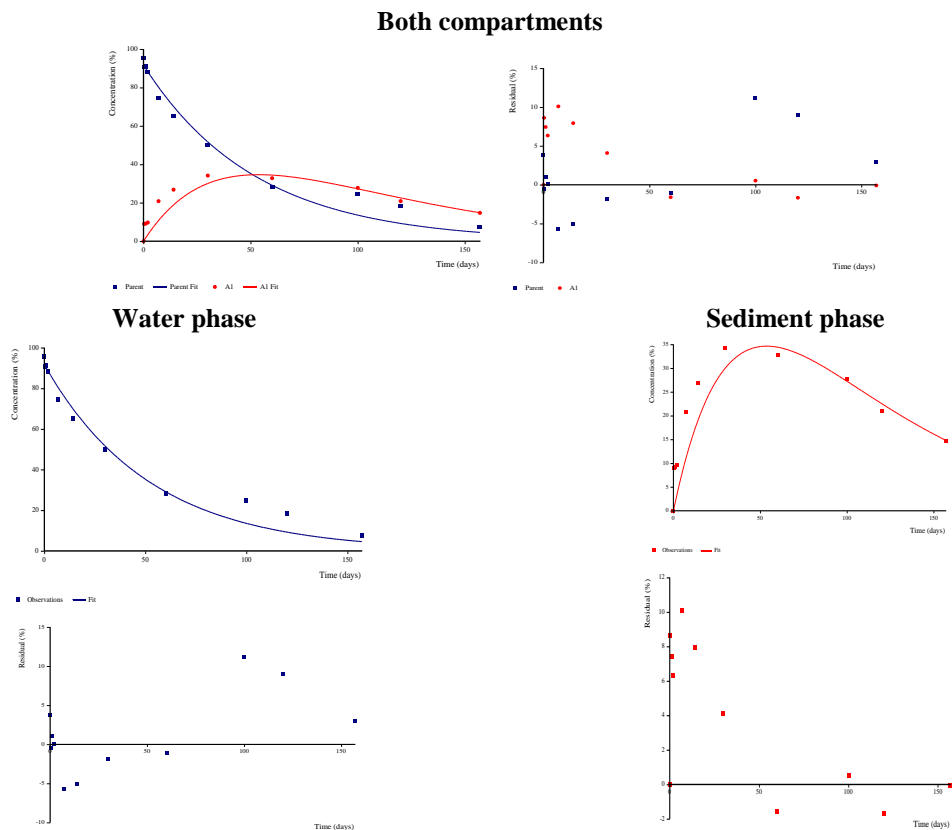


Figure B.8.2.2.3._CA-29: The graphical results of the kinetic fitting of the data for Flufenacet in water and sediment phases obtained in BRP system, study by [Kelley et al.; 1995], using SFO model for water phase.

Table B.8.2.2.3._CA-52: The numerical results of the kinetic fitting of the data for Flufenacet in water and sediment phases obtained in BRP system, study by [Kelley et al.; 1995], using SFO model for water phase.

Compartment	Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
			Value	Error	Confidence intervals		Prob. > t	χ^2 % error	Visual assessment; R
					Lower	Upper			
Water phase	SFO	M_0	91.69	2.728	86.94	96.43	----	12.1	Good fit; R = 0.983
		k	0.001911	2.02 E-3	0.01559	0.02262	1.73 E-8		
Sediment phase	SFO	M_0	0.00	----	----	----	----	23.3	Acceptable fit; R = 0.879
		k	0.01811	5.21 E-3	9.04 E-3	0.02718	0.001457		
		ff	1.00	0.229	0.6012	1.399	----		

b) Fitting using the FOMC as kinetic model for water phase:

The results of the fitting are presented below in graphical form on the figure B.8.2.2.3._CA-30 and in the numerical form in the table B.8.2.2.3._CA-53.

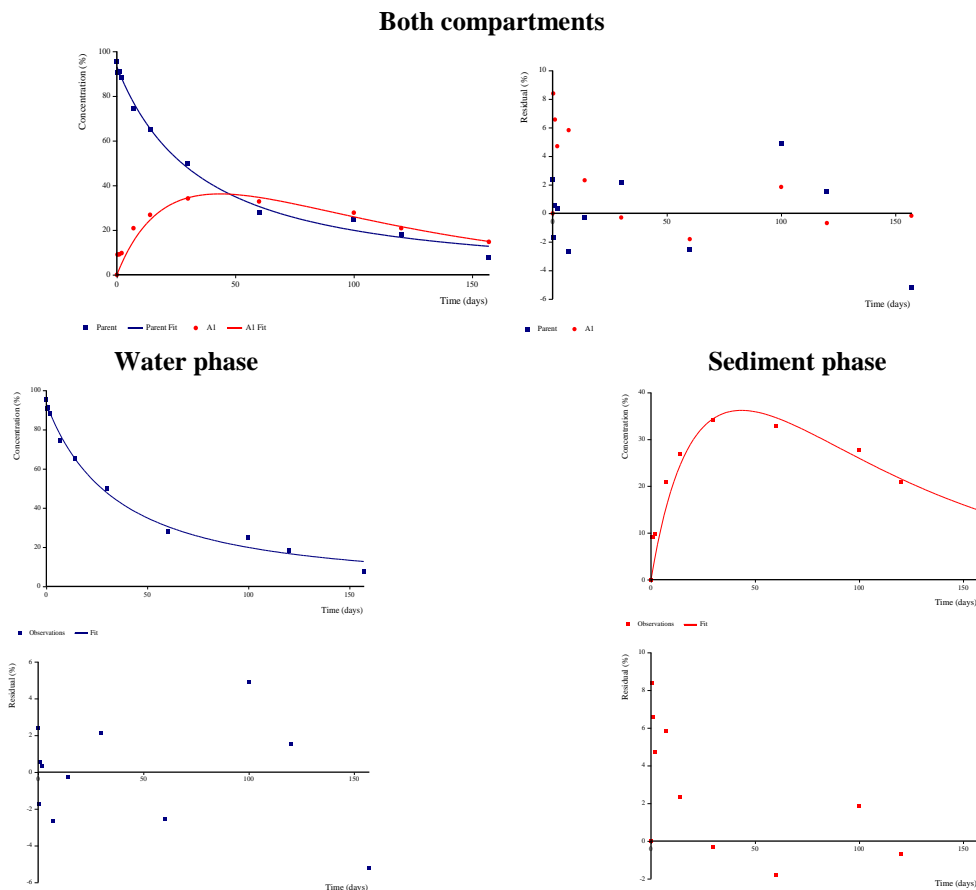


Figure B.8.2.2.3._CA-30: The graphical results of the kinetic fitting of the data for Flufenacet in water and sediment phases obtained in BRP system, study by [Kelley et al.; 1995], using FOMC model for water phase.

Table B.8.2.2.3._CA-53: The numerical results of the kinetic fitting of the data for Flufenacet in water and sediment phases obtained in BRP system, study by [Kelley et al.; 1995], using FOMC model for water phase.

Compartment	Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
			Value	Error	Confidence intervals		Prob. > t	χ^2 % error	Visual assessment; R
					Lower	Upper			
Water phase	FOMC	M_0	93.1	1.706	90.12	96.08	----	3.96	Good fit; $R = 0.9902$
		α	1.357	0.344	0.7558	1.958	----		
		β	47.19	17.98	15.8	78.57	----		
Sediment phase	SFO	M_0	0.00	----	----	----	----	16.6	Good fit; $R = 0.9441$
		k	0.01589	3.355 E-3	0.01003	0.02175	1.12 E-4		
		ff	1.00	0.151	0.7364	1.264	----		

c) Fitting using the DFOP as kinetic model for water phase:

The results of the fitting are presented below in graphical form on the figure B.8.2.2.3._CA-31 and in the numerical form in the table B.8.2.2.3._CA-54.

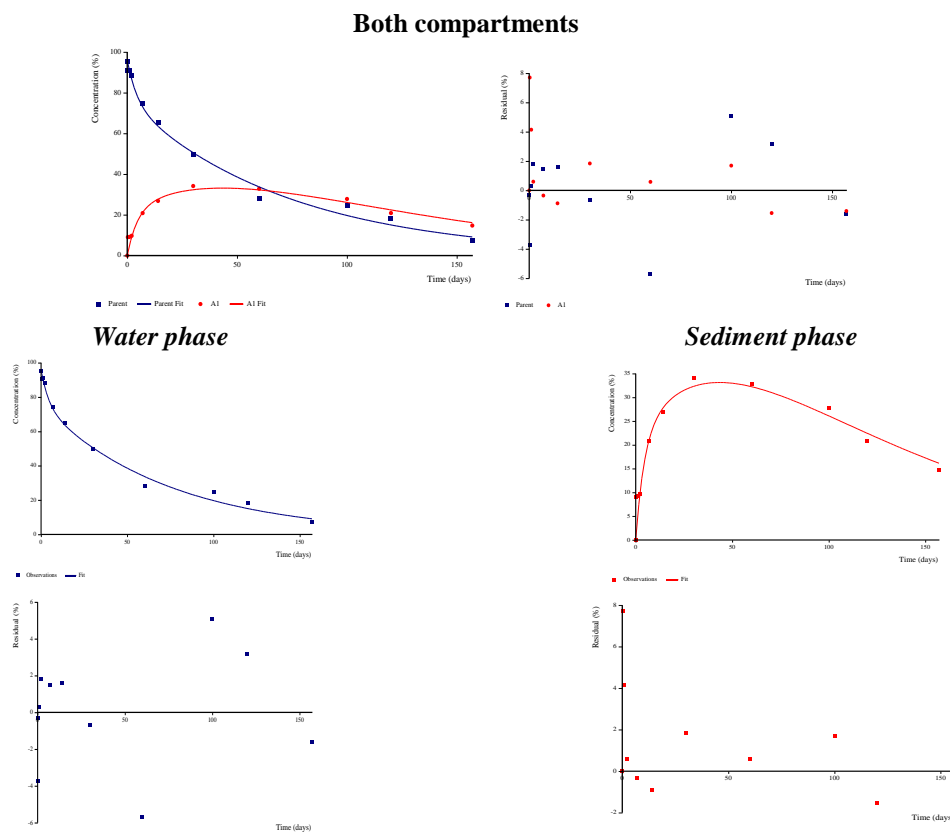


Figure B.8.2.2.3._CA-31: The graphical results of the kinetic fitting of the data for Flufenacet in water and sediment phases obtained in BRP system, study by [Kelley et al.; 1995], using DFOP model for water phase.

Table B.8.2.2.3._CA-54: The numerical results of the kinetic fitting of the data for Flufenacet in water and sediment phases obtained in BRP system, study by [Kelley et al.; 1995], using DFOP model for water phase.

Compartment	Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
			Value	Error	Confidence intervals		Prob. > t	χ^2 % error	Visual assessment; R
					Lower	Upper			
Water phase	DFOP	M_0	95.79	2.155	92.01	99.57	----	4.47	Good fit; $R = 0.992$
		k_1	0.2243	0.1009	0.04744	0.4011	0.02099		
		k_2	0.01346	0.00135	0.01109	0.01583	2.60 E-8		
		g	0.2103	0.05249	0.1183	0.3023	----		
Sediment phase	SFO	M_0	0.00	----	----	----	----	11.6	Good fit; $R = 0.951$
		k	0.01714	0.002905	0.01204	0.02223	1.46 E-5		
		ff	1.00	0.1323	0.7681	1.232	----		

Evaluation of the fits:

Of the three tested options DFOP-SFO returned the best fits for both phases in visual and statistical terms. The improvement was observed already for the combination FOMC-SFO, what may indicate that the dissipation of Flufenacet from water phase may follow bi-phasic pattern. While the kinetic fit for the water phase was visually and statistically acceptable for all three kinetic models used, it was not possible to obtain the fully acceptable fit, mainly in statistical terms, for the combinations SFO-SFO and FOMC-SFO. Only the combination DFOP-SFO returned visually and statistically acceptable fits for both water and sediment phase. At the same time it shall be indicated that the DFOP fit for water phase cannot be considered acceptable because of the lack of reliability of the determined kinetic parameters – k_1 in particular. Therefore, as the combination FOMC-SFO returned the fits visually and statistically better than the combination SFO-SFO, and the kinetic parameters of the fits were acceptable, it shall be regarded as appropriate description of kinetic behaviour of Flufenacet in water and sediment compartments. For the water phase the kinetic model identified as returning the best fit is the same as indicated by the Applicant in the kinetic examination carried out at the Level P-I.

The kinetic endpoints obtained for each tested combination are presented below in the table B.8.2.2.3._CA-55.

Table B.8.2.2.3._CA-55: The kinetic endpoints obtained in the fitting for each combination of the kinetic models.

Compartment	Kinetic endpoint	Kinetic model tested for water phase:		
		SFO	FOMC	DFOP
Water phase	DT ₅₀ [days]	36.3	31.5	34
	DT ₉₀ [days]	121	210	154
Sediment phase (SFO model used only)	DT ₅₀ [days]	38.3	43.6	40.5
	DT ₉₀ [days]	127	145	134
	Kinetic formation fraction ff	1.00	1.00	1.00

Analysing the values of the kinetic formation fractions – ff , representing here the flow from water to the sediment phase, RMS noticed that for all three combinations of the kinetic models tested they were equal to 1. That may indicate that the dominant mechanism of dissipation of Flufenacet from water phase is its migration to sediment. Also that is indicated by the fact that FOMC – bi-phasic model, returned the best fit, statistically and visually, with fully reliable kinetic parameters. Therefore the kinetic parameters determined for Flufenacet in water phase in that test system should be regarded as persistence endpoints not to be used in modelling.

The comparison of the results obtained for Flufenacet in water phase by RMS and the Applicant showed, that they were similar. For that reason RMS decided to keep as reliable the values determined by the Applicant.

As for the kinetic endpoints for the sediment phase, RMS decided to consider the values determined by the Applicant as reliable kinetic characteristic of the persistence of Flufenacet in sediment phase. That was due to the fact that they displayed higher reliability.

Finally, in RMS's opinion the results of this fitting, and in particular that of ff (representing the flow from water to sediment compartment), clearly indicate that the whole system DT₅₀ value is more appropriate for SW modelling at higher tiers as representing the degradation in the sediment phase. Therefore the appropriate value for SW modelling at higher tiers as representing the degradation in water will be DT₅₀ = 1000 days (FOCUS default).

- 3) The results of the kinetic analysis of the data for Flufenacet at the Level P-II obtained for NESA test system treated with [Thiadiazole-2-¹⁴C]Flufenacet (study by [Halarnkar and Irwin, 1997]):

The kinetic analysis was performed for the results obtained in water and sediment compartments fitted together, as shown on figure B.8.2.2.3._CA-25. For the results obtained in water phase, defined in the fitting as “parent” compartment, the fitting was performed using all four kinetic models – SFO, FOMC, DFOP and HS. The results obtained in the sediment phase were kinetically analysed using solely SFO kinetic model, due to the fact that in the conceptual model within the tool they were defined as the compartment “A1”. The results of the fitting are presented below, individually for each combination of the kinetic models.

a) Fitting using the SFO as kinetic model for water phase:

The results of the fitting are presented below in graphical form on the figure B.8.2.2.3._CA-32 and in the numerical form in the table B.8.2.2.3._CA-56.

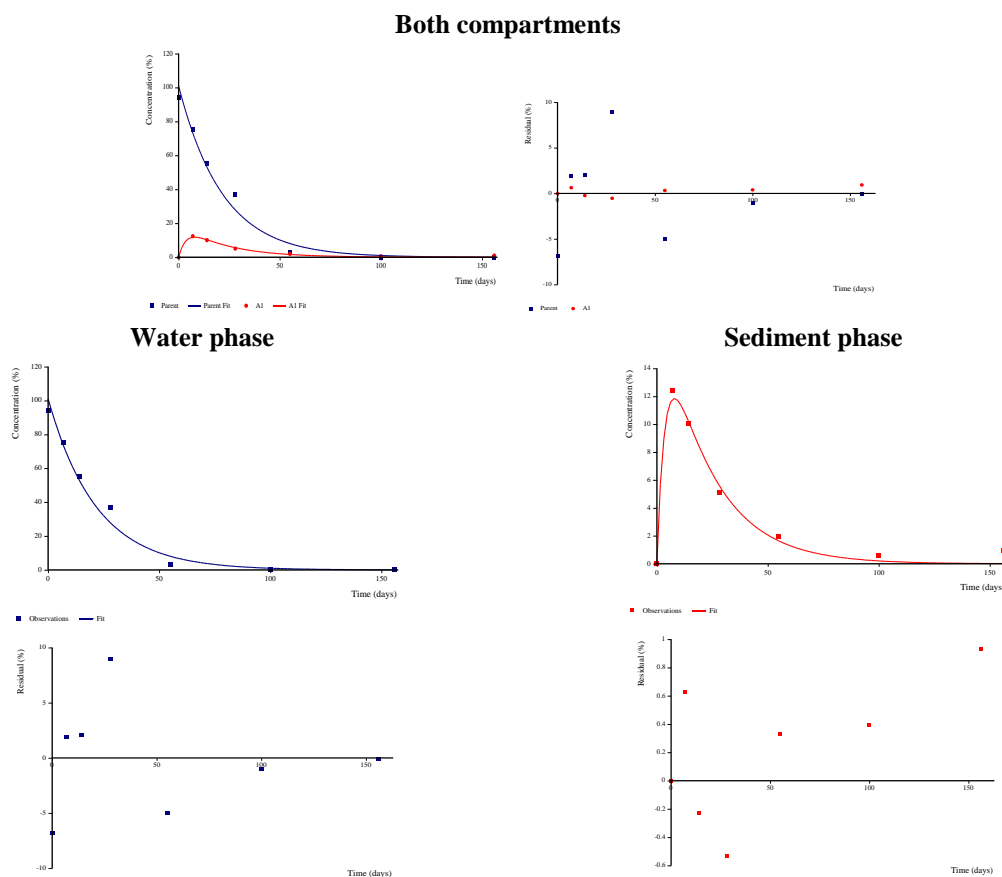


Figure B.8.2.2.3._CA-32: The graphical results of the kinetic fitting of the data for Flufenacet in water and sediment phases obtained in NESAsystem, study by [Halarnkar and Irwin; 1997], using SFO model for water phase.

Table B.8.2.2.3._CA-56: The numerical results of the kinetic fitting of the data for Flufenacet in water and sediment phases obtained in NESAsystem, study by [Halarnkar and Irwin; 1997], using SFO model for water phase.

Compartment	Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
			Value	Error	Confidence intervals		Prob. > t	χ^2 % error	Visual assessment; R
					Lower	Upper			
Water phase	SFO	M_0	101.0	5.072	91.72	110.3	----	10.1	Good fit; R = 0.983
		k	0.04594	0.00483	0.03709	0.05479	2.71 E-6		
Sediment phase	SFO	M_0	0.00	----	----	----	----	8.57	Good fit; R = 0.990
		k	0.2731	0.07009	0.1464	0.4016	0.001818		
		ff	1.00	0.2948	0.4596	1.540	----		

b) Fitting using the FOMC as kinetic model for water phase:

The results of the fitting are presented below in graphical form on the figure B.8.2.2.3._CA-33 and in the numerical form in the table B.8.2.2.3._CA-57.

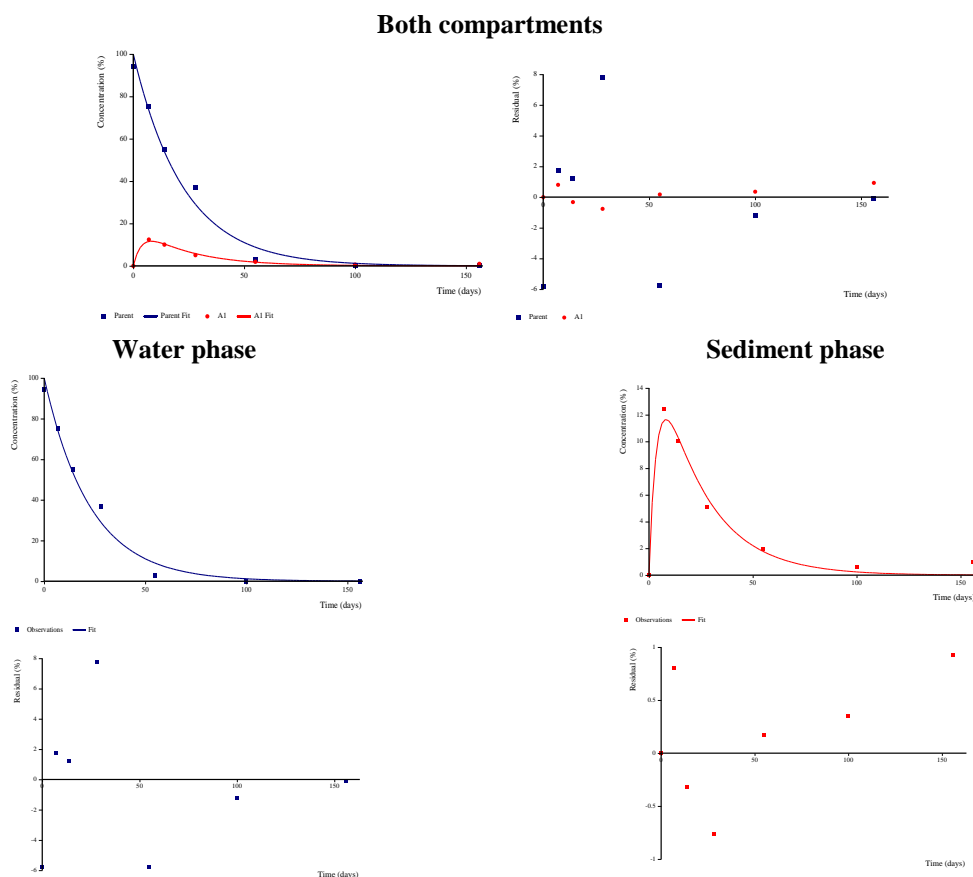


Figure B.8.2.2.3._CA-33: The graphical results of the kinetic fitting of the data for Flufenacet in water and sediment phases obtained in NESAs system, study by [Halarnkar and Irwin; 1997], using FOMC model for water phase.

Table B.8.2.2.3._CA-57: The numerical results of the kinetic fitting of the data for Flufenacet in water and sediment phases obtained in NESAs system, study by [Halarnkar and Irwin; 1997], using FOMC model for water phase.

Compartment	Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
			Value	Error	Confidence intervals		Prob. > t	χ^2 % error	Visual assessment; R
					Lower	Upper			
Water phase	FOMC	M_0	100.0	4.379	91.85	108.1	----	9.93	Good fit; $R = 0.985$
		α	6900	321.7	6300	7500	----		
		β	1.57 E5	305.2	1.56 E5	1.57 E5	----		
Sediment phase	SFO	M_0	0.00	----	----	----	----	9.61	Acceptable fit; $R = 0.986$
		k	0.2644	0.02255	0.2224	0.3063	1.28 E-6		
		ff	1.00	7.07 E-4	0.9987	1.001	----		

c) Fitting using the DFOP as kinetic model for water phase:

The results of the fitting are presented below in graphical form on the figure B.8.2.2.3._CA-34 and in the numerical form in the table B.8.2.2.3._CA-58.

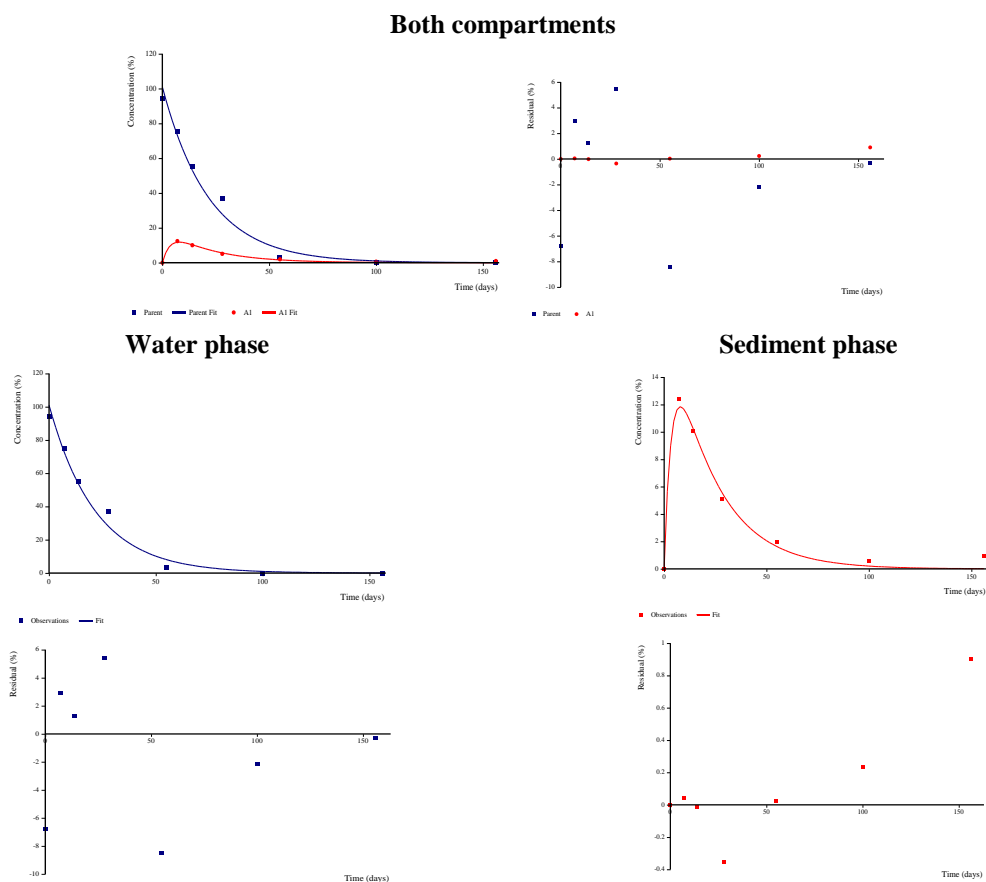


Figure B.8.2.2.3._CA-34: The graphical results of the kinetic fitting of the data for Flufenacet in water and sediment phases obtained in NESA system, study by [Halarnkar and Irwin; 1997], using DFOP model for water phase.

Table B.8.2.2.3._CA-58: The numerical results of the kinetic fitting of the data for Flufenacet in water and sediment phases obtained in NESA system, study by [Halarnkar and Irwin; 1997], using DFOP model for water phase.

Compartment	Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
			Value	Error	Confidence intervals		Prob. > t	χ^2 % error	Visual assessment; R
					Lower	Upper			
Water phase	DFOP	M_0	101.0	5.09	91.37	110.7	----	12.1	Good fit; R = 0.983
		k_1	0.1902	0.177	-0.1452	0.5255	0.1591		
		k_2	0.04594	0.00896	0.02896	0.06291	6.79 E-4		
		g	6.9 E-7	0.1764	-0.3343	0.3343	----		
Sediment phase	SFO	M_0	0.00	----	---	----	----	6.27	Good fit; R = 0.995
		k	0.2731	0.0275	0.221	0.3252	1.12 E-5		
		ff	1.00	7.56 E-4	0.9986	1.001	----		

Evaluation of the fits:

Of the three tested options SFO-SFO returned the best fits for both phases in visual and statistical terms. The combination FOMC-SFO returned statistically slightly better fit for water phase, but worse, in both statistical and visual terms, for the sediment phase. Finally, the use of the combination of DFOP-SFO kinetic models resulted in the best fit for the sediment phase, but the worst of the three for water phase. Additionally, while combinations SFO-SFO and FOMC-SFO returned reliable sets of the kinetic parameters, the same cannot be stated for the combination DFOP-SFO – the k_i in the DFOP fit for the water phase did not pass the acceptability criteria of the t-test.

Therefore, on the basis of the weight of evidence, SFO-SFO fit shall be regarded as appropriate description of kinetic behaviour of Flufenacet in water and sediment compartments. For the water phase the kinetic model identified as returning the best fit is the same as indicated by the Applicant in the kinetic examination carried out at the Level P-I.

The kinetic endpoints obtained for each tested combination are presented below in the table B.8.2.2.3._CA-59.

Table B.8.2.2.3._CA-59: The kinetic endpoints obtained in the fitting for each combination of the kinetic models.

Compartment	Kinetic endpoint	Kinetic model tested for water phase:		
		<i>SFO</i>	<i>FOMC</i>	<i>DFOP</i>
<i>Water phase</i>	DT ₅₀ [days]	15.1	15.7	15.1
	DT ₉₀ [days]	50.1	52.2	50.1
<i>Sediment phase</i> (<i>SFO model used only</i>)	DT ₅₀ [days]	2.54	2.62	2.54
	DT ₉₀ [days]	8.43	8.71	8.43
	Kinetic formation fraction ff	1.00	1.00	1.00

Analysing the values of the kinetic formation fractions – ff , representing here the flow from water to the sediment phase, RMS noticed that for all three combinations of the kinetic models tested they were equal to 1. That may indicate that the dominant mechanism of dissipation of Flufenacet from water phase is its migration to sediment. Therefore the kinetic parameters determined for Flufenacet in water phase in that test system should be regarded as persistence endpoints not to be used in modelling.

The comparison of the results obtained for Flufenacet in water phase by RMS and the Applicant showed, that they were very similar. For that reason RMS decided to keep as reliable the values determined by the Applicant.

As for the kinetic endpoints for the sediment phase, RMS decided to consider the values determined by the Applicant as reliable kinetic characteristic of the persistence of Flufenacet in sediment phase. That was due to the fact that they displayed higher reliability.

Finally, in RMS's opinion the results of this fitting, and in particular that of ff (representing the flow from water to sediment compartment), clearly indicate that the whole system DT₅₀ value is more appropriate for SW modelling at higher tiers as representing the degradation in the sediment phase. Therefore the appropriate value for SW modelling at higher tiers as representing the degradation in water will be DT₅₀ = 1000 days (FOCUS default).

- 4) The results of the kinetic analysis of the data for Flufenacet at the Level P-II obtained for NESA test system treated with [Thiadiazole-2-¹⁴C]Flufenacet (study by [Halarnkar and Irwin; 1997]):

The kinetic analysis was performed for the results obtained in water and sediment compartments fitted together, as shown on figure B.8.2.2.3._CA-25. For the results obtained in water phase, defined in the fitting as “parent” compartment, the fitting was performed using all four kinetic models – SFO, FOMC, DFOP and HS. The results obtained in the sediment phase were kinetically analysed using solely SFO kinetic model, due to the fact that in the conceptual model within the tool they were defined as the compartment “A1”. The results of the fitting are presented below, individually for each combination of the kinetic models.

a) Fitting using the SFO as kinetic model for water phase:

The results of the fitting are presented below in graphical form on the figure B.8.2.2.3._CA-35 and in the numerical form in the table B.8.2.2.3._CA-60.

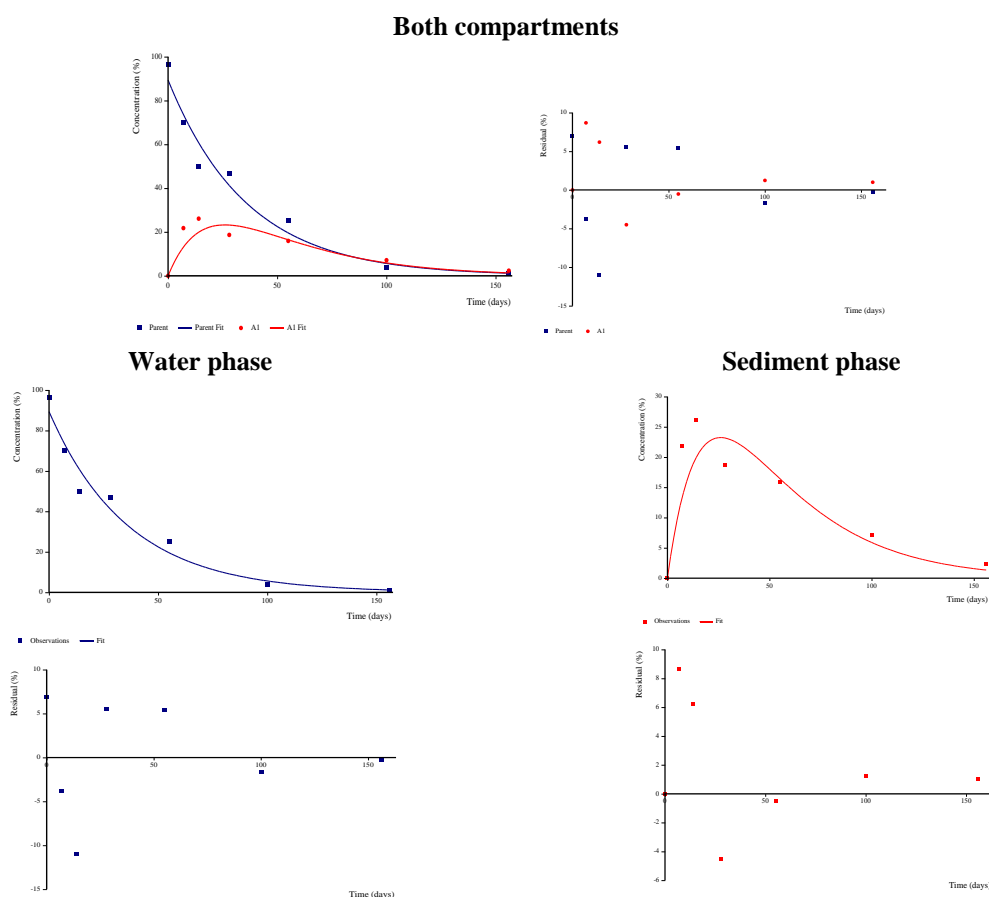


Figure B.8.2.2.3._CA-35: The graphical results of the kinetic fitting of the data for Flufenacet in water and sediment phases obtained in BRP system, study by [Halarncar and Irwin; 1997], using SFO model for water phase.

Table B.8.2.2.3._CA-60: The numerical results of the kinetic fitting of the data for Flufenacet in water and sediment phases obtained in BRP system, study by [Halarncar and Irwin; 1997], using SFO model for water phase.

Compartment	Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
			Value	Error	Confidence intervals		Prob. > t	χ^2 % error	Visual assessment; R
					Lower	Upper			
Water phase	SFO	M_0	89.37	5.936	78.49	100.3	----	11.3	Acceptable fit; $R = 0.966$
		k	0.02759	0.00468	0.01901	0.03617	1.15 E-4		
Sediment phase	SFO	M_0	0.00	----	----	----	----	24.8	Acceptable fit; $R = 0.809$
		k	0.05172	0.02361	8.44 E-3	0.09501	0.0281		
		ff	1.00	0.387	0.2913	1.709	----		

b) Fitting using the FOMC as kinetic model for water phase:

The results of the fitting are presented below in graphical form on the figure B.8.2.2.3._CA-36 and in the numerical form in the table B.8.2.2.3._CA-61.

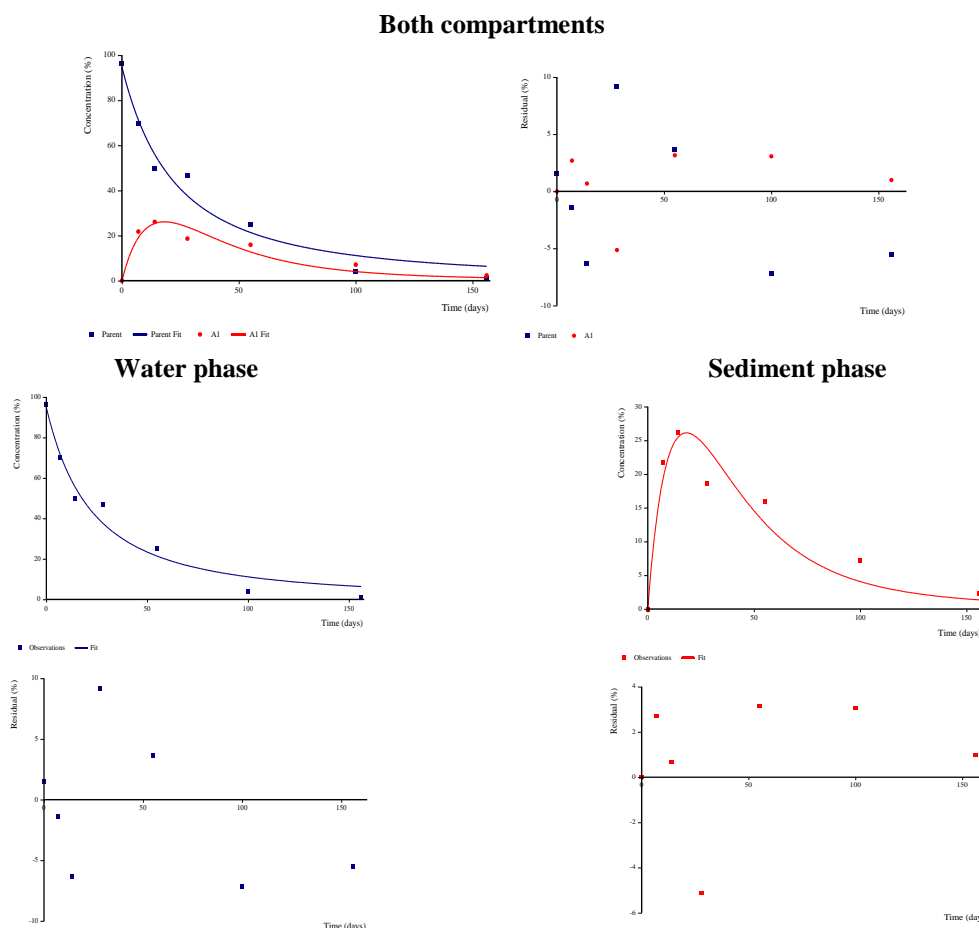


Figure B.8.2.2.3._CA-36: The graphical results of the kinetic fitting of the data for Flufenacet in water and sediment phases obtained in BRP system, study by [Halarikar and Irwin; 1997], using FOMC model for water phase.

Table B.8.2.2.3._CA-61: The numerical results of the kinetic fitting of the data for Flufenacet in water and sediment phases obtained in BRP system, study by [Halarikar and Irwin; 1997], using FOMC model for water phase.

Compartment	Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
			Value	Error	Confidence intervals		Prob. > t	χ^2 % error	Visual assessment; R
					Lower	Upper			
Water phase	FOMC	M_0	94.76	7.118	81.53	108.0	----	11.6	Acceptable fit; $R = 0.971$
		α	1.626	1.111	-0.4392	3.692	----		
		β	36.71	36.08	-30.38	103.8	----		
Sediment phase	SFO	M_0	0.00	----	----	----	----	15.6	Acceptable fit; $R = 0.928$
		k	0.0559	0.0224	0.0144	0.0975	0.0184		
		ff	1.00	0.366	0.318	1.682	----		

c) Fitting using the DFOP as kinetic model for water phase:

The results of the fitting are presented below in graphical form on the figure B.8.2.2.3._CA-37 and in the numerical form in the table B.8.2.2.3._CA-62.

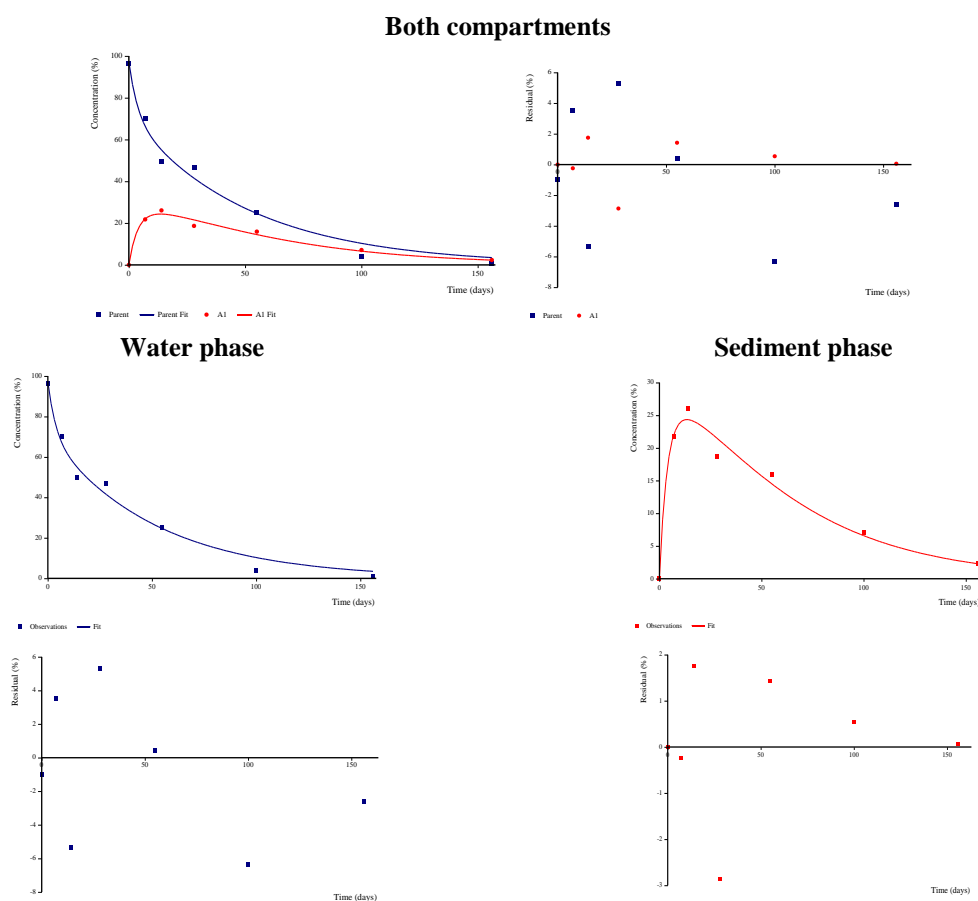


Figure B.8.2.2.3._CA-37: The graphical results of the kinetic fitting of the data for Flufenacet in water and sediment phases obtained in BRP system, study by [Halarncar and Irwin; 1997], using DFOP model for water phase.

Table B.8.2.2.3._CA-62: The numerical results of the kinetic fitting of the data for Flufenacet in water and sediment phases obtained in BRP system, study by [Halarncar and Irwin; 1997], using DFOP model for water phase.

Compartment	Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
			Value	Error	Confidence intervals		Prob. > t	χ^2 % error	Visual assessment ; R
					Lower	Upper			
Water phase	DFOP	M_0	97.30	5.707	86.49	108.1	----	9.27	Good fit; $R = 0.986$
		k_1	0.2645	0.1708	-0.0591	0.5882	0.0827		
		k_2	0.01933	3.88 E-3	0.01198	0.02668	7.97 E-4		
		g	0.2668	0.1047	0.06856	0.4651	----		
Sediment phase	SFO	M_0	0.00	----	---	----	----	7.83	Good fit; $R = 0.978$
		k	0.04435	0.01103	0.02346	0.06524	2.52 E-3		
		ff	0.8566	0.2072	0.4641	1.249	----		

Evaluation of the fits:

Of the three tested options DFOP-SFO returned the best fits for both phases in visual and statistical terms. The improvement of the fit for the sediment phase was observed already for the combination FOMC-SFO. dissipation of Flufenacet from water phase may follow bi-phasic pattern. The kinetic fit for the water phase was visually and statistically acceptable for all three kinetic models used, but it was not possible to obtain the fully acceptable fit, mainly in statistical terms, for the combinations SFO-SFO and FOMC-SFO. It shall be indicated that none of the bi-phasic models tested for water phase returned reliable kinetic parameters. Therefore SFO-SFO fit shall be regarded as appropriate description of kinetic behaviour of Flufenacet in water and sediment compartments. For the water phase the kinetic model identified as returning the best fit is the same as indicated in the kinetic examination carried out at the Level P-I.

The kinetic endpoints obtained for each tested combination are presented below in the table B.8.2.2.3._CA-63.

Table B.8.2.2.3._CA-63: The kinetic endpoints obtained in the fitting for each combination of the kinetic models.

Compartment	Kinetic endpoint	Kinetic model tested for water phase:		
		<i>SFO</i>	<i>FOMC</i>	<i>DFOP</i>
<i>Water phase</i>	DT ₅₀ [days]	25.1	19.5	19.9
	DT ₉₀ [days]	83.5	115	103
<i>Sediment phase (SFO model used only)</i>	DT ₅₀ [days]	13.4	12.4	15.6
	DT ₉₀ [days]	44.5	41.2	51.9
	Kinetic formation fraction <i>ff</i>	1.00	1.00	0.8566

Analysing the values of the kinetic formation fractions – *ff*, representing here the flow from water to the sediment phase, RMS noticed that for all three combinations of the kinetic models tested they were very close or equal to 1. That may indicate that the dominant mechanism of dissipation of Flufenacet from water phase is its migration to sediment. Therefore the kinetic parameters determined for Flufenacet in water phase in that test system should be regarded as persistence endpoints not to be used in modelling.

The comparison of the results obtained for Flufenacet in water phase by RMS and the Applicant showed, that they were similar. For that reason RMS decided to keep as reliable the values determined by the Applicant.

As for the kinetic endpoints for the sediment phase, RMS decided to consider the values determined by the Applicant as reliable kinetic characteristic of the persistence of Flufenacet in sediment phase. That was due to the fact that they displayed higher reliability.

Finally, in RMS's opinion the results of this fitting, and in particular that of *ff* (representing the flow from water to sediment compartment), clearly indicate that the whole system DT₅₀ value is more appropriate for SW modelling at higher tiers as representing the degradation in the sediment phase. Therefore the appropriate value for SW modelling at higher tiers as representing the degradation in water will be DT₅₀ = 1000 days (FOCUS default).

Final conclusion of the kinetic analysis:

On the basis of the obtained results it may be stated that the kinetic endpoints determined for the dissipation of Flufenacet from water phase shall be regarded only as persistence endpoints and cannot be considered as modelling endpoints. Additionally, it was demonstrated that the kinetic endpoints determined for the whole system in each experiment shall be regarded, for the modelling purpose, as representing the degradation of Flufenacet in sediment compartment. Therefore, for degradation in water compartment the default value of DT₅₀ = 1000 days should be used.

Finally, RMS is of the opinion that the kinetic parameters determined by the Applicant the the Level P-I for the whole system, water phase and sediment phase shall be regarded as reliable kinetic endpoints characterising persistence of Flufenacet in water/sediment system. Additionally the whole-system DT₅₀ values shall be used to derive the geomean value to be used as input parameter in SW model exposure assessment.

Finally, the Applicant performed the kinetic analysis of the data for the parent compound and identified major degradation products – FOE Methylsulfide and FOE Thiadone. That was done in order to derive the kinetic endpoints for these two compounds that could be subsequently used in SW modelling assessment.

The kinetic analysis of the data for the major degradation products (performed by the Applicant)

In the water/sediment studies two major degradation products – formed in the whole test system at any time point in amount >10% AR, were identified. In case of the study by [Kelley et al.; 1995] it was FOE Methylsulfide and in that by [Halarnkar and Irwin; 1997] FOE Thiadone. The Applicant performed their kinetical analysis in attempt to derive the kinetic endpoints suitable for deriving kinetic input parameters for the SW modelling.

The kinetic analysis was carried out in line with the recommendations of FOCUS Kinetics Guidelines ([FOCUS; 2006], [FOCUS; 2011]) at the Level M-I using the whole-system data. It was a multi-stage procedure consisting of the following steps:

- **Step 1:** Processing of the raw input data for parent – Flufenacet, and the given degradation product;
- **Step 2:** Kinetic evaluation of the processed data for the using the SFO kinetic model for both parent compound and the given degradation product and KinGUI 2 as a modelling tool; the fitting was carried out using the transformation schemes for Flufenacet → FOE Methylsulfone and Flufenacet → FOE Thiadone presented on figure B.8.2.2.3._CA-38.
- **Step 3:** Evaluation of the results of kinetic examination of the data;
- **Step 4:** Reporting of the obtained results, in particular kinetic parameters (not normalised) recommended for modelling.

The raw input data for Flufenacet were processes following the recommendations given by FOCUS. In general terms it looked as follows:

- The total AR recovery recorded in DAT-0 samples was used as concentration of Flufenacet at that time point, but the M_0 value was allowed to be estimated by the model;
- Values between LOD and LOQ were set to measured values;
- All single values <LOD or the non-detects (n. d.) were set to $\frac{1}{2}$ LOD. The same procedure was applied to the first appearances. However, when the values <LOD/n.d. appeared consecutively for second and next times, the kinetic curve was cut off until the appearance of the first value >LOQ;
- Sampling times for sediment phases were shifted, starting with the time point DAT 0 at the day of the maximum measured concentration of Flufenacet.
- For the whole system the pre-processed values in water and sediment compartments were summed up and used as the input.

The pre-processing of the raw input data for the degradation products followed the similar pattern, and looked as follows:

- The initial (DAT-0) concentration was set to 0. That value, unlike the free-fitted M_0 concentration for the parent compound, was a fixed value;
- The values for subsequent time points, if reported as <LOD or non-detects were also set to 0 until the last time point before the first detectable amount was recorded;
- The value reported as <LOD/n.d. appearing just before the first detectable amount was recorded was set to $\frac{1}{2}$ LOD.
- Values between LOD and LOQ were set to measured values;
- In the decline phase the first values <LOD/n.d. were also set $\frac{1}{2}$ LOD. For the consecutive second and next such appearances the kinetic curve was cut off until, eventually, the first value >LOQ appeared;
- Data sets with insufficient number of data points (less than 4 after peak concentration) were not further processed.

The raw and pre-processed data, used as input data for the kinetic examination, are presented below in two tables: the table B.8.2.2.3._CA-64 for the experiment in which FOE Methylsulfide was identified and table B.8.2.2.3._CA-65 for the experiment in which FOE Thiadone was detected. In case the values were the non-detects occurring before or after the value >LOD appeared for the first/last time (except DAT-0 time point) they were set to NaN (“Not a Number” – KinGUI default when numbers are not available).

Table B.8.2.2.3._CA-64: The not processed and pre-processed whole-system data for Flufenacet and FOE Methylsulfide used as input in kinetic analysis.

Study	Test system/test compound	The whole-system concentrations – the not processed data			The whole-system concentrations – the pre-processed data		
		Time Point – DAT ¹⁾ [days]	Concentration [% AR] of:		Time Point – DAT ¹⁾ [days]	Concentration [% AR] in:	
			Flufenacet	FOE Methylsulfide		Flufenacet	FOE Methylsulfide
[Kelley et al.; 1995]	NESA	0	98.4	0.00	0	100.9	0
		0.25	96.6	0.00	0.25	96.59	NaN
		1	100.8	0.00	1	100.77	NaN
		2	99.5	0.00	2	99.53	0.05
		7	98.1	0.5	7	98.11	0.45
		14	91.5	1.0	14	91.46	0.96
		30	83.4	2.0	30	83.43	1.97
		60	65.8	6.6	60	65.84	6.63
		100	47.9	8.6	100	47.93	8.56
		120	38.8	9.2	120	38.76	9.22
[Kelley et al.; 1995]	BRP	157	27.7	11.4	157	27.67	11.41
		0	95.5	0.00	0	96.2	0
		0.25	99.8	0.00	0.25	99.79	NaN
		1	100.2	0.00	1	100.18	NaN
		2	98.0	0.00	2	98.05	0.05
		7	95.4	0.7	7	95.38	0.68
		14	92.0	0.5	14	.99	0.51
		30	84.1	0.3	30	84.05	0.34
		60	60.9	1.3	60	60.88	1.33
		100	52.6	2.4	100	52.57	2.39
		120	39.1	3.0	120	39.13	2.96
		157	22.3	4.5	157	22.28	4.53

Footnotes to the table:

1) DAT stands for “Days After Treatment”;

Table B.8.2.2.3._CA-65: The not processed and pre-processed whole-system data for Flufenacet and FOE Thiadone used as input in kinetic analysis.

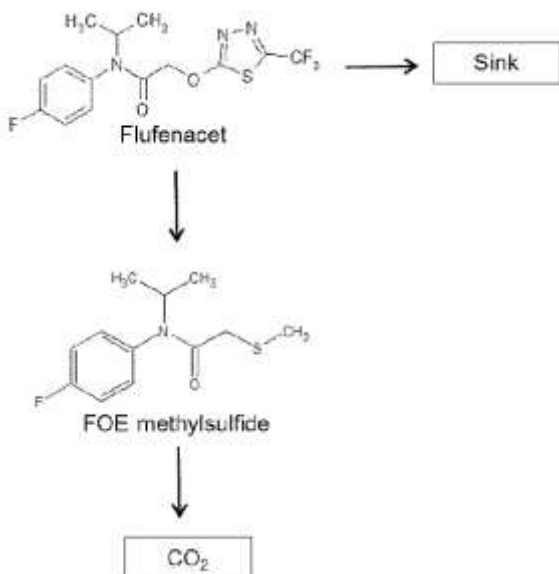
Study	Test system/test compound	The whole-system concentrations – the not processed data			The whole-system concentrations – the pre-processed data		
		Time Point – DAT ¹⁾ [days]	Concentration [% AR] of:		Time Point – DAT ¹⁾ [days]	Concentration [% AR] in:	
			Flufenacet	FOE Thiadone		Flufenacet	FOE Thiadone
[Halarnkar and Irwin; 1997]	NESA	0	94.2	0.0	0	97.90	0
		7	87.9	0.6	7	87.59	0.76
		14	65.2	18.8	14	65.22	18.76
		28	42.1	51.3	28	41.97	51.34
		55	5.0	84.3	55	5.02	84.22
		100	0.6	81.7	100	0.65	81.72
[Halarnkar and Irwin; 1997]	BRP	156	0.9	68.7	156	0.95	68.60
		0	96.3	0.2	0	100.50	0.0
		7	91.8	0.6	7	91.70	0.81
		14	75.6	12.7	14	75.82	12.42
		28	65.4	22.6	28	65.52	22.42
		55	41.0	44.0	55	40.99	43.92
		100	11.1	63.8	100	11.12	63.78
		156	3.3	54.2	156	3.25	54.15

Footnotes to the table:

1) DAT stands for “Days After Treatment”;

The processed data were kinetically examined using KinGUI ver. 2 modelling tool, developed by Bayer. The optimisation was performed using IRLS (Iteratively Reweighed Nonlinear Least Squares) algorithm. The fitting was performed assuming the transformation schemes presented below on figure B.8.2.2.3._CA-38.

Transformation pathway for kinetic examination of the data for Flufenacet and FOE Methylsulfide



Transformation pathway for kinetic examination of the data for Flufenacet and FOE Thiadone

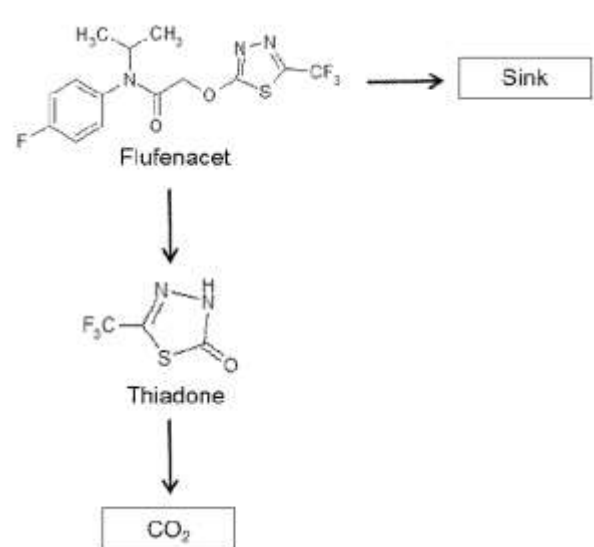


Figure B.8.2.2.3_CA-38: The transformation pathways assumed in the kinetic analysis of the whole-system data for Flufenacet and its major degradation products at the Level M-I (copied from the study report).

The obtained results of the kinetic analysis of the data were evaluated by the Applicant. That was done by means of a detailed statistical analysis, comprising the following components:

- visual assessment of the fit;
- χ^2 -error statistics;
- t-test significance;
- correlation analysis.

Characterising the adopted approach to the visual assessment of the fit, considered to be the first step in the evaluation, the Applicant stated that it focused on the following features:

- the conformity of the fitted decline curve with measured residue concentrations;
- the distribution of the residuals, which should be random and not systematic;
- level of residuals, which should be as small as possible – in such case even if their distribution is rather systematic, the fit may be still qualified as acceptable.

Based on these criteria the fit could be classified as:

- **good fit**, when the conformity of the kinetic curve and measured residues was good, levels of residuals were low, they were randomly scattered and no obvious systematic deviation in residual plot was visible;
- **acceptable fit**, when the conformity of the kinetic curve and measured residues was acceptable, levels of residuals were medium and they were more-or-less randomly scattered, and the absolute level of residuals was low;
- **poor fit**, when the fitted decline curve significantly deviated from the measured residues and did not match the observed pattern, the level of residuals was high and they were clearly not randomly scattered around zero line.

Characterising the next component of the assessment – χ^2 -error statistics, the Applicant indicated that 15% threshold value was not considered to be an absolute cut-off criterion, especially in case of the degradation products. That was indicated to be due to the fact that that threshold value is strictly appropriate for optimal experimental conditions only. It was therefore indicated that in some cases, even though χ^2 -error > 15%, the fit may be acceptable. Additionally, for degradation products it was indicated that for them usually measurements in comparison to the mean of all measurements are low, what strongly influences the χ^2 test.

Finally, characterising the t-test, the Applicant stated that the t-test probability of 0.05 was sufficiently small and should be used as acceptability criterion, in case however of degradation products, or the results of field dissipation studies the $prob > t$ value of 0.10 or even higher may be still acceptable.

Analysing the proposed assessment procedure RMS stated that it complied with the procedure presented in FOCUS Kinetics Guidance Document [FOCUS; 2006].

The results of the kinetic examination of the data and their evaluation are provided below, individually for each test system.

- 1) The kinetic evaluation of the whole-system data for Flufenacet and FOE Methylsulfide obtained in the test system NESA treated with [Phenyl- $U-^{14}C$]Flufenacet (study by [Kelley et al.; 1995]):

The kinetic analysis of the whole-system data for Flufenacet and FOE Methylsulfide was carried out SFO kinetic model for both compounds. Its graphical results are presented on figure B.8.2.2.3._CA-39 and the numerical results in the table B.8.2.2.3._CA-66. Additionally, in the table B.8.2.2.3._CA-67 are provided the kinetic endpoints returned by the modelling tool for each compound.

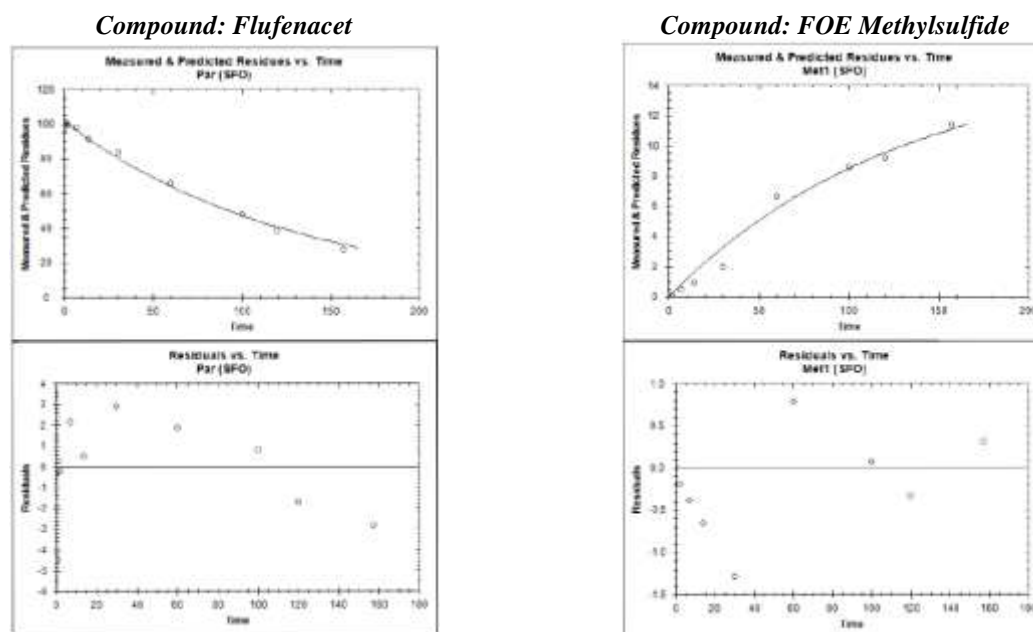


Figure B.8.2.2.3._CA-39: The graphical results of the kinetic analysis (copied from the study report).

Table B.8.2.2.3._CA-66: The numerical results of the kinetic analysis.

Compound	Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
			Value	Error	Confidence intervals		Prob. > t	χ^2 % error	Visual assessment ¹⁾
					Lower	Upper			
Flufenacet	SFO	M_0	101.30	0.991	99.32	103.21	<2 E-16	2.186	Not provided
		k	7.65 E-3	2.74 E-4	7.11 E-3	0.008	2.73 E-15		
FOE Methylsulfide	SFO	M_0	0.0	----	----	----	----	10.076	Good
		k	4.51 E-9	1.54 E-3	-3.03 E-3	0.003	0.5		
		ff	0.1568	0.01854	----	----	----		

1) Visual assessment of the kinetic curve as proposed by the Applicant.

Table B.8.2.2.3._CA-67: The kinetic endpoints obtained as a result of the fitting.

Determined parameter	Compound	
	<i>Flufenacet</i>	<i>FOE Methylsulfide</i>
DT ₅₀ [days]	90.64	Reliable value not determined
DT ₉₀ [days]	301.10	Reliable value not determined
Kinetic formation fraction <i>ff</i>	Not applicable – parent compound	0.157 ± 0.0185
Precursor	Not applicable – parent compound	Flufenacet
Kinetic model	FOMC	SFO

Evaluation:

The values obtained for the parent compound are very similar to those obtained for Flufenacet fitted alone. In case of the degradation product – FOE Methylsulfide it was not possible to obtain the reliable kinetic endpoints for degradation because the concentrations were still increasing at the study's end.

- 2) The kinetic evaluation of the whole-system data for Flufenacet and FOE Methylsulfide obtained in the test system **BRP** treated with [Phenyl-U-¹⁴C]Flufenacet (study by [Kelley et al.; 1995]):

The kinetic analysis of the whole-system data for Flufenacet and FOE Methylsulfide was carried out SFO kinetic model for both compounds. Its graphical results are presented on figure B.8.2.2.3._CA-40 and the numerical results in the table B.8.2.2.3._CA-68. Additionally, in the table B.8.2.2.3._CA-69 are provided the kinetic endpoints returned by the modelling tool for each compound.

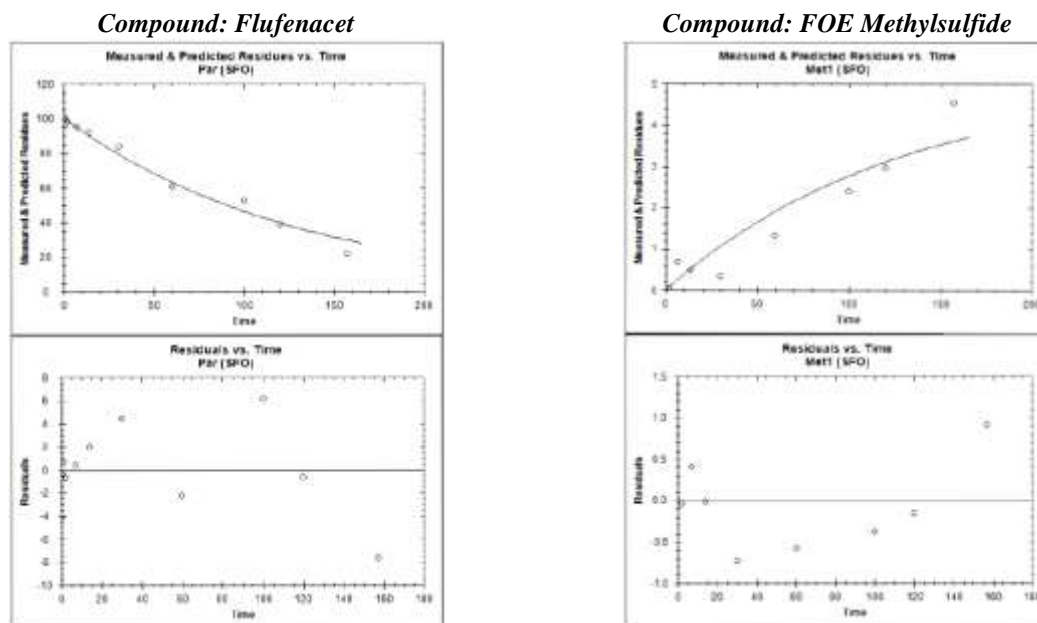
**Figure B.8.2.2.3._CA-40:** The graphical results of the kinetic analysis (copied from the study report).

Table B.8.2.2.3._CA-68: The numerical results of the kinetic analysis.

Compound	Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
			Value	Error	Confidence intervals		Prob. > t	χ^2 % error	Visual assessment ¹⁾
					Lower	Upper			
Flufenacet	SFO	M ₀	100.30	1.707	96.96	103.65	<2 E-16	3.810	Not provided
		k	7.71 E-3	4.78 E-4	6.77 E-3	0.009	1.29 E-11		
FOE Methylsulfide	SFO	M ₀	0.0	----	----	----	----	25.098	Poor
		k	3.49 E-9	4.35 E-3	-8.53 E-3	0.009	0.5		
		ff	0.0514	0.0156	----	----	----		

1) Visual assessment of the kinetic curve as proposed by the Applicant.

Table B.8.2.2.3._CA-69: The kinetic endpoints obtained as a result of the fitting.

Determined parameter	Compound	
	Flufenacet	FOE Methylsulfide
DT ₅₀ [days]	89.91	Reliable value not determined
DT ₉₀ [days]	298.70	Reliable value not determined
Kinetic formation fraction ff	Not applicable – parent compound	0.051 ± 0.0043
Precursor	Not applicable – parent compound	Flufenacet
Kinetic model	FOMC	SFO

Evaluation:

The values obtained for the parent compound are very similar to those obtained for Flufenacet fitted alone. In case of the degradation product – FOE Methylsulfide it was not possible to obtain the reliable kinetic endpoints for degradation because the concentrations were still increasing at the study's end.

- 3) The kinetic evaluation of the whole-system data obtained for Flufenacet and FOE Thiadone in the test system **NESA** treated with [Thiadiazole-2-¹⁴C]Flufenacet (study by [Halarnkar and Irwin; 1997]):

The kinetic analysis of the whole-system data for Flufenacet and FOE Thiadone was carried out SFO kinetic model for both compounds. Its graphical results are presented on figure B.8.2.2.3._CA-41 and the numerical results in the table B.8.2.2.3._CA-70. Additionally, in the table B.8.2.2.3._CA-71 are provided the kinetic endpoints returned by the modelling tool for each compound.

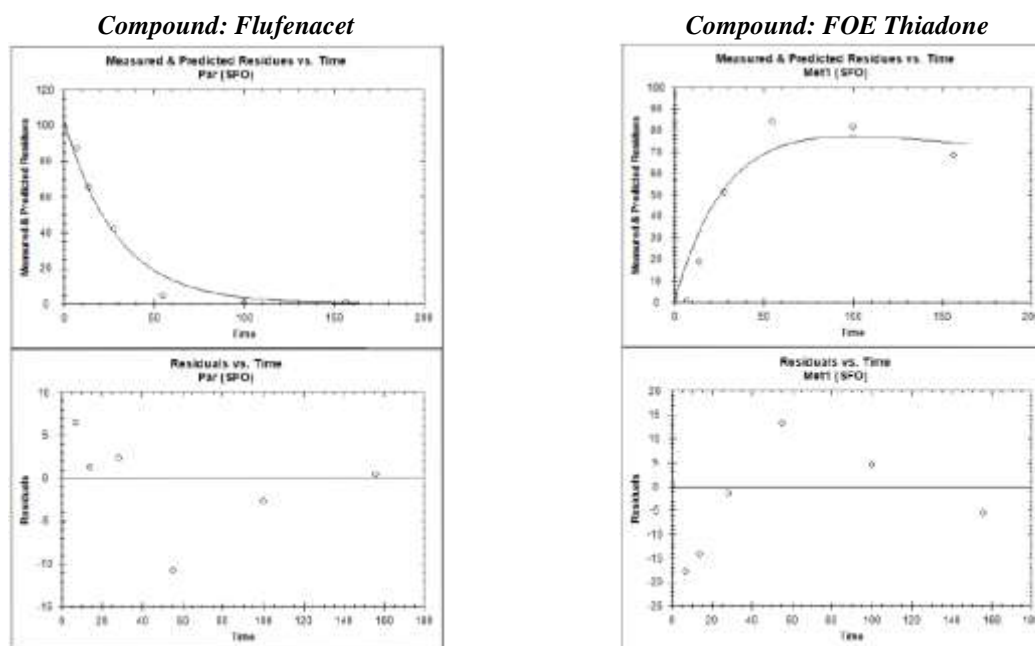


Figure B.8.2.2.3_CA-41: The graphical results of the kinetic analysis (copied from the study report).

Table B.8.2.2.3_CA-70: The numerical results of the kinetic analysis.

Compound	Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
			Value	Error	Confidence intervals		Prob. > t	χ^2 % error	Visual assessment ¹⁾
					Lower	Upper			
Flufenacet	SFO	M ₀	102.99	5.151	92.90	113.089	1.08 E-9	9.905	Not provided
		k	0.03411	0.00392	0.02643	0.042	2.80 E-6		
FOE Thiadone	SFO	M ₀	0.0	----	----	----	----	17.448	Poor
		k	1.26 E-3	2.02 E-3	-2.71 E-3	0.005	0.2736		
		ff	0.8504	----	----	----	----		

1) Visual assessment of the kinetic curve as proposed by the Applicant.

Table B.8.2.2.3_CA-71: The kinetic endpoints obtained as a result of the fitting.

Determined parameter	Compound	
	Flufenacet	FOE Thiadone
DT ₅₀ [days]	89.91	Reliable value not determined
DT ₉₀ [days]	298.70	Reliable value not determined
Kinetic formation fraction ff	Not applicable – parent compound	0.850
Precursor	Not applicable – parent compound	Flufenacet
Kinetic model	FOMC	SFO

Evaluation:

The values obtained for the parent compound are very similar to those obtained for Flufenacet fitted alone. In case of the degradation product – FOE Thiadone it was not possible to obtain the reliable kinetic endpoints for degradation because of the too few data points after the maximum was reached and the poor fitting results.

- 4) The kinetic evaluation of the whole-system data obtained for Flufenacet and FOE Thiadone in the test system **BRP** treated with [Thiadiazole-2-¹⁴C]Flufenacet (study by [Halarikar and Irwin; 1997]):

The kinetic analysis of the whole-system data for Flufenacet and FOE Thiadone was carried out SFO kinetic model for both compounds. Its graphical results are presented on figure B.8.2.2.3._CA-42 and the numerical results in the table B.8.2.2.3._CA-72. Additionally, in the table B.8.2.2.3._CA-73 are provided the kinetic endpoints returned by the modelling tool for each compound.

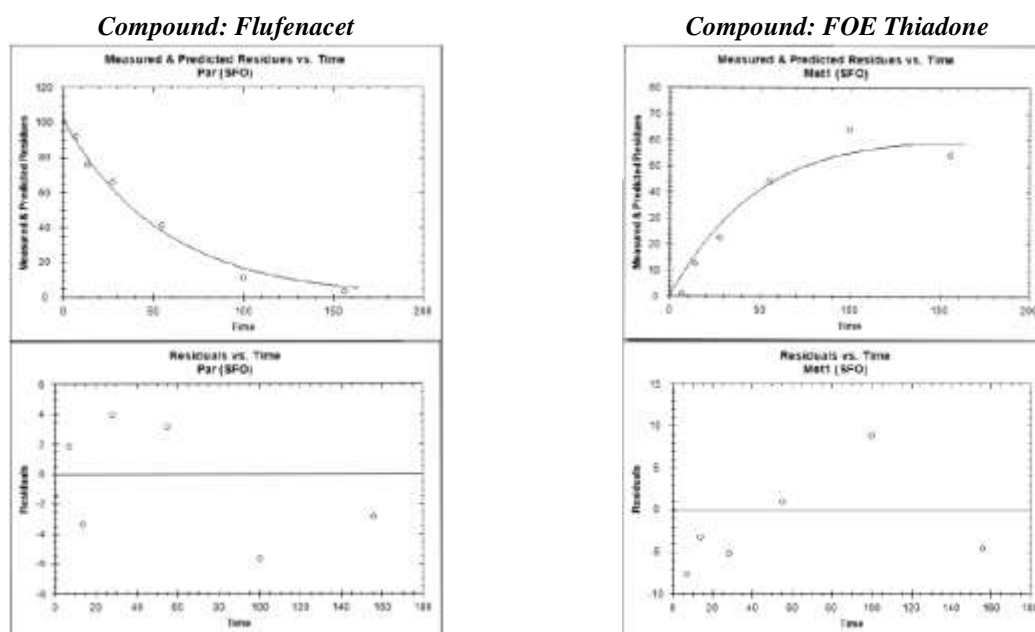


Figure B.8.2.2.3._CA-42: The graphical results of the kinetic analysis (copied from the study report).

Table B.8.2.2.3._CA-72: The numerical results of the kinetic analysis.

Compound	Kinetic model	Model parameters	Statistical evaluation of the parameter					Evaluation of the fit	
			Value	Error	Confidence intervals		Prob. > t	χ^2 % error	Visual assessment ¹⁾
					Lower	Upper			
Flufenacet	SFO	M ₀	101.940	2.908	96.240	107.639	4.23 E-12	4.941	Not provided
		k	0.01802	0.001345	0.01538	0.021	5.15 E-8		
FOE Thiadone	SFO	M ₀	0.0	----	----	----	----	13.718	Good
		k	1.15 E-3	0.00179	-0.00237	0.005	0.269		
		ff	0.6949	0.1084	----	----	----		

1) Visual assessment of the kinetic curve as proposed by the Applicant.

Table B.8.2.2.3._CA-73: The kinetic endpoints obtained as a result of the fitting.

Determined parameter	Compound	
	Flufenacet	FOE Thiadone
DT ₅₀ [days]	38.47	Reliable value not determined
DT ₉₀ [days]	127.80	Reliable value not determined
Kinetic formation fraction ff	Not applicable – parent compound	0.6949
Precursor	Not applicable – parent compound	Flufenacet
Kinetic model	FOMC	SFO

Evaluation:

The values obtained for the parent compound are very similar to those obtained for Flufenacet fitted alone. In case of the degradation product – FOE Thiadone it was not possible to obtain the reliable kinetic endpoints for degradation because of the too few data points after the maximum was reached.

Conclusions of the fitting:

The kinetic examination of the whole-system data for Flufenacet and its identified major degradation products – either FOE Methylsulfide or FOE Thiadone, showed that it was not possible to derive reliable kinetic endpoints for both metabolites. In case of FOE Methylsulfide that was due to the fact that by the end of the study the maximum of formation and decline phase were not reached. For FOE Thiadone such maximum was reached in both test systems, but the decline phase that followed comprised too few data points – two for NESA test system and only one for BRP test system, to obtain the reliable kinetic endpoints.

Additionally it was demonstrated that neither for FOE Methylsulfide nor FOE Thiadone it was possible to obtain fully reliable kinetic fits using the available data sets.

Final conclusions of the study:

The Applicant presented the kinetic evaluation of the data on the fate and behaviour of Flufenacet in water/sediment systems obtained in two separate studies: by [Kelley et al.; 1995] using [Phenyl-U-¹⁴C]Flufenacet and by [Halarnkar and Irwin; 1997] using [Thiadiazole-2-¹⁴C]Flufenacet. In these studies two major degradation products were identified – FOE Methylsulfide in the experiment by [Kelley et al.; 1995] and FOE Thiadone in that by [Halarnkar and Irwin; 1997]. The kinetic analysis was performed for the data obtained for Flufenacet in the whole test systems as well as in water and sediment phases of each test system and was carried out on the Level P-I. Its aim was, in case of the whole-system data to determine the persistence endpoints for Flufenacet and the modelling endpoints. In case of water and sediment phases the kinetic analysis was aimed on the determination of the persistence endpoints. The analysis was performed in line with the recommendations given by FOCUS Kineits Guidance document [FOCUS; 2006].

The key results of that examination are presented below in the table B.8.2.2.3._CA-74.

Table B.8.2.2.3._CA-74: The key results of the kinetic examination at the Level P-I of the data obtained for Flufenacet in water/sediment studies.

Study	Test system	Compartment	Kinetic model	Evaluation of fit		Kinetic parameter(s)		Kinetic endpoints	
				Visual	χ^2 % error	Parameter	Value	DT ₅₀ [days]	DT ₉₀ [days]
[Kelley et al.; 1995]	NESA	Whole system	SFO	Good	2.185	<i>k</i>	0.00767	90.34	300.10
		Water	SFO	Good	4.936	<i>k</i>	0.0118	58.72	195.10
		Sediment	SFO – top down	Good	2.079	<i>k</i>	0.00493	140.50	466.80
	BRP	Whole system	SFO	Good	3.804	<i>k</i>	0.00779	89.00	295.70
		Water	FOMC	Good	4.041	α	1.339	31.23	211.00
		Sediment	SFO – top down	not reported	7.534	<i>k</i>	0.005754		
[Halarnkar and Irwin; 1997]	NESA	Whole system	SFO	Good	9.836	<i>k</i>	0.03525	19.67	65.33
		Water	SFO	Good	6.823	<i>k</i>	0.04083	16.98	56.40
		Sediment	SFO – top down	Good	7.312	<i>k</i>	0.03929	17.64	58.61
	BRP	Whole system	SFO	Good	4.933	<i>k</i>	0.01819	38.11	126.60
		Water	SFO	Good	12.50	<i>k</i>	0.02908	23.84	79.20
		Sediment	SFO – top down	Good	7.738	<i>k</i>	0.01447	47.91	159.10

The calculated geomean values for the kinetic endpoints – DT₅₀ and DT₉₀, determined in the whole system are following **DT₅₀ = 49.54 days**, **DT₉₀ = 164.59 days**. These values are determined by the RMS. The geomean

whole-system DT_{50} value given in the study report is following: **$DT_{50} = 49.6$ days**. The difference between the two values is minimal and can be attributed to the rounding procedure used by the Applicant. Therefore the value proposed by the Applicant may be considered a reliable kinetic endpoint to be used as input parameter in SW model exposure assessment.

For water and sediment phases at the Level P-I the Applicant derived two sets of the kinetic endpoints – those representing persistence and those suitable for modelling. RMS however noticed that Flufenacet displayed quite high adsorption potential onto soil, with the geomean $K_{fOC} = 245.9$ mL/g (range 161.6 – 643.48 mL/g) and rather low solubility in water – 56 mg/L. That may indicate that the compound would display substantial affinity to the sediment phase. The examination of degradation of Flufenacet in natural water, not containing suspended sediment, showed that that process take long – more than 600 days. Additionally, studies on abiotic degradation of Flufenacet in water showed that only indirect photolysis may substantially contribute to the dissipation of Flufenacet from water, while abiotic hydrolysis is not a relevant degradation mechanism for Flufenacet. All that taken into account, also bearing in mind that the water/sediment studies were performed in absence of light, it may be assumed that the process of dissipation of Flufenacet from water column is, at least of mixed nature, partly being degradation and to some extent, if not predominantly, migration to the sediment, where the proper degradation occurs.

In order to verify that RMS decided to perform additional kinetic examination of the data for Flufenacet using the procedure corresponding to the Level P-II assessment. In that fitting the data for Flufenacet in water phase were treated as those for the parent compound, while the sediment phase was defined as the metabolite A1 compartment.

Unlike at the Level P-I for the sediment phase whole data set was fitted together with that for water phase.

The results obtained for water phase were comparable to those obtained for that compartment by the Applicant at the Level P-I. The kinetic endpoints obtained for the sediment phase were usually shorter than those obtained by the Applicant at the Level P-I, what also reflected differences in the kinetic approach. It shall be indicated that the fits obtained for Flufenacet in the sediment phase were also not always fully reliable, but of sufficient quality to draw the conclusions.

Finally, it was noticed that the values of the kinetic formation fraction – ff , characterising the flux from water to sediment phases were in all cases very close or equal to 1. That may indicate that the dominant mechanism of dissipation from water column is migration to the sediment.

On that basis the RMS stated that the geomean whole-system DT_{50} value when used in the modelling should be considered as representing the degradation of Flufenacet in sediment, not in the water column.

The Applicant also made an attempt to derive the kinetic endpoints for the two identified major degradation products – FOE Methylsulfide and FOE Thiadone. The kinetic analysis aimed on that was performed at the Level M-I using the whole-system data for Flufenacet and related degradation products kinetically fitted together. The results obtained for Flufenacet were very similar to those obtained for the same compound fitted alone at the Level P-I. However, it was not possible to obtain the reliable kinetic endpoints for the degradation products, due to the fact that the concentrations stillm increased at the end of the experiment – which was the case for FOE Methylsulfide, or the number of data point after maximum was reached was too low to obtain the reliable decline curve, what was observed in case of FOE Thiadone. Additionally, it shall be indicated that due to the poor fitting results the kinetic formation fractions determined for both degradation products shall be considered with care.

Study 4:

Report: Pangilinan N. C., Smith D. M., (1995): “Anaerobic Aquatic Metabolism of [Thiadiazole-2-¹⁴C]FOE 5043.”; Miles Inc., Agriculture Division, Research and Development Department, P. O. Box 4913, Kansas City, Missouri 64120-0013, USA; (performing laboratory) *for* Miles Inc., Agriculture Division, 17745 South Metvcalf Avenue, Stilwell, Kansas 66085, USA; study No. F3042102; unpublished Miles Report No. MR 106440; 24 February 1995; study reference number: M-002215-01-1;

Guidelines: The study was performed to comply with the following Guidelines:

- US. EPA Guidelines for Pesticide Registration, Subdivision N, Section 162-3, Anaerobic Aquatic Metabolism.

GLP: Yes;

RMS comments: The study had been evaluated for the previous authorisation of Flufenacet in the EU, by its inclusion into the Annex I of the Directive 91/414/EEC. Its summary can be found under the point B.7.4.3.2.2., in section B.7 of the Annex B to the Monograph prepared by the RMS – France, for Flufenacet. The study was evaluated for its compliance with OECD Guideline 308 – Aerobic and Anaerobic Transformation in Aquatic Sediment Systems. RMS stated that the study deviated from the reference Guideline in the following areas:

- **selection of sediment:** in the study soil was used instead of anaerobic sediment; the water overlying “sediment layer” was not that associated with it, but taken from pond located at the test facility, in the vicinity of the soil sampling area;
- **number of water/sediment systems:** the Guideline recommends at least two types of water/sediment systems to be used in experiment; in this case only one type was used;
- **duration of the experiment:** Guideline recommends that the study should usually not be longer than 100 days; in this case the study lasted for 388 days;
- the anaerobic conditions were not maintained throughout the incubation period and there is no indication in the study report when the change occurred; although in the study report it is declared that anaerobic conditions for ~99 days of incubation there is no experimental evidence conforming that statement;
- although the study lasted for 388 days and the test soil, used as a surrogate for sediment, was known, from other studies, to have problems with maintaining biological viability, in the study report the biological viability of the test system was not reported.

As a result, RMS stated that the study cannot be considered as complying with the provisions of the reference Guideline, hence it cannot be considered acceptable for the present assessment. It shall be indicated that the fully reliable study in aerobic water/sediment system for Flufenacet radiolabelled in exactly the same position as used here is summarised above as **Study 2**. Therefore RMS decided not to summarise it in order not to overburden the report, nor include its results into the List of End Points. The former summary can be found in the Draft Assessment Report prepared by the then-RMS – France, for the previous authorisation of Flufenacet in the EU.

Summary:

The evaluation of the study performed by the RMS showed that it was not acceptable. For that reason, in order not to overburden the Renewal Assessment Report, RMS decided not to summarise it.

Additionally the search of the open literature resulted in identifying a paper containing the data relevant for the determination of fate and behaviour of Flufenacet in water/sediment system. The paper is characterising the fate and behaviour of Trifluoroacetic acid (TFA) in water/sediment systems, the issue not covered by any of water/sediment studies submitted for Flufenacet for regulatory purposes. It is summarised below as **Study 5**.

Study 5:

Report: Ellis D. A.^{a)}, Hanson M. L.^{b)}, Sibley P. K.^{b)}, Shahid T.^{a)}, Fineberg N. A.^{a)}, Solomon K. R.^{b)}, Muir D. C. G.^{c)}, Mabury S. A.^{a)}, (2001): "The fate and persistence of trifluoroacetic and chloroacetic acids in pond water."; Department of Chemistry, University of Toronto, Toronto, Canada (a), Department of Environmental Biology, University of Guelph, Guelph, Canada (b), National Water Research Institute, Environment Canada, Burlington, Canada (c); published study - published in: "Chemosphere", vol. 42, 2001, pp 309-318.

Guidelines: : None declared as this is an open-source study, therefore not submitted for the regulatory purposes.

GLP: no, not applicable – peer-reviewed scientific paper

RMS comments: The paper presents the results of the examination of fate of selected haloacetic acids, including trifluoroacetic acid in the aquatic environment. The investigation was carried out using the outdoor aquatic mesocosms (artificial ponds) and laboratory water/sediment systems. In the paper it was not indicated that the experiments were performed in line with any relevant guidelines. However, the study protocol is well characterised, what enables the evaluation of the validity of the study for regulatory purposes. The study may be considered valid, and therefore is summarised below, in its part dealing specifically with the examination of the fate and behaviour of TFA in aquatic, water/sediment, systems. The study provides the pieces of information giving the good insight into the persistence of TFA in SW water bodies and its behaviour there. However, RMS is of the opinion that the results it provides may be regarded only as supplementary and should not be used as a source of regulatory endpoints.

Summary:

The paper contains an abstract, outlining the aims of the experiment and its key results, which was made available on-line. However, due to the copyright restrictions RMS could not present it here and the readers are kindly asked to consult the relevant document. Instead, below is presented the extended summary prepared by the RMS.

Extended summary prepared by RMS:

The aim of the study was to investigate the fate of four haloacetic acids (HAAs) – three chloroacetic acids (monochloroacetic acid – MCA, Dichloroacetic acid – DCA and trichloroacetic acid – TCA) and Trifluoroacetic acid (TFA) in the aquatic environment – field and laboratory microcosms. That was done in order to demonstrate that the degradation of chloroacetic acids is the biologically mediated process and to establish the degradation pathways and the residence times of the test HAAs in natural (pond) water.

The selected HAAs are common pollutants belonging to that group, for which the routes of entering the environment as well as concentrations in various environmental compartments was extensively examined. However, prior to that study little was known about their fate and behaviour in the environment, and in particular in SW water bodies.

The outdoor part of the experiment was performed at the University of Guelph Microcosm Facility, located at the Guelph Turfgrass Institute (Canada) and consisting of 30 artificial ponds. The microcosms were each 1.2 m deep, 3.9 m in diameter, having a surface area of 11.95 m² and a capacity of holding approx. 12 m³ of water. The water layer in each of them had a depth of 1 m. In order to avoid the potential run-off from precipitation the ponds were located on the top of a raised mound. The surface of water layer in each pond was on the same level as the surrounding ground and the its rim was elevated 5-10 cm above that level.

The microcosm systems were created using galvanized steel panels and support struts to provide a basic frame and food grade PVC to create the closed system relative to other microcosm.

The sediment layer in each mesocosm was created by placing at the bottom 46 trays, 52-cm long and 25-cm wide, having the depth of 7cm. They were filled with a sediment consisting of a mixture of sand and loam in even amounts and in 20% of organic matter. The so prepared sediment was sieved thorough ½ in. mesh screen. The so prepared trays covered approx. 50% of the total bottom surface of the microcosm. Water filling

microcosm during pre-treatment period originated from an irrigation pond located on the trial site and supplied from the on-site located well. It was circulated among all microcosm at rate 12 m³/24 hours for at least two weeks prior to the treatment with any test compounds. To each microcosm were introduced at least five potted macrophytes – *Myriophyllum spicatum* in order to provide the habitat for juvenile fish and zooplankton. Additionally individual plants of *Myriophyllum spicatum* and *Myriophyllum sibiricum* were introduced for toxicity testing. In each microcosm cages with breeding pairs (four pairs per cage) of fish – fathead minnow (*Pimephales promelas*) were introduced. In some studies the additional fish species – pumpkinseed sunfish (*Lepomis gibbosus*) were introduced in hanging mesh cages. Microcosms were open to aerial colonisation by insects and PVC sides allowed for periphyton growth.

The circulation of water in microcosms was stopped before the treatment with the test compounds, each administered individually.

The HAA were administered as a solution in bi-distilled deionised water, adjusted to pH = 8.5, prepared on the day of treatment. The treatment solutions were injected to the microcosms using a low-pressure high-volume pump system. After treatment water in each microcosm, including the untreated controls was circulated for 15 minutes.

The experiments with TFA, each lasting one year, were performed in two periods – in years 1997-1998 and 1998-1999. The treatment rates in 1997 were following: 10 µg/L – four microcosms, 100 µg/L – another four microcosms, 300 µg/L – two microcosms, 1000 µg/L – another two microcosms. In 1998 the treatment rates were: 100 µg/L, 1000 µg/L, 3000 µg/L and 10000 µg/L, each applied to three individual microcosms. The experiment for each year comprised also three untreated microcosms as controls.

The experiments lasted 1 year each.

During the experiment the maximum and minimum temperature and dissolved O₂ were measured on the daily basis. Additionally, on selected sampling days other water parameters, such as pH hardness, alkalinity, DOC total N and total P, were measured.

Water samples for the determination of the content of the given HAA were taken one day before treatment, on the day of the treatment, 1 hour after introduction of the test compound, on DAT 1 (Days After Treatment), DAT 2, DAT 4, DAT 7 and from that time point in one- or two-week intervals. They were taken using the metal integrated water column sample, characterised in one of the previous publications by Solomon. From each microcosm at least four samples were collected, having a total volume of 250, 500 or 1000 mL. They were stored at T = 4°C until being analysed by IC.

The indoor experiment, in design similar to water/sediment study, was carried out in 120-mL clear narrow-mouth Boston round bottles to which 5-g aliquots of the dried sediment, characterised above, were introduced. Next, to each bottle the appropriate amount of the test solution, containing 20 µg/mL of the given HAA, was added in such way to not disturb the sediment. The bottles were then loosely capped and placed on the windowsill facing north to be exposed to sunlight – 12-14 hours in June-July 1999. At predefined sampling points 5-mL water samples were taken for the analysis. The experiment for TFA lasted for 2880 hours (120 days).

The quantitative analysis of TFA was performed by means of the Ion Chromatography (IC), on Dionex Ionopac AS14 IC column. The chromatographic separation was performed in isocratic mode using an aqueous solution of 3.5 mmol NaHCO₃/0.5 mmol Na₂CO₃ as a mobile phase.

In case of the low-concentration samples – <100 µg/L a pre-concentration step was used. Firstly 50-mL aqueous samples were filtered through 0.45-µm paper filter and then passed sequentially through an IC-Ba cartridge and two 500-mg SAX columns. Next cartridges were eluted with 2M NaOH_{aq}, the eluates combined and analysed using IC. For these samples the standard solutions, containing the known amounts of TFA, were prepared in a similar way.

In the field studies with TFA no global change in concentration of that compound over the period of one experimental year was observed. As the results of the concurrent project showed the input of TFA from precipitation was negligible (in amounts of ng/L), it was stated that no degradation of TFA occurred. However, the temporal fluctuations in concentration were recorded. During the period June – October no change in concentrations of TFA in water column was observed, from November to the end of January they dropped by 35%. Then in February and March it gradually returned to the initial levels.

The possible explanation of that phenomenon was the forced partition to the not identified phase, possibly enhanced by low temperatures. It was noticed that formation of ice caused the increase of the concentration of TFA in water phase due to its thermodynamic exclusion from ice. That phenomenon however was observed for one 1-year experimental period, while in the second experiment no such decrease was observed. For that reason further experiments were conducted.

One of the possible explanation of the phenomenon, provided in the paper were the observed differences in the content of biotic and/or suspended organic matter content, what could have indicated that TFA partitioned to that phase.

In the laboratory water/sediment experiments with TFA no degradation of that compound was observed in the course of experiment, conforming its high persistence.

It shall be indicated that unlike TFA all chlorinated HAAs used in the experiment underwent degradation, at rate specific for the given compound. TFA was not degraded even in solutions previously containing TCA, so pre-adapted to degradation of HAAs. That indicated that TFA is very resistant to microbial transformation.

On the basis of the obtained results it was stated that TFA was demonstrated to be persistent in natural SW water bodies, but its concentrations may be subjected to the temporal fluctuations related to the changes of the temperature. It was indicated however that the nature of that phenomenon required further examination.

RMS comments:

The results of this study demonstrate the high persistence of TFA in SW water bodies under natural conditions. Therefore they may be considered as fully supporting the default $DT_{50} = 1000$ days values for TFA in the whole system. water and sediment, proposed to be used as the input values in the SW modelling.

Summary – Water/sediment studies

The transformation pattern of Flufenacet in aerobic water/sediment systems was examined in two separate studies, using Flufenacet radiolabelled at two different positions – uniformly in fluorophenyl ring as [Phenyl-U- ^{14}C]Flufenacet – one of the studies ([Kelley et al.; 1995]), and in C2 position of Thiadiazole moiety as [Thiadiazole -2- ^{14}C]Flufenacet – second study ([Halarnkar and Irwin; 1997]). In each study two water/sediment systems were used, bearing codenames (common for both studies) NESA and BRP. It shall be indicated however that, although sampled on the same locations, the test systems did not bear the same characteristics, therefore shall be considered as individual test systems and not the replicates. RMS examining the data set noticed that the examination of the transformation of the thiadiazole moiety of Flufenacet was performed for only C2 radiolabelling position, while C5 radiolabelling position was not covered. That resulted in the lack of data concerning the potential formation of TFA and, possibly (if the degradation pattern was similar to that observed in aerobic soil) FOE TFESA. RMS considers this to be a potential data gap with regard to the full examination of the transformation of Flufenacet in the water/sediment systems.

In the study with [Phenyl-U- ^{14}C]Flufenacet two water/sediment systems were used:

- NESA test system (NESA), containing silty clay loam sediment, having pH = 7.9, OC content of 0.7% and CEC of 33.5 meq/100 g, and associated water, having pH = 7.5, dissolved O_2 content of 9.2 ppm and the content of total dissolved solids of 82 ppm;
- BRP test system (BRP), containing silty clay loam sediment, having pH = 7.8, OC content of 1.4% and CEC of 25.6 meq/100 g, and associated water, having pH = 7.3, dissolved O_2 content of 8.5 ppm and the content of total dissolved solids of 120 ppm.

The experiment lasted for 156 days and the samples were incubated in the darkness at constant temperature $T = 20^{\circ}C$.

In the study with [Thiadiazole-2- ^{14}C]Flufenacet two water/sediment systems were used:

- NESA test system (NESA 1), containing silty clay sediment, having pH = 7.8, OC content of 0.38% and CEC of 22.0 meq/100 g, and associated water, having pH = 7.2, dissolved O_2 content of 9.2 ppm and the OC content of 331 ppm;
- BRP test system (BRP 1), containing silty clay loam sediment, having pH = 7.8, OC content of 1.54% and CEC of 13.02 meq/100 g, and associated water, having pH = 6.9, dissolved O_2 content of 10.0 ppm and the OC content of 415 ppm.

The experiment lasted for 156 days and the samples were incubated in the darkness at constant temperature $T = 20^{\circ}C$.

The key results of both studies with regard to the distribution of radioactivity in the test systems are presented below in the table B.8.2.2.3._CA-75. The detailed results of the profiling of radioactivity in the test water/sediment systems are presented in the table B.8.2.2.3._CA-76.

Table B.8.2.2.3._CA-75: Distribution of the Applied Radioactivity (AR) in the test water/sediment systems.

Water/ Sediment system and test compound	Characteristic of the system:			AR distribution in the system [%]:				Identified metabolites ¹⁾
				<i>In water phase max/min</i>	<i>Max. in sediment - extractable</i>	<i>NER</i>	<i>Minerali- sation level (¹⁴CO₂)</i>	
NESA; [Phenyl-U- ¹⁴ C] Flufenacet	<i>Sediment's texture class - USDA</i>		Slity clay loam	<u>total:</u> max. 97.1%, DAT 0; min. 38.1%, DAT 157 <u>Flufenacet:</u> max. 94.9%, DAT 0; Min. 15.8% DAT 157	<u>total:</u> max. 23.5%, DAT 120; min. 3.5%, DAT 0 <u>Flufenacet:</u> max. 22.9%, DAT 30; min. 3.5% DAT 0	28.5%; DAT 157	3.4%; DAT 157	FOE Oxalate – max. 4.6%; FOE Alcohol – max. 0.7%; FOE Sulfonic acid – max. 1.7%; FOE Methyl- sulfide – max. 11.4%; FOE Methyl- sulfone – max. 6.4%; FOE Methyl- sulfoxide – max. 3.2%; FOE TGS – max. 2.0%
	<i>pH</i>	Water phase	7.5					
		Sediment	7.9					
	<i>OC content</i>	Sediment [%]	0.7					
	<i>Incubation temperature [°C]</i>		20					
BRP; [Phenyl-U- ¹⁴ C] Flufenacet	<i>Sediment's texture class - USDA</i>		Slity clay loam	<u>total:</u> max. 95.5%, DAT 0; min. 21.9%, DAT 157 <u>Flufenacet:</u> max. 95.0%, DAT 0; min. 7.53% DAT 157	<u>total:</u> max. 35.0%, DAT 30; min. 0.5%, DAT 0 <u>Flufenacet:</u> max. 34.2%, DAT 30; min. 0.5% DAT 0	46.4%; DAT 157	1.5%; DAT 157	FOE Oxalate – max. 5.4%; FOE Alcohol – max. 1.3%; FOE Sulfonic acid – max. 3.2%; FOE Methyl- sulfide – max. 4.5%; FOE Methyl- sulfone – max. 7.2%; FOE Methyl- sulfoxide – max. 2.2%; FOE TGS – max. 1.9%
	<i>pH</i>	Water phase	7.3					
		Sediment	7.8					
	<i>OC content</i>	Sediment [%]	1.4					
	<i>Incubation temperature [°C]</i>		20					
NESA 1; [Thiadiazole-2- ¹⁴ C]Flufenacet	<i>Sediment's texture class - USDA</i>		Slity clay	<u>total:</u> max. 88.0%, DAT 28; min. 68.0%, DAT 156 <u>Flufenacet:</u> max. 83.99%, DAT 0; min. 3.1% DAT 55	<u>total:</u> max. 12.8%, DAT 7; min. 2.7%, DAT 100 <u>Flufenacet:</u> max. 12.4%, DAT 7; min. 0.6% DAT 100	3.3%; DAT 55	15.3%; DAT 156	FOE Thiadone – max. 84.3%
	<i>pH</i>	Water phase	7.2					
		Sediment	7.8					
	<i>OC content</i>	Sediment [%]	0.38					
	<i>Incubation temperature [°C]</i>		20					
BRP 1; [Thiadiazole-2- ¹⁴ C]Flufenacet	<i>Sediment's texture class - USDA</i>		Slity clay loam	<u>total:</u> max. 84.5%, DAT 0; min. 0.9%, DAT 156 <u>Flufenacet:</u> max. 83.2%, DAT 0; min. 0.9% DAT 156	<u>total:</u> max. 29.9%, DAT 14; min. 4.4%, DAT 156 <u>Flufenacet:</u> max. 26.1%, DAT 14; min. 2.3% DAT 156	9.6%; DAT 100	15.0%; DAT 156	FOE Thiadone – max 63.8%.
	<i>pH</i>	Water phase	6.9					
		Sediment	7.8					
	<i>OC content</i>	Sediment [%]	1.54					
	<i>Incubation temperature [°C]</i>		20					

Footnotes to the table:

1) FOE TGS = FOE Thioglycolate sulfoxide;

Table B.8.2.2.3._CA-76: The results of the profiling of radioactivity in the test water/sediment systems.

Water/ Sediment system and test compound	Compound	Concentration [% AR] in:								
		Whole system			Water phase			Sediment phase:		
		Begin- ning of the study ¹⁾	End of the study ²⁾	Max. amount (DAT)	Begin- ning of the study ¹⁾	End of the study ²⁾	Max. amount (DAT)	Begin- ning of the study ¹⁾	End of the study ²⁾	Max. amount (DAT)
NESA; [Phenyl- U- ¹⁴ C] Flufenacet	Flufenacet	98.4	27.7	98.4; (0)	94.9	15.8	94.9; (0)	3.5	11.9	22.9; (30)
	FOE Oxalate	0.0	4.6	4.6; (157)	0.0	4.6	4.6; (157)	0.0	0.0	0.2; (100)
	FOE Alcohol	0.0	0.6	0.7; (120)	0.0	0.2	0.2; (157)	0.0	0.4	0.6; (120)
	FOE Sulfonic acid	0.0	1.7	1.7; (157)	0.0	1.7	1.7; (157)	0.0	0.0	0.0
	FOE Methylsulfide	0.0	11.4	11.4; (157)	0.0	8.0	8.0; (157)	0.0	3.5	3.5; (157)
	FOE Methylsulfone	0.0	5.3	6.4; (100)	0.0	4.4	5.0; (100)	0.0	0.9	1.4; (100)
	FOE Methylsulfoxide	0.4	3.2	3.2; (157)	0.4	0.0	0.4; (0)	0.0	3.2	3.2; (157)
	FOE TGS ³⁾	0.0	2.0	2.0; (157)	0.0	2.0	2.0; (157)	0.0	0.0	0.0
BRP; [Phenyl- U- ¹⁴ C] Flufenacet	Flufenacet	95.5	22.3	100.2; (1)	95.0	7.5	95.0; (0)	0.5	14.8	34.2; (30)
	FOE Oxalate	0.0	5.4	5.4; (157)	0.0	4.8	4.8; (157)	0.0	0.6	0.6; (157)
	FOE Alcohol	0.0	1.3	1.3; (157)	0.0	0.0	0.0;	0.0	1.3	1.3; (157)
	FOE Sulfonic acid	0.0	3.2	3.2; (157)	0.5	3.0	3.0; (157)	0.0	0.3	0.3; (156)
	FOE Methylsulfide	0.0	4.5	4.5; (157)	0.0	1.9	2.7; (120)	0.0	2.7	2.7; (157)
	FOE Methylsulfone	0.0	3.8	7.2; (120)	0.0	2.9	6.5; (120)	0.0	0.9	1.0; (100)
	FOE Methylsulfoxide	0.0	1.7	2.2; (120)	0.0	0.5	1.0; (60)	0.0	1.2	2.2; (120)
	FOE TGS ³⁾	0.0	1.4	1.9; (60)	0.0	1.4	2.0; (60)	0.0	0.0	0.0
NESA 1; [Thia- diazole-2- ¹⁴ C] Flu- fenacet	Flufenacet	94.2	0.9	94.2; (0)	83.9	0.0	83.9; (0)	10.4	1.0	12.4; (7)
	FOE Thiadone	0.0	68.7	84.3; (55)	0.0	65.5	81.8; (55)	0.0	3.0	3.0; (156)
BRP 1; [Thia- diazole-2- ¹⁴ C] Flu- fenacet	Flufenacet	96.3	3.3	96.3; (0)	83.2	0.9	83.2; (0)	12.2	2.39	26.1; (14)
	FOE Thiadone	0.2	54.2	63.8; (100)	0.0	52.2	60.0; (100)	0.1	1.9	3.8; (100)

Footnotes to the table:

- 1) DAT 0 for all experiments;
- 2) DAT 157 for experiments with [Phenyl-U-¹⁴C] Flufenacet and DAT 156 for experiments with [Thiadiazole-2-¹⁴C] Flufenacet;
- 3) FOE TGS = FOE Thioglycolate sulfoxide.

The results obtained in the water/sediment systems confirm that Flufenacet cannot be considered readily biodegradable. It was also stated that the transformation pathway of Flufenacet in aerobic water/sediment systems was very similar to that determined in aerobic soil. It is presented below on figure B.8.2.2.3._CA-43. As already stated that transformation scheme cannot be considered complete due to the fact that the transformation of the thiadiazole moiety was not fully examined. In particular not examined was the formation of TFA from FOE Thiadone, the mechanism indicated in some literature studies (please refer to the point **B.8.2.6. – Impact on water treatment procedures**). That would result in the underestimation of the exposure in SW compartment based on the model calculations.

RMS was able to identify one open literature study examining the fate of several halogenoacetic acids, including TFA, in the test systems similar to the design used in water/sediment studies. On that basis it may be concluded that TFA, when formed from FOE Thiadone, will not undergo any substantial transformation in natural SW bodies and it will occur predominantly in water column.

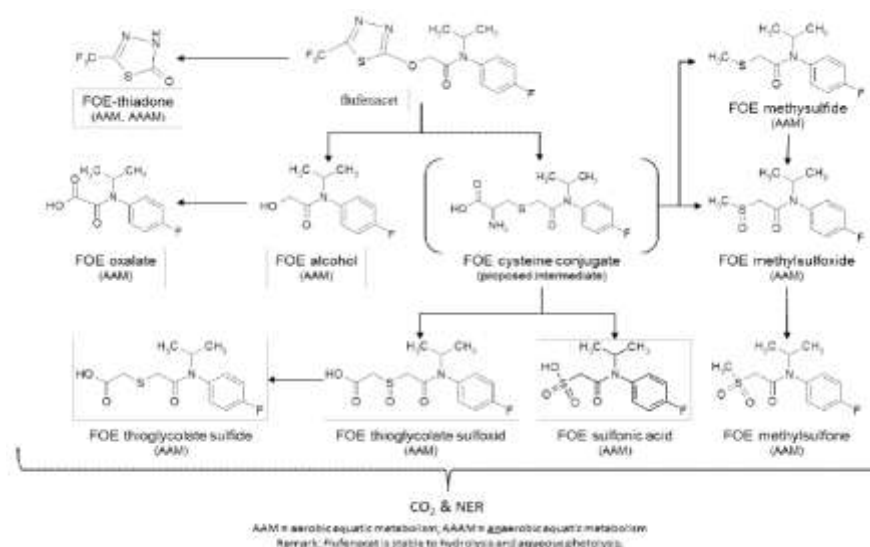


Figure B.8.2.2.3_CA-43: The transformation pathway of Flufenacet determined in aerobic water/sediment system (copied from the Applicant's report).

The results of the regulatory water/sediment studies were subjected to the kinetic examination in a separate study.

The kinetic analysis was performed for the data obtained for Flufenacet in the whole test systems as well as in water and sediment phases of each test system and was carried out on the Level P-I. Its aim was, in case of the whole-system data to determine the persistence endpoints for Flufenacet and the modelling endpoints. In case of water and sediment phases the kinetic analysis was aimed on the determination of the persistence endpoints. The analysis was performed in line with the recommendations given by FOCUS Kinetics Guidance document [FOCUS; 2006].

The key results of that examination are presented below in the table B.8.2.2.3_CA-77.

Table B.8.2.2.3_CA-77: The key results of the kinetic examination at the Level P-I of the data obtained for Flufenacet in water/sediment studies.

Study	Test system	Compartment	Kinetic model	Evaluation of fit		Kinetic parameter(s)		Kinetic endpoints	
				Visual	χ^2 % error	Parameter	Value	DT ₅₀ [days]	DT ₉₀ [days]
[Kelley <i>et al.</i> ; 1995]	NESA	Whole system	SFO	Good	2.185	k	0.00767	90.34	300.10
		Water	SFO	Good	4.936	k	0.0118	58.72	195.10
		Sediment	SFO – top down	Good	2.079	k	0.00493	140.50	466.80
	BRP	Whole system	SFO	Good	3.804	k	0.00779	89.00	295.70
		Water	FOMC	Good	4.041	α	1.339	31.23	211.00
		Sediment	SFO – top down	not reported	7.534	k	0.005754		
[Halarnkar and Irwing; 1997]	NESA	Whole system	SFO	Good	9.836	k	0.03525	19.67	65.33
		Water	SFO	Good	6.823	k	0.04083	16.98	56.40
		Sediment	SFO – top down	Good	7.312	k	0.03929	17.64	58.61
	BRP	Whole system	SFO	Good	4.933	k	0.01819	38.11	126.60
		Water	SFO	Good	12.50	k	0.02908	23.84	79.20
		Sediment	SFO – top down	Good	7.738	k	0.01447	47.91	159.10

The calculated geomean values for the kinetic endpoints – DT₅₀ and DT₉₀, determined in the whole system are following **DT₅₀ = 49.54 days**, **DT₉₀ = 164.59 days**. These values are determined by the RMS. The geomean

whole-system DT_{50} value given in the study report is following: $DT_{50} = 49.6$ days. The difference between the two values is minimal and can be attributed to the rounding procedure used by the Applicant. Therefore the value proposed by the Applicant may be considered a reliable kinetic endpoint to be used as input parameter in SW model exposure assessment.

For water and sediment phases at the Level P-I the Applicant derived two sets of the kinetic endpoints – those representing persistence and those suitable for modelling. RMS however noticed that Flufenacet displayed quite high adsorption potential onto soil, with the geomean $K_{fOC} = 245.9$ mL/g (range 161.6 – 643.48 mL/g) and rather low solubility in water – 56 mg/L. That may indicate that the compound would display substantial affinity to the sediment phase. The examination of degradation of Flufenacet in natural water, not containing suspended sediment, showed that that process take long – more than 600 days. Additionally, studies on abiotic degradation of Flufenacet in water showed that only indirect photolysis may substantially contribute to the dissipation of Flufenacet from water, while abiotic hydrolysis is not a relevant degradation mechanism for Flufenacet. All that taken into account, also bearing in mind that the water/sediment studies were performed in absence of light, it may be assumed that the process of dissipation of Flufenacet from water column is, at least of mixed nature, partly being degradation and to some extent, if not predominantly, migration to the sediment, where the proper degradation occurs.

In order to verify that RMS decided to perform additional kinetic examination of the data for Flufenacet using the procedure corresponding to the Level P-II assessment. In that fitting the data for Flufenacet in water phase were treated as those for the parent compound, while the sediment phase was defined as the metabolite A1 compartment.

Unlike at the Level P-I for the sediment phase whole data set was fitted together with that for water phase.

The results obtained for water phase were comparable to those obtained for that compartment by the Applicant at the Level P-I. The kinetic endpoints obtained for the sediment phase were usually shorter than those obtained by the Applicant at the Level P-I, what also reflected differences in the kinetic approach. It shall be indicated that the fits obtained for Flufenacet in the sediment phase were also not always fully reliable, but of sufficient quality to draw the conclusions.

Finally, it was noticed that the values of the kinetic formation fraction – ff , characterising the flux from water to sediment phases were in all cases very close or equal to 1. That may indicate that the dominant mechanism of dissipation from water column is migration to the sediment.

On that basis the RMS stated that the geomean whole-system DT_{50} value when used in the modelling should be considered as representing the degradation of Flufenacet in sediment, not in the water column.

The Applicant also made an attempt to derive the kinetic endpoints for the two identified major degradation products – FOE Methylsulfide and FOE Thiadone. The kinetic analysis aimed on that was performed at the Level M-I using the whole-system data for Flufenacet and related degradation products kinetically fitted together. The results obtained for Flufenacet were very similar to those obtained for the same compound fitted alone at the Level P-I. However, it was not possible to obtain the reliable kinetic endpoints for the degradation products, due to the fact that the concentrations stillm increased at the end of the experiment – which was the case for FOE Methylsulfide, or the number of data point after maximum was reached was too low to obtain the reliable decline curve, what was observed in case of FOE Thiadone. Additionally, it shall be indicated that due to the poor fitting results the kinetic formation fractions determined for both degradation products shall be considered with care.

Also was submitted the study examining the fate and behaviour of Flufenacet in anaerobic water/sediment system. The study was evaluated for its compliance with OECD Guideline 308 – Aerobic and Anaerobic Transformation in Aquatic Sediment Systems. RMS stated that the study deviated from the reference Guideline in the following areas:

- **selection of sediment:** in the study soil was used instead of anaerobic sediment; the water overlying “sediment layer” was not that associated with it, but taken from pond located at the test facility, in the vicinity of the soil sampling area;
- **number of water/sediment systems:** the Guideline recommends at least two types of water/sediment systems to be used in experiment; in this case only one type was used;
- **duration of the experiment:** Guideline recommends that the study should usually not be longer than 100 days; in this case the study lasted for 388 days;
- the anaerobic conditions were not maintained throughout the incubation period and there is no indication in the study report when the change occurred; although in the study report it is declared that anaerobic conditions for ~99 days of incubation there is no experimental evidence conforming that statement;
- although the study lasted for 388 days and the test soil, used as a surrogate for sediment, was known, from other studies, to have problems with maintaining biological viability, in the study report the biological viability of the test system was not reported.

As a result, RMS stated that the study could not be considered as complying with the provisions of the reference Guideline, hence it was found not acceptable for the present assessment. Therefore RMS decided not to summarise it and use its results in the evaluation.

The results of the examination of fate and behaviour of Flufenacet in aerobic water/sediment systems, in format recommended for reporting the regulatory endpoints in the EU, are presented below. In that form the values will be inserted into the proposal for the EU List of End Points.

Water / sediment study (Regulation (EU) N° 283/2013, Annex Part A, point 7.2.2.3 and Regulation (EU) N° 284/2013, Annex Part A, point 9.2.2)

Parent: Flufenacet		Distribution: NESA test system: max. in water 94.9% on DAT 0, max. in sediment 22.9% on DAT 30; BRP test system: max. in water 95.0% on DAT 0, max. in sediment 34.2% on DAT 30; NESA 1 test system: max. in water 83.99% on DAT 0, max. in sediment 12.4% on DAT 7; BRP 1 test system: max. in water 83.2% on DAT 0, max. in sediment 26.1% on DAT 14								
Water / sediment system	pH water phase	pH sed ^{a)}	t. °C	DT ₅₀ /DT ₉₀ whole sys.	St. (χ ²)	DT ₅₀ /DT ₉₀ water	St. (χ ²)	DT ₅₀ /DT ₉₀ sed	St. (χ ²)	Method of calculation
NESA; silty clay loam sediment	7.5	7.9 ^{a)}	20	90.34 d./ 300.10 d.	2.18	58.72 d./ 195.10 d	4.94	140.50 d./ 466.80 d.	2.08	Whole sys.: SFO; Water: SFO - persistence; Sed.: SFO top-down
BRP; silty clay loam sediment	7.3	7.8 ^{a)}	20	89.00 d./ 295.70 d.	3.80	31.23 d./ 211.00 d	4.04	120.50 d./ 400.20 d.	7.53	Whole sys.: SFO; Water: SFO - persistence; Sed.: SFO top-down
NESA 1; silty clay sediment	7.2	7.8 ^{b)}	20	19.57 d./ 65.33 d.	9.84	16.98 d./ 56.40 d.	6.82	17.64 d./ 58.61 d.	7.31	Whole sys.: SFO; Water: SFO - persistence; Sed.: SFO top-down
BRP 1; silty clay loam sediment	6.9	7.8 ^{b)}	20	38.11 d./ 126.60 d.	4.93	23.84 d./ 79.20 d.	12.5	47.91 d./ 159.10 d.	7.74	Whole sys.: SFO; Water: SFO - persistence; Sed.: SFO top-down
Geometric mean at 20°C ^{b)}				49.55 d./ 164.54 d.	n. a. ^{c)}	29.35 d./ 116.45 d	n. a. ^{c)}	61.50 d./ 204.30 d.	n. a. ^{c)}	

^{a)} Medium, in which pH was measured, not specified;

^{b)} Measured in H₂O;

^{c)} n. a. = not applicable.

Metabolite FOE Oxalate		Distribution : NESA test system: max. in water - 4.6% on DAT 157, max. in sediment - 0.2% on DAT 30, max. in whole system - 4.6% on DAT 157; BRP test system: max. in water - 4.8% on DAT 157, max. in sediment - 0.6% on DAT 157, max. in whole system - 5.4% on DAT 157; kinetic formation fraction (k_f/k_{dp}): reliable values not determined;								
Water / sediment system	pH water phase	pH sed ^{a)}	t. °C	DT ₅₀ /DT ₉₀ whole sys.	St. (χ ²)	DT ₅₀ /DT ₉₀ water	St. (χ ²)	DT ₅₀ /DT ₉₀ sed	St. (χ ²)	Method of calculation
NESA; silty clay loam sediment	7.5	7.9 ^{a)}	20	Not determined	n. a. ^{b)}	Not determined	n. a. ^{b)}	Not determined	n. a. ^{b)}	Not applicable
BRP; silty clay loam sediment	7.3	7.8 ^{a)}	20	Not determined	n. a. ^{b)}	Not determined	n. a. ^{b)}	Not determined	n. a. ^{b)}	Not applicable
Geometric mean at 20°C ^{b)}				Not applicable	n. a. ^{b)}	Not applicable	n. a. ^{b)}	Not applicable	n. a. ^{b)}	Not applicable

^{a)} Medium, in which pH was measured, not specified;

^{b)} n. a. = not applicable.

Metabolite FOE Sulfonic acid		Distribution : NESA test system: max. in water - 1.7% on DAT 157, max. in sediment – not found, max. in whole stsem – 1.7% on DAT 157; BRP test system: max. in water – 3.0% on DAT 157, max. in sediment – 0.6% on DAT 157, max. in whole system – 3.2% on DAT 157; kinetic formation fraction (k_f/k_{dp}): reliable values not determined;								
Water / sediment system	pH water phase	pH sed ^{a)}	t. °C	DT ₅₀ /DT ₉₀ whole sys.	St. (χ^2)	DT ₅₀ /DT ₉₀ water	St. (χ^2)	DT ₅₀ /DT ₉₀ sed	St. (χ^2)	Method of calculation
NESA; silty clay loam sediment	7.5	7.9 ^{a)}	20	Not determined	n. a. ^{b)}	Not determined	n. a. ^{b)}	Not determined	n. a. ^{b)}	Not applicable
BRP; silty clay loam sediment	7.3	7.8 ^{a)}	20	Not determined	n. a. ^{b)}	Not determined	n. a. ^{b)}	Not determined	n. a. ^{b)}	Not applicable
Geometric mean at 20°C ^{b)}				Not applicable	n. a. ^{b)}	Not applicable	n. a. ^{b)}	Not applicable	n. a. ^{b)}	Not applicable

^{a)} Medium, in which pH was measured, not specified;

^{b)} n. a. = not applicable.

Metabolite FOE Methylsulfone		Distribution : NESA test system: max. in water – 5.0% on DAT 100, max. in sediment – 1.4% on DAT 100, max. in whole system – 6.4% on DAT 100; BRP test system: max. in water – 6.5% on DAT 120, max. in sediment – 1.0% on DAT 100, max. in whole system – 7.2% on DAT 120; kinetic formation fraction (k_f/k_{dp}): reliable values not determined;								
Water / sediment system	pH water phase	pH sed ^{a)}	t. °C	DT ₅₀ /DT ₉₀ whole sys.	St. (χ^2)	DT ₅₀ /DT ₉₀ water	St. (χ^2)	DT ₅₀ /DT ₉₀ sed	St. (χ^2)	Method of calculation
NESA; silty clay loam sediment	7.5	7.9 ^{a)}	20	Not determined	n. a. ^{b)}	Not determined	n. a. ^{b)}	Not determined	n. a. ^{b)}	Not applicable
BRP; silty clay loam sediment	7.3	7.8 ^{a)}	20	Not determined	n. a. ^{b)}	Not determined	n. a. ^{b)}	Not determined	n. a. ^{b)}	Not applicable
Geometric mean at 20°C ^{b)}				Not applicable	n. a. ^{b)}	Not applicable	n. a. ^{b)}	Not applicable	n. a. ^{b)}	Not applicable

^{a)} Medium, in which pH was measured, not specified;

^{b)} n. a. = not applicable.

Metabolite FOE Methylsulfide		Distribution : NESA test system: max. in water – 8.0% on DAT 157, max. in sediment – 3.5% on DAT 157, max. in whole system – 11.4% on DAT 157; BRP test system: max. in water – 2.7% on DAT 120, max. in sediment 2.7% on DAT 157; max. in whole system – 4.5% on DAT 157; kinetic formation fraction (k_f/k_{dp}): reliable values not determined;								
Water / sediment system	pH water phase	pH sed ^{a)}	t. °C	DT ₅₀ /DT ₉₀ whole sys.	St. (χ^2)	DT ₅₀ /DT ₉₀ water	St. (χ^2)	DT ₅₀ /DT ₉₀ sed	St. (χ^2)	Method of calculation
NESA; silty clay loam sediment	7.5	7.9 ^{a)}	20	Not determined	n. a. ^{b)}	Not determined	n. a. ^{b)}	Not determined	n. a. ^{b)}	Not applicable
BRP; silty clay loam sediment	7.3	7.8 ^{a)}	20	Not determined	n. a. ^{b)}	Not determined	n. a. ^{b)}	Not determined	n. a. ^{b)}	Not applicable
Geometric mean at 20°C ^{b)}				Not applicable	n. a. ^{b)}	Not applicable	n. a. ^{b)}	Not applicable	n. a. ^{b)}	Not applicable

^{a)} Medium, in which pH was measured, not specified;

^{b)} n. a. = not applicable.

Metabolite FOE Thiadone		Distribution : NESA 1 test system: max. in water – 81.8% on DAT 55, max. in sediment – 3.0 on DAT 156, max. in whole system – 84.3% on DAT 55; BRP 1 test system: max. in water – 60.0% on DAT 100, max. in sediment – 3.8% on DAT 100, max. in whole system – 63.8% on DAT 100; kinetic formation fraction (k_f/k_{dp}): reliable values not determined;								
Water / sediment system	pH water phase	pH sed ^{a)}	t. °C	DT ₅₀ /DT ₉₀ whole sys.	St. (χ^2)	DT ₅₀ /DT ₉₀ water	St. (χ^2)	DT ₅₀ /DT ₉₀ sed	St. (χ^2)	Method of calculation
NESA 1; silty clay sediment	7.2	7.8 ^{a)}	20	Not determined	n. a. ^{b)}	Not determined	n. a. ^{b)}	Not determined	n. a. ^{b)}	Not applicable
BRP 1; silty clay loam sediment	6.9	7.8 ^{a)}	20	Not determined	n. a. ^{b)}	Not determined	n. a. ^{b)}	Not determined	n. a. ^{b)}	Not applicable
Geometric mean at 20°C ^{b)}				Not applicable	n. a. ^{b)}	Not applicable	n. a. ^{b)}	Not applicable	n. a. ^{b)}	Not applicable

^{a)} Measured in H₂O;

^{b)} n. a. = not applicable.

Mineralisation and non extractable residues (from parent dosed experiments)					
Water / sediment system	pH water phase	pH sed	Mineralisation x % after n d. (end of the study).	Non-extractable residues in sed. max x % after n d	Non-extractable residues in sed. max x % after n d (end of the study)
NESA; silty clay loam sediment	7.5	7.9 ^{a)}	3.4% on DAT 157 (end of the study)	28.5% on DAT 157 (end of the study)	28.5% on DAT 157 (end of the study)
BRP; silty clay loam sediment	7.3	7.8 ^{a)}	1.5% on DAT 157 (end of the study)	46.4% on DAT 157 (end of the study)	46.4% on DAT 157 (end of the study)
NESA 1; silty clay sediment	7.2	7.8 ^{b)}	15.3% on DAT 156 (end of the study)	3.3% on DAT 55	2.2% on DAT 156 (end of the study)
BRP 1; silty clay loam sediment	6.9	7.8 ^{b)}	15.0% on DAT 156 (end of the study)	9.6% on DAT 100	7.5% on DAT 156 (end of the study)

^{a)} Medium, in which pH was measured, not specified;

^{b)} Measured in H₂O.

B.8.2.2.4. – Irradiated water/sediment study

The Applicant did not submit any study report specifically covering this data point. However, in the Document M-II, Section 7: Fate and behaviour in the environment, it was stated that such data were provided in the study, also submitted for the purpose of the previous authorisation of Flufenacet in the EU, examining fate and biological effects of that, formulated, compound in aquatic indoor mesocosm. The results obtained in that study with regard to the fate of Flufenacet in the test system were kinetically examined and the results presented in the study report submitted specifically for the purpose of the current evaluation.

The evaluation of both studies performed by the RMS is presented below.

Study 1:

Report: Foekema E. M., Jak R. G., (1999): “The fate and biological effects of Flufenacet WG 60 in aquatic indoor microcosms.”; TNO Institute of Environmental Sciences, Energy Research and Process Innovation, Business Part E. T. V., Laan van Westenenk 501, P. O. Box 342, 7300 AH Apeldoorn, The Netherlands (performing laboratory) for Bayer AG, Crop Protection, Institute for Environmental Biology, Agricultural Centre Monheim, D-51368 Leverkusen, Germany; study No. 30210 (TNO), TNO report No. TNO-MEP-R99/423; 29 November 1999; study reference number: M-023412-01-1;

Guidelines: The study was performed to comply with the following Guidelines:

- OECD Guidance document “Freshwater Lentic Field Tests”, July 1996 (Draft);
- Guidance document on Testing Procedures for Pesticides in Freshwater Mesocosm (SETAC-Europe Workshop, Monks Wood, UK, July 1991).

GLP: Yes;

RMS comments: The study is indicated by the Applicant as an existing mesocosm study, evaluated for the previous authorisation of Flufenacet in the EU, but it was then evaluated only as ecotox study. Therefore as the study aimed on the examination of fate and behaviour of Flufenacet in the aquatic systems it may be considered as a newly submitted study, and hence evaluated specifically for the purpose of the current assessment. It shall be indicated that it was not listed by the Applicant as one of the studies examining the fate and behaviour of Flufenacet in aquatic system. RMS however decided to include it, because it was a data-source study for the next study, aimed on the kinetic examination of its results, presented further down this data point as **Study 2**.

It was evaluated for its compliance with the provisions of the OECD 308 Guideline – “Aerobic and Anaerobic Transformation in Aquatic Sediment Systems”, in line with the provisions of the Commission Regulation (EU) No. 283/2013 and the European Commission Communication 2013/C95/01, indicating that Guideline as the reference test guideline for the experiments carried out under the data requirement set by the point 7.2.2.4. of the Annex to the Commission Regulation (EU) No. 283/2013. The examination of the study report for its compliance with the evoked test Guideline showed that:

- the study was performed in the test system containing water phase and sediment sampled at two different locations – sediment from Geesteambach lake located in Northern Holland (mesotrophic lake) and water from lake Markermeer, which is a southwestern part of the lake IJsselmeer located in central part of the Netherlands (eutrophic lake); the OECD Guideline, in point 28, recommends to use sediment and water associated with it (from the same SW body) and at the same period;
- sediment used in the experiment was only characterised for its texture while other parameters required by the reference Guideline, such as CEC, pH, WHC, content of macro- and microelements, were not provided;
- the experiment was performed in open polyethylene containers (test tanks), while OECD 308 Guideline recommends the use of glass containers attached to the trap system for volatile compounds;
- The sediment layer used in the experiment was 10-cm thick, while the guideline recommends 2.5 ± 0.5 cm-layer, and the height of the water column above it was 50 cm;
- OECD 308 Guideline recommends to use radiolabelled test compound, what enables the determination of the mass balance as well as identification and quantitation of the degradation products, while in the experiment the non-radiolabelled Flufenacet was used;

- The experiment was performed using several initial concentrations of the test compound: 0 µg/L, 0.75 µg/L, 1.5 µg/L, 3.0 µg/L, 6.0 µg/L, 12.0 µg/L and 24.0 µg/L, while OECD 308 Guideline recommends one test concentration of the given compound should be used, reflecting the would-be maximum environmental concentration resulting from the use of the test compound in maximum label-recommended rate; it is admissible to use second concentration in case it is expected that the compound may reach the SW bodies via different migration routes and at significantly different concentrations;
- The test compound was applied as formulated product – WG 60 formulation, while OECD 308 states that “*The use of formulated products is not routinely recommended as formulation ingredients may affect the distribution of the test substance and/or transformation products between water and sediment phases.*” The use of formulated products is indicated as an alternative for poorly water-soluble products, which is not a case of Flufenacet;
- The average temperature of the test vessels during the experiment was $T = 16.4^{\circ}\text{C}$, but it varied from 15.3°C to 18.0°C ; the OECD 308 states that the experiment shall be performed at constant temperature within the range $10 - 30^{\circ}\text{C}$, but preferably (indicated appropriate temperature) at $T = 20 \pm 2^{\circ}\text{C}$;
- The concentration of Flufenacet in the test system was determined only in the water phase, by taking the representative samples from each test tank, while sediment was not analysed for the content of Flufenacet at the given time point (OECD 308 Guideline recommends the analysis of both water and sediment phase); as a result from that experiment solely the information on the dissipation of Flufenacet from water phase, including the uptake by plants introduced to the test tanks.

On the basis of the assessment presented above RMS stated that the experiment did not comply with the provisions of the OECD 308 Guideline and therefore cannot be considered acceptable as representing irradiated water/sediment study. It shall be also indicated that the study was also not considered acceptable, for the purpose of the current assessment, as a microcosm study (for more details please refer to the B.9 section of this Renewal Assessment Report). Therefore it was decided not to summarise the study report in its part relevant for the elucidation of the fate and behaviour of Flufenacet in water/sediment system, in order not to overburden the report.

Summary:

The evaluation of the study performed by the RMS showed that it was not acceptable. For that reason, in order not to overburden the Renewal Assessment Report, RMS decided not to summarise it.

Study 2:

Report: Reinken G., Maassen K., (2014): “Kinetic Evaluation of the Dissipation Behaviour of Flufenacet in Aquatic Microcosm Systems According to FOCUS Kinetics Using the KinGUI 2 Tool. Flufenacet (FOE 5043).”; Bayer CropScience AG, Environmental Safety, Alfred-Nobel-Strasse 50, 40789 Monheim, Germany; Report No. En-Sa-14-0127; 2014. 02. 18; study reference number: M-478447-01-1

Guidelines: The study was performed to comply with the following Guidelines:

- FOCUS (2006): “Guidance Document on Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration.”; Report of the Work Group on Degradation Kinetics, EC Document Reference SANCO/10058/2005, version 2.0, 434 pp.;
- FOCUS (2011): “Generic Guidance for Estimating Persistence and Degradation Kinetics from Environmental Fate Studies in EU Registration, version 1.0, 436 pp.

GLP: No, not applicable – this is a modelling study;

RMS comments: This is a newly submitted study, providing the kinetic examination of the results of the determination of concentration of Flufenacet in water phase of the indoor microcosms, presented in the study by [Foekema and Jak; 1999]. RMS, for the purpose of the current

assessment evaluated the study for its compliance with the Guidelines evoked above. It can be stated that the kinetic assessment presented in the study was in line with the provisions of the FOCUS Kinetics Guidance Document. The Applicant justifying the submission of the study in LCA-Section-7 document provided the following statement: *“Additional data: Kinetic analysis of the dissipation of flufenacet in aquatic indoor microcosm system for modelling purpose and trigger evaluation.”* It shall be indicated that RMS, having evaluated the source study stated that it cannot be considered acceptable. As a result also the kinetic analysis of its results cannot be considered acceptable for registration purposes. Therefore RMS decided not to summarise this study report in order not to overburden the Renewal Assessment Report.

Summary:

The evaluation of the study performed by the RMS showed that although it was acceptable from the methodological point of view, it was aimed on the assessment of the data presented in the study report that was found not acceptable. Therefore the study cannot be considered as providing the reliable kinetic endpoints. For that reason, in order not to overburden the Renewal Assessment Report, RMS decided not to summarise it.

B.8.2.4 – Degradation in the saturated zone

The problem of the degradation of Flufenacet in the saturated zone was not examined for the purpose of the present evaluation. Instead the Applicant in the document MCA for the Section 7: Environmental Fate and Behaviour, in order to address the problem, made the following statement: *“The degradation of flufenacet in the saturated zone was not studied since flufenacet is not expected to reach the saturated zone after its use according to good agricultural practices.”*. That statement may be considered justified as long as it concerns GW recharge, however it cannot be excluded that the problem of the degradation of Flufenacet in the saturated zone may be relevant with regard to other issues, in particular bank filtration as a first stage of drinking water abstraction from the surface water (riverine). The problem is discussed in a more detailed way under the point B.8.2.6 of this document, therefore RMS is of the opinion that it does not require more extensive consideration under this point.

It shall be indicated that for the purpose of the former evaluation of Flufenacet for its authorisation in the EU the then-RMS – France, made the following statement in this area (please also refer to the point B.7.4.4 of the Annex B.7 of the Assessment Report): *“No special studies were performed on the degradation of FOE 5043 and its metabolites in the saturated zone. However, this requirement is considered to be covered by the lysimeter studies under the point 7.2.4. Additional information can be derived from the studies on the metabolism in soil (section 7.1.1.) and on hydrolytic degradation (section 7.4.1.).”*.

RMS – Poland, is of the opinion that for the purpose of the current assessment this statement may be considered valid.

Finally, it shall be indicated that the results of the examination of the transformation pathways of Flufenacet in the aquatic systems, in particular water/sediment studies, showed that it should be very similar, if not identical, to that determined in soil. Therefore RMS is of the opinion that there is no need for more extensive examination of that problem and that it may be covered by the data obtained in the other areas of the assessment.

B.8.2.5 – Summary of persistence in surface water and degradation in the saturated zone

The determination of transformation pathways and persistence of Flufenacet in the aquatic environment was performed by examining potentially relevant abiotic and biologically-mediated processes.

The examination of abiotic degradation of Flufenacet in the aquatic environment comprised the following processes:

- abiotic aqueous hydrolysis;
- direct aqueous photolysis;
- indirect aqueous photolysis.

The **abiotic hydrolysis of Flufenacet** was examined at three different pH – pH = 5, pH = 7 and pH = 9 (environmentally relevant pH range) and T = 25°C. The results of that examination, presented in one study report, demonstrated that Flufenacet was hydrolytically stable within the whole examined pH range. The determined in that experiment half-lives at T = 25°C were: DT₅₀ > 1000 days for pH 5-7 and DT₅₀ = 655 days for pH = 9.

Additionally the results presented in the open source paper identified as a relevant for the evaluation of Flufenacet showed that the pH of the aqueous solution, and hence the hydrolysis, had only minimal influence on the rate of dissipation/degradation of Flufenacet from water (biologically viable). The results of that study were considered however only as indicative and were not used to derive the regulatory endpoints.

Also stable to abiotic hydrolysis in the aquatic environment, for the same environmentally relevant conditions, was demonstrated to be the major soil and aquatic major degradation product of Flufenacet – FOE Thiadone. The determined half-lives were DT₅₀ > 1000 days for the whole tested range pH = 5-9 and T = 25°C.

The **direct aqueous photolysis of Flufenacet** was examined in a sterile buffer solution having pH = 5 and T = 21°C. The samples were exposed to UV-Vis radiation generated by the artificial light source. The irradiation conditions were similar to those recorded during 30-days exposure to natural summer sunlight in Phoenix, Arizona, USA. The results demonstrated that Flufenacet was not prone to the direct aqueous photolysis – practically no photodegradation of Flufenacet, in comparison to what was observed in the dark control samples, was stated. The determined half-lives were: for irradiated sample DT₅₀ = 7430 days when expressed in Natural Sunlight days, and for the dark control samples DT₅₀ = 4160 days.

In a separate experiment the quantum yield of the process of direct photodegradation of Flufenacet in water was determined. The quantum yield value determined in that experiment was $\phi = 0.00096$ [mol/Einstein]. The calculated using that value environmental photolytical half-lives for Flufenacet, calculated using GC-Solar method in water were:

- for the latitude 30°N in range DT₅₀ = 126 – 308 days;
- for the latitude 40°N in range DT₅₀ = 131 – >365 days;
- for the latitude 50°N in range DT₅₀ = 142 – >365 days;
- for the latitude 60°N in range DT₅₀ = 160 – >365 days;

Additionally, in a separate study, was examined the direct aquatic photolysis of the major soil and aquatic degradation product of Flufenacet – FOE Thiadone. The experiment was performed in a sterile buffer solution having pH = 7 and T = 25°C. The samples were exposed to UV-Vis radiation generated by the artificial light source. The irradiation conditions were similar to those recorded during 30-days exposure to natural summer sunlight in Phoenix, Arizona, USA. The results demonstrated that FOE Thiadone not prone to the direct aqueous photolysis – practically no photodegradation of that compound was observed in either irradiated samples or in dark control and it was not possible to determine the reliable DT₅₀ values.

The **indirect aqueous photolysis of Flufenacet** was examined in four types of aqueous solutions:

- natural pond water having pH = 6.5, TOC = 20.7 mg/L and containing 160 mg/L of suspended solids (total), subsequently named Howe pond water;
- natural pond water having pH = 7.8, TOC = 1.55 mg/L and containing 9 mg/L of suspended solids, subsequently named Stilwell pond water;
- ultrapure water containing 15 ppm of humic material;
- ultrapure water containing 50 ppm KNO₃.

The samples were exposed to UV-Vis radiation generated by artificial light source, but bearing the characteristic of the natural sunlight. The irradiation conditions were similar to those recorded during the

30-days exposure to natural summer light in Phoenix, Arizona, USA. The experiment showed that Flufenacet was prone to indirect photolysis in water, although that process should not be regarded as one of the driving mechanisms in disappearance of Flufenacet from natural waters. The experiments were aimed on the determination of the kinetic parameters of the process – the rates of the indirect photodegradation of Flufenacet in water, therefore no attempt was made to identify and quantify the formed degradation products.

The calculated, net, half-lives for the indirect photodegradation of Flufenacet in water were following:

- for Howe pond water the experimentally derived (continuous irradiation) **DT₅₀ = 160.08 days**, what corresponded to **DT₅₀ = 468.53 days** for exposure to natural summer sunlight at 33° 26' N (in June at Phoenix, Arizona, USA);
- for Stilwell pond water the experimentally derived (continuous irradiation) **DT₅₀ = 281 days**, what corresponded to **DT₅₀ = 822 days** for exposure to natural summer sunlight at 33° 26' N (in June at Phoenix, Arizona, USA);
- for ultrapure water containing 15 ppm of Humic material the experimentally derived (continuous irradiation) **DT₅₀ = 114 days**, what corresponded to **DT₅₀ = 332 days** for exposure to natural summer sunlight at 33° 26' N (in June at Phoenix, Arizona, USA);
- for ultrapure water containing 50 ppm of KNO₃ the experimentally derived (continuous irradiation) **DT₅₀ = 27.5 days**, what corresponded to **DT₅₀ = 158 days** for exposure to natural summer sunlight at 33° 26' N (in June at Phoenix, Arizona, USA).

It shall be however indicated that these values were determined using the results obtained in non-GLP experiments (being an additional part of a GLP study aimed on the examination of the direct aqueous photolysis of Flufenacet). For that reason RMS decided to consider them as only indicative and not to include them into the EU List of Endpoints.

Additionally, in a separate experiment, was examined the indirect aqueous photolysis of FOE Thiadone – the major soil and aquatic degradation product of Flufenacet. The test medium was sterilised natural (riverine) water. The samples were exposed to UV-Vis radiation generated by artificial light source, but bearing the characteristic of the natural sunlight. The irradiation conditions were similar to those recorded during the 30-days exposure to natural summer light in Phoenix, Arizona, USA. The experiment showed that FOE Thiadone was prone to indirect photolysis in water, although that process should not be regarded as one of the driving mechanisms in disappearance of Flufenacet from natural waters. The experiment was performed with the test compound radiolabelled at C2 position in thiadiazole ring, what resulted in identification only CO and CO₂ as degradation products. Therefore it remains unknown what are the degradation products associated with the second carbon atom within the thiadiazole ring – C5. However, it may be assumed that one of such products could be TFA. The calculated, net, rate of indirect photodegradation of FOE Thiadone in water was **k = 0.1194 [days⁻¹]**, corresponding to **DT₅₀ = 5.8 days** in samples continuously irradiated with artificial sunlight. When recalculated to the natural conditions that value corresponded to:

- **DT₅₀ = 15.8 days** determined for summer sunlight conditions (June) in Phoenix, Arizona, USA (33° 26' N);
- **DT₅₀ = 24.4 days** determined for summer sunlight conditions (June) in Athens, Greece, EU (38° 03' N);
- **DT₅₀ = 30.5 days** determined for summer sunlight conditions (July) in London, UK, EU (51° 30' N).

These results were reported in the EU List of Endpoints for Flufenacet.

The assessment of biologically-mediated transformation of Flufenacet in the aquatic environment covered the following issues:

- examination of the ready biodegradability;
- examination of the aerobic mineralisation in surface water;
- examination of the fate and behaviour of Flufenacet in aerobic water/sediment systems;
- examination of the fate and behaviour of Flufenacet in irradiated aerobic water/sediment systems;
- examination of the degradation of Flufenacet in saturated zone (anaerobic water/sediment system).

The Applicant has not submitted any study report presenting the results of the examination of **ready biodegradability of Flufenacet**. Instead the following justification for non-submission was provided:

“Flufenacet was stated to be not ready biodegradable. This was accepted by the European Commission (7469/VI/98-Final -3rd July 2003). Therefore no additional study was performed for the flufenacet renewal of approval.” The justification for non-provision of the adequate study may be considered acceptable. RMS examining the submitted documentation stated that the Applicant submitted a study examining the degradation of Flufenacet in natural water. Also are available two studies examining the fate and behaviour of Flufenacet in aerobic water/sediment systems. These studies provided information on the mineralisation of Flufenacet in

aquatic environment. Their results confirm that Flufenacet shall be classified as not readily biodegradable, hence the conclusion drawn during the previous evaluation of Flufenacet for its authorisation in the EU remains valid.

The **aerobic mineralisation of Flufenacet in surface water** was examined in pelagic (pond) freshwater collected from the pond representative for the agricultural area of the use of Flufenacet. The test water had the following characteristics:

- type of water sample: pelagic water (no associated sediment);
- pH: 7.5;
- total alkalinity: 230 mg CaCO₃/L;
- total hardness: 329 mg CaCO₃/L;
- specific conductivity: 500 µmhos/cm;
- [O₂]: 9.6 mg/L;
- Suspended solids: 8.5 mg/L;
- Microbial activity, expressed in number of the colony forming units (CFU): 5.9 E3 CFU/mL.

The examination of the degradation of Flufenacet in water was performed in irradiated test systems, under light regime similar to natural sunlight conditions. The mean temperature of incubation was in range 23.1 – 24.4 (mean estimated by the RMS is 23.75°C), therefore slightly deviating from the assumed $T = 25 \pm 1^\circ\text{C}$.

The experiment was performed with Flufenacet radiolabelled in only one position – in fluorophenyl ring, therefore the proposed transformation scheme cannot be considered as complete. In case of the biologically viable samples three degradation products were identified and quantified:

- FOE Alcohol, recorded for the first time on DAT 60, peaking at 4.4% of the applied amount of the parent compound on DAT 368 (end of the study) and that amount was still seemingly increasing;
- FOE Oxalate, recorded for the first time on DAT 60, peaking at 24.0% of the applied amount of the parent compound on DAT 368 (end of the study) and that amount was still increasing;
- FOE Sulfonic acid, recorded for the first time on DAT 278, peaking at 8.6% of the applied amount of the parent compound on DAT 368 (end of the study) and that amount was still increasing;

In sterilised samples only one degradation product was identified – FOE Alcohol, observed for the first time on DAT 278 and formed in amount up to 6.8% of the applied amount of the parent compound (value recorded at the end of the study – on DAT 368).

The proposed, partial, transformation scheme for Flufenacet in natural, microbiologically viable water, resulting from that examination, is presented below on figure B.8.2.5._CA-1.

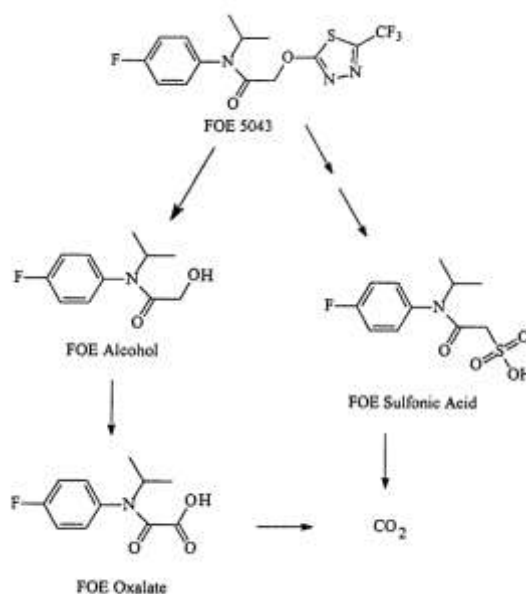


Figure B.8.2.5._CA-1: The proposed, partial transformation pathway of Flufenacet in natural, microbiologically viable water (copied from the study report).

During that experiment, lasting for 368 days, it was stated that Flufenacet radiolabelled in fluorophenyl moiety, underwent very limited mineralisation – up to 3.0% of the applied dose was fully mineralised in the biologically viable samples. That indicates that Flufenacet cannot be considered ready biodegradable. In the sterilised samples the level of mineralisation was up to 0.8% at the end of incubation period – DAT 368.

It shall be pointed out that the so determined transformation pathway of Flufenacet was only partial, as it fully covered only one moiety within the molecule – that comprising fluorophenyl ring and attached to it n-alkyl chain. At the same time however it shall be indicated that the main functional group within that moiety – fluorophenyl ring, displayed high persistence, what enabled to estimate with quite good accuracy not only persistence of Flufenacet in natural, microbiologically viable water, but also overall level of mineralisation of the molecule.

The process of degradation of Flufenacet in pelagic water was slow, with $DT_{50} = 473$ days and $DT_{90} = 1570$ days in non sterilised water, and it followed the SFO kinetic model. When recalculated to the standard temperature – $T = 20^{\circ}\text{C}$ (using Arrhenius activation energy $E_a = 65.4$ kJ/mol) these values were: $DT_{50} = 664$ days and $DT_{90} = 2204.1$ days.

In sterilised water the rate of degradation, also following the SFO kinetics, was much slower, with $DT_{50} = 2230$ days and $DT_{90} = 7410$ days. When recalculated to the standard temperature – $T = 20^{\circ}\text{C}$ (using Arrhenius activation energy $E_a = 65.4$ kJ/mol) these values were: $DT_{50} = 3130.7$ days and $DT_{90} = 10402.9$ days.

The kinetic examination of the results for any of the identified and quantified degradation products was not possible due to the fact that all they were still forming at the study end.

These results demonstrated that the process of the degradation of Flufenacet in natural pelagic water was predominantly biologically mediated and that the abiotic degradation processes – hydrolysis and aqueous photolysis (direct and indirect) played only minor role, if any.

The transformation pattern of Flufenacet in aerobic water/sediment systems was examined in two separate studies, using Flufenacet radiolabelled at two different positions – uniformly in fluorophenyl ring as [Phenyl- $U\text{-}^{14}\text{C}$]Flufenacet – one of the studies ([Kelley et al.; 1995]), and in C2 position of Thiadiazole moiety as [Thiadiazole - $2\text{-}^{14}\text{C}$]Flufenacet – second study ([Halarnkar and Irwin; 1997]). In each study two water/sediment systems were used, bearing codenames (common for both studies) NESAs and BRPs. It shall be indicated however that although sampled on the same locations the test systems did not bear the same characteristics, therefore shall be considered as individual test systems and not the replicates. RMS examining the data set noticed that the examination of the transformation of the thiadiazole moiety of Flufenacet was performed for only C2 radiolabelling position, while C5 radiolabelling position was not covered. That resulted in the lack of data concerning the potential formation of TFA and, possibly (if the degradation pattern was similar to that observed in aerobic soil) FOE TFESA. RMS considers this to be a potential data gap with regard to the full examination of the transformation of Flufenacet in the water/sediment systems.

In the study with [Phenyl- $U\text{-}^{14}\text{C}$]Flufenacet two water/sediment systems were used:

- NESAs test system (NESAs), containing silty clay loam sediment, having $\text{pH} = 7.9$, OC content of 0.7% and CEC of 33.5 meq/100 g, and associated water, having $\text{pH} = 7.5$, dissolved O_2 content of 9.2 ppm and the content of total dissolved solids of 82 ppm;
- BRPs test system (BRPs), containing silty clay loam sediment, having $\text{pH} = 7.8$, OC content of 1.4% and CEC of 25.6 meq/100 g, and associated water, having $\text{pH} = 7.3$, dissolved O_2 content of 8.5 ppm and the content of total dissolved solids of 120 ppm.

The experiment lasted for 156 days and the samples were incubated in the darkness at constant temperature $T = 20^{\circ}\text{C}$.

In the study with [Thiadiazole- $2\text{-}^{14}\text{C}$]Flufenacet two water/sediment systems were used:

- NESAs test system (NESAs 1), containing silty clay sediment, having $\text{pH} = 7.8$, OC content of 0.38% and CEC of 22.0 meq/100 g, and associated water, having $\text{pH} = 7.2$, dissolved O_2 content of 9.2 ppm and the OC content of 331 ppm;
- BRPs test system (BRPs 1), containing silty clay loam sediment, having $\text{pH} = 7.8$, OC content of 1.54% and CEC of 13.02 meq/100 g, and associated water, having $\text{pH} = 6.9$, dissolved O_2 content of 10.0 ppm and the OC content of 415 ppm.

The experiment lasted for 156 days and the samples were incubated in the darkness at constant temperature $T = 20^{\circ}\text{C}$.

The key results of both studies with regard to the distribution of radioactivity in the test systems are presented below in the table B.8.2.5._CA-1. The detailed results of the profiling of radioactivity in the test water/sediment systems are presented in the table B.8.2.5._CA-2.

Table B.8.2.5._CA-1: Distribution of the Applied Radioactivity (AR) in the test water/sediment systems.

Water/ Sediment system and test compound	Characteristic of the system:			AR distribution in the system [%]:				Identified metabolites ¹⁾
				<i>In water phase max/min</i>	<i>Max. in sediment - extractable</i>	<i>NER</i>	<i>Minerali- sation level (¹⁴CO₂)</i>	
NESA; [Phenyl-U- ¹⁴ C] Flufenacet	<i>Sediment's texture class - USDA</i>		Slity clay loam	<u>total:</u> max. 97.1%, DAT 0; min. 38.1%, DAT 157 <u>Flufenacet:</u> max. 94.9%, DAT 0; Min. 15.8% DAT 157	<u>total:</u> max. 23.5%, DAT 120; min. 3.5%, DAT 0 <u>Flufenacet:</u> max. 22.9%, DAT 30; min. 3.5% DAT 0	28.5%; DAT 157	3.4%; DAT 157	FOE Oxalate – max. 4.6%; FOE Alcohol – max. 0.7%; FOE Sulfonic acid – max. 1.7%; FOE Methyl- sulfide – max. 11.4%; FOE Methyl- sulfone – max. 6.4%; FOE Methyl- sulfoxide – max. 3.2%; FOE TGS – max. 2.0%
	<i>pH</i>	Water phase	7.5					
		Sediment	7.9					
	<i>OC content</i>	Sediment [%]	0.7					
	<i>Incubation temperature [°C]</i>		20					
BRP; [Phenyl-U- ¹⁴ C] Flufenacet	<i>Sediment's texture class - USDA</i>		Slity clay loam	<u>total:</u> max. 95.5%, DAT 0; min. 21.9%, DAT 157 <u>Flufenacet:</u> max. 95.0%, DAT 0; min. 7.53% DAT 157	<u>total:</u> max. 35.0%, DAT 30; min. 0.5%, DAT 0 <u>Flufenacet:</u> max. 34.2%, DAT 30; min. 0.5% DAT 0	46.4%; DAT 157	1.5%; DAT 157	FOE Oxalate – max. 5.4%; FOE Alcohol – max. 1.3%; FOE Sulfonic acid – max. 3.2%; FOE Methyl- sulfide – max. 4.5%; FOE Methyl- sulfone – max. 7.2%; FOE Methyl- sulfoxide – max. 2.2%; FOE TGS – max. 1.9%
	<i>pH</i>	Water phase	7.3					
		Sediment	7.8					
	<i>OC content</i>	Sediment [%]	1.4					
	<i>Incubation temperature [°C]</i>		20					
NESA 1; [Thiadiazole-2- ¹⁴ C]Flufenacet	<i>Sediment's texture class - USDA</i>		Slity clay	<u>total:</u> max. 88.0%, DAT 28; min. 68.0%, DAT 156 <u>Flufenacet:</u> max. 83.99%, DAT 0; min. 3.1% DAT 55	<u>total:</u> max. 12.8%, DAT 7; min. 2.7%, DAT 100 <u>Flufenacet:</u> max. 12.4%, DAT 7; min. 0.6% DAT 100	3.3%; DAT 55	15.3%; DAT 156	FOE Thiadone – max. 84.3%
	<i>pH</i>	Water phase	7.2					
		Sediment	7.8					
	<i>OC content</i>	Sediment [%]	0.38					
	<i>Incubation temperature [°C]</i>		20					
BRP 1; [Thiadiazole-2- ¹⁴ C]Flufenacet	<i>Sediment's texture class - USDA</i>		Slity clay loam	<u>total:</u> max. 84.5%, DAT 0; min. 0.9%, DAT 156 <u>Flufenacet:</u> max. 83.2%, DAT 0; min. 0.9% DAT 156	<u>total:</u> max. 29.9%, DAT 14; min. 4.4%, DAT 156 <u>Flufenacet:</u> max. 26.1%, DAT 14; min. 2.3% DAT 156	9.6%; DAT 100	15.0%; DAT 156	FOE Thiadone – max 63.8%.
	<i>pH</i>	Water phase	6.9					
		Sediment	7.8					
	<i>OC content</i>	Sediment [%]	1.54					
	<i>Incubation temperature [°C]</i>		20					

Footnotes to the table:

1) FOE TGS = FOE Thioglycolate sulfoxide;

Table B.8.2.5._CA-2: The results of the profiling of radioactivity in the test water/sediment systems.

Water/ Sediment system and test compound	Compound	Concentration [% AR] in:								
		Whole system			Water phase			Sediment phase:		
		Begin- ning of the study ¹⁾	End of the study ²⁾	Max. amount (DAT)	Begin- ning of the study ¹⁾	End of the study ²⁾	Max. amount (DAT)	Begin- ning of the study ¹⁾	End of the study ²⁾	Max. amount (DAT)
NESA; [Phenyl- U- ¹⁴ C] Flufenacet	Flufenacet	98.4	27.7	98.4; (0)	94.9	15.8	94.9; (0)	3.5	11.9	22.9; (30)
	FOE Oxalate	0.0	4.6	4.6; (157)	0.0	4.6	4.6; (157)	0.0	0.0	0.2; (100)
	FOE Alcohol	0.0	0.6	0.7; (120)	0.0	0.2	0.2; (157)	0.0	0.4	0.6; (120)
	FOE Sulfonic acid	0.0	1.7	1.7; (157)	0.0	1.7	1.7; (157)	0.0	0.0	0.0
	FOE Methylsulfide	0.0	11.4	11.4; (157)	0.0	8.0	8.0; (157)	0.0	3.5	3.5; (157)
	FOE Methylsulfone	0.0	5.3	6.4; (100)	0.0	4.4	5.0; (100)	0.0	0.9	1.4; (100)
	FOE Methylsulfoxide	0.4	3.2	3.2; (157)	0.4	0.0	0.4; (0)	0.0	3.2	3.2; (157)
	FOE TGS ³⁾	0.0	2.0	2.0; (157)	0.0	2.0	2.0; (157)	0.0	0.0	0.0
BRP; [Phenyl- U- ¹⁴ C] Flufenacet	Flufenacet	95.5	22.3	100.2; (1)	95.0	7.5	95.0; (0)	0.5	14.8	34.2; (30)
	FOE Oxalate	0.0	5.4	5.4; (157)	0.0	4.8	4.8; (157)	0.0	0.6	0.6; (157)
	FOE Alcohol	0.0	1.3	1.3; (157)	0.0	0.0	0.0;	0.0	1.3	1.3; (157)
	FOE Sulfonic acid	0.0	3.2	3.2; (157)	0.5	3.0	3.0; (157)	0.0	0.3	0.3; (156)
	FOE Methylsulfide	0.0	4.5	4.5; (157)	0.0	1.9	2.7; (120)	0.0	2.7	2.7; (157)
	FOE Methylsulfone	0.0	3.8	7.2; (120)	0.0	2.9	6.5; (120)	0.0	0.9	1.0; (100)
	FOE Methylsulfoxide	0.0	1.7	2.2; (120)	0.0	0.5	1.0; (60)	0.0	1.2	2.2; (120)
	FOE TGS ³⁾	0.0	1.4	1.9; (60)	0.0	1.4	2.0; (60)	0.0	0.0	0.0
NESA 1; [Thia- diazole-2- ¹⁴ C] Flu- fenacet	Flufenacet	94.2	0.9	94.2; (0)	83.9	0.0	83.9; (0)	10.4	1.0	12.4; (7)
	FOE Thiadone	0.0	68.7	84.3; (55)	0.0	65.5	81.8; (55)	0.0	3.0	3.0; (156)
BRP 1; [Thia- diazole-2- ¹⁴ C] Flu- fenacet	Flufenacet	96.3	3.3	96.3; (0)	83.2	0.9	83.2; (0)	12.2	2.39	26.1; (14)
	FOE Thiadone	0.2	54.2	63.8; (100)	0.0	52.2	60.0; (100)	0.1	1.9	3.8; (100)

Footnotes to the table:

- 1) DAT 0 for all experiments;
- 2) DAT 157 for experiments with [Phenyl-U-¹⁴C] Flufenacet and DAT 156 for experiments with [Thiadiazole-2-¹⁴C] Flufenacet;
- 3) FOE TGS = FOE Thioglycolate sulfoxide.

The results obtained in the water/sediment systems conform that Flufenacet cannot be considered readily biodegradable. It was also stated that the transformation pathway of Flufenacet in aerobic water/sediment systems was very similar to that determined in aerobic soil. It is presented below on figure B.8.2.5._CA-2. As already stated that transformation scheme cannot be considered complete due to the fact that the transformation of the thiadiazole moiety was not fully examined. In particular not examined was the formation of TFA from FOE Thiadone, the mechanism indicated in some literature studies (please refer to the point **B.8.2.6. – Impact on water treatment procedures**). That would result in the underestimation of the exposure in SW compartment based on the model calculations.

RMS was able to identify one open literature study examining the fate of several halogenoacetic acids, including TFA, in the test systems similar to the design used in water/sediment studies. On that basis it may be concluded that TFA, when formed from FOE Thiadone, will not undergo any substantial transformation in natural SW bodies and it will occur predominantly in water column.

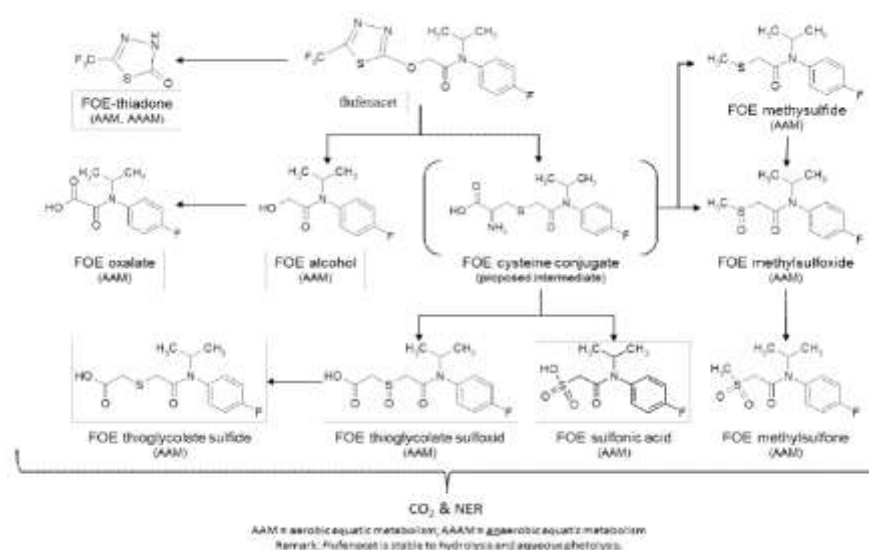


Figure B.8.2.5_CA-2: The transformation pathway of Flufenacet determined in aerobic water/sediment system (copied from the Applicant's report).

The results of the regulatory water/sediment studies were subjected to the kinetic examination in a separate study.

The kinetic analysis was performed for the data obtained for Flufenacet in the whole test systems as well as in water and sediment phases of each test system and was carried out on the Level P-I. Its aim was, in case of the whole-system data to determine the persistence endpoints for Flufenacet and the modelling endpoints. In case of water and sediment phases the kinetic analysis was aimed on the determination of the persistence endpoints. The analysis was performed in line with the recommendations given by FOCUS Kineitics Guidance document [FOCUS; 2006].

The key results of that examination are presented below in the table B.8.2.5_CA-3.

Table B.8.2.5_CA-3: The key results of the kinetic examination at the Level P-I of the data obtained for Flufenacet in water/sediment studies.

Study	Test system	Compartment	Kinetic model	Evaluation of fit		Kinetic parameter(s)		Kinetic endpoints	
				Visual	χ^2 % error	Parameter	Value	DT ₅₀ [days]	DT ₉₀ [days]
[Kelley <i>et al.</i> ; 1995]	NESA	Whole system	SFO	Good	2.185	k	0.00767	90.34	300.10
		Water	SFO	Good	4.936	k	0.0118	58.72	195.10
		Sediment	SFO – top down	Good	2.079	k	0.00493	140.50	466.80
	BRP	Whole system	SFO	Good	3.804	k	0.00779	89.00	295.70
		Water	FOMC	Good	4.041	α	1.339	31.23	211.00
		Sediment	SFO – top down	not reported	7.534	k	0.005754		
[Halarnkar and Irwing; 1997]	NESA	Whole system	SFO	Good	9.836	k	0.03525	19.67	65.33
		Water	SFO	Good	6.823	k	0.04083	16.98	56.40
		Sediment	SFO – top down	Good	7.312	k	0.03929	17.64	58.61
	BRP	Whole system	SFO	Good	4.933	k	0.01819	38.11	126.60
		Water	SFO	Good	12.50	k	0.02908	23.84	79.20
		Sediment	SFO – top down	Good	7.738	k	0.01447	47.91	159.10

The calculated geomean values for the kinetic endpoints – DT₅₀ and DT₉₀, determined in the whole system are following **DT₅₀ = 49.54 days**, **DT₉₀ = 164.59 days**. These values are determined by the RMS. The geomean

whole-system DT_{50} value given in the study report is following: $DT_{50} = 49.6$ days. The difference between the two values is minimal and can be attributed to the rounding procedure used by the Applicant. Therefore the value proposed by the Applicant may be considered a reliable kinetic endpoint to be used as input parameter in SW model exposure assessment.

For water and sediment phases at the Level P-I the Applicant derived two sets of the kinetic endpoints – those representing persistence and those suitable for modelling. RMS however noticed that Flufenacet displayed quite high adsorption potential onto soil, with the geomean $K_{fOC} = 245.9$ mL/g (range 161.6 – 643.48 mL/g) and rather low solubility in water – 56 mg/L. That may indicate that the compound would display substantial affinity to the sediment phase. The examination of degradation of Flufenacet in natural water, not containing suspended sediment, showed that that process take long – more than 600 days. Additionally, studies on abiotic degradation of Flufenacet in water showed that only indirect photolysis may substantially contribute to the dissipation of Flufenacet from water, while abiotic hydrolysis is not a relevant degradation mechanism for Flufenacet. All that taken into account, also bearing in mind that the water/sediment studies were performed in absence of light, it may be assumed that the process of dissipation of Flufenacet from water column is, at least of mixed nature, partly being degradation and to some extent, if not predominantly, migration to the sediment, where the proper degradation occurs.

In order to verify that RMS decided to perform additional kinetic examination of the data for Flufenacet using the procedure corresponding to the Level P-II assessment. In that fitting the data for Flufenacet in water phase were treated as those for the parent compound, while the sediment phase was defined as the metabolite A1 compartment.

Unlike at the Level P-I for the sediment phase whole data set was fitted together with that for water phase.

The results obtained for water phase were comparable to those obtained for that compartment by the Applicant at the Level P-I. The kinetic endpoints obtained for the sediment phase were usually shorter than those obtained by the Applicant at the Level P-I, what also reflected differences in the kinetic approach. It shall be indicated that the fits obtained for Flufenacet in the sediment phase were also not always fully reliable, but of sufficient quality to draw the conclusions.

Finally, it was noticed that the values of the kinetic formation fraction – ff , characterising the flux from water to sediment phases were in all cases very close or equal to 1. That may indicate that the dominant mechanism of dissipation from water column is migration to the sediment.

On that basis the RMS stated that the geomean whole-system DT_{50} value when used in the modelling should be considered as representing the degradation of Flufenacet in sediment, not in the water column.

The Applicant also made an attempt to derive the kinetic endpoints for the two identified major degradation products – FOE Methylsulfide and FOE Thiadone. The kinetic analysis aimed on that was performed at the Level M-I using the whole-system data for Flufenacet and related degradation products kinetically fitted together. The results obtained for Flufenacet were very similar to those obtained for the same compound fitted alone at the Level P-I. However, it was not possible to obtain the reliable kinetic endpoints for the degradation products, due to the fact that the concentrations still increased at the end of the experiment – which was the case for FOE Methylsulfide, or the number of data point after maximum was reached was too low to obtain the reliable decline curve, what was observed in case of FOE Thiadone. Additionally, it shall be indicated that due to the poor fitting results the kinetic formation fractions determined for both degradation products shall be considered with care.

Also was submitted the study examining the **fate and behaviour of Flufenacet in anaerobic water/sediment system**. The study was evaluated for its compliance with OECD Guideline 308 – Aerobic and Anaerobic Transformation in Aquatic Sediment Systems. RMS stated that the study deviated from the reference Guideline in the following areas:

- **selection of sediment:** in the study soil was used instead of anaerobic sediment; the water overlying “sediment layer” was not that associated with it, but taken from pond located at the test facility, in the vicinity of the soil sampling area;
- **number of water/sediment systems:** the Guideline recommends at least two types of water/sediment systems to be used in experiment; in this case only one type was used;
- **duration of the experiment:** Guideline recommends that the study should usually not be longer than 100 days; in this case the study lasted for 388 days;
- the anaerobic conditions were not maintained throughout the incubation period and there is no indication in the study report when the change occurred; although in the study report it is declared that anaerobic conditions for ~99 days of incubation there is no experimental evidence conforming that statement;
- although the study lasted for 388 days and the test soil, used as a surrogate for sediment, was known, from other studies, to have problems with maintaining biological viability, in the study report the biological viability of the test system was not reported.

As a result, RMS stated that the study could not be considered as complying with the provisions of the reference Guideline, hence it was found not acceptable for the present assessment. Therefore RMS decided not to summarise it and use its results in the evaluation.

The issue of the determination of **fate and behaviour of Flufenacet in irradiated water/sediment system** was covered by the Applicant by submitting a study report presenting the kinetic evaluation of the results obtained in the indoor mesocosm study. The indoor mesocosm study ([Foekema and Jak.; 1999]) was indicated by the Applicant as the study covering the problem of transformation in irradiated water/sediment systems. RMS evaluated the study and stated that it displayed several deficiencies not enabling to consider it a reliable regulatory study addressing the problem of fate and behaviour in irradiated water/sediment systems. As a result also the study presenting the kinetic analysis of its results cannot be considered valid for regulatory purposes. At the same time it shall be indicated that the kinetic analysis it presents was performed in line with the recommendations of the FOCUS Work Group on the Degradation Kinetics ([FOCUS; 2006]), therefore formally meeting the acceptability criteria.

It shall be however indicated that the lack of the proper regulatory study examining the problem of the transformation of Flufenacet in the irradiated water/sediment systems does not result in the data gap, as the issue is satisfactorily covered by the other studies submitted for this assessment.

The problem of the **degradation of Flufenacet in the saturated zone** was not examined for the purpose of the present evaluation. Instead the Applicant in the document MCA for the Section 7: Environmental Fate and Behaviour, in order to address the problem, made the following statement: *“The degradation of flufenacet in the saturated zone was not studied since flufenacet is not expected to reach the saturated zone after its use according to good agricultural practices.”*. That statement may be considered justified as long as it concerns GW recharge, however it cannot be excluded that the problem of the degradation of Flufenacet in the saturated zone may be relevant with regard to other issues, in particular bank filtration as a first stage of drinking water abstraction from the surface water (riverine). The problem is discussed in a more detailed way under the point B.8.2.6 of this document, therefore RMS is of the opinion that it does not require more extensive consideration under this point.

It shall be indicated that for the purpose of the former evaluation of Flufenacet for its authorisation in the EU the then-RMS – France, made the following statement in this area (please also refer to the point B.7.4.4 of the Annex B.7 of the Assessment Report): *“No special studies were performed on the degradation of FOE 5043 and its metabolites in the saturated zone. However, this requirement is considered to be covered by the lysimeter studies under the point 7.2.4. Additional information can be derived from the studies on the metabolism in soil (section 7.1.1.) and on hydrolytic degradation (section 7.4.1.).”*.

RMS – Poland, is of the opinion that for the purpose of the current assessment this statement may be considered valid.

Finally, it shall be indicated that the results of the examination of the transformation pathways of Flufenacet in the aquatic systems, in particular water/sediment studies, showed that it should be very similar, if not identical, to that determined in soil. Therefore RMS is of the opinion that there is no need for more extensive examination of that problem and that it may be covered by the data obtained in the other areas of the assessment.

Summarising the data presented above it may be stated that in the aquatic compartment of the environment Flufenacet is expected to be moderately persistent, with half life in water $DT_{50} = 29.4$ days (geomean; range 16.9 – 58.8 days) and that in sediment $DT_{50} = 61.5$ days (geomean; range 17.6 – 140.5 days). The half life in the whole compartment (water and sediment together) is estimated to be $DT_{50} = 49.6$ days (geomean; range 19.6 – 90.3 days). The dissipation from water column was demonstrated to occur mainly by migration to sediment, where the compound will be degraded to several degradation products, identical to those identified in soil.

The degradation of Flufenacet in the aquatic environment was demonstrated to be biologically-mediated process, while the abiotic processes – abiotic hydrolysis and direct photolysis were shown to be not relevant degradation mechanism for Flufenacet in that component of the environment. Of the abiotic degradation processes only indirect aqueous photolysis may be considered relevant, contributing to degradation of Flufenacet in water column (understood as the decomposition of the molecule) to similar extent as the microbial transformation.

Flufenacet was demonstrated to be not readily biodegradable.

B.8.2.6 - Impact on water treatment procedures

In the documentation submitted by the Applicant this issue was not addressed. Therefore the whole assessment presented below is based on the results of the repeated literature search performed by the RMS.

The analysis performed by the RMS focused mainly on the potential impact of Flufenacet and its identified major degradation products on drinking water abstraction procedures. The identified publications also enabled to briefly evaluate the possible impact of the residues of Flufenacet on wastewater treatment processes. However, as the problem is also dealt with, and to greater extent in section B.9. – Ecotoxicology, of this Renewal Assessment Report, RMS decided to signalise the issue instead of examining it thoroughly.

The assessment of the impact on the processes of abstraction of drinking water consisted of the following steps:

- a) examination of the available data resulting from the assessment of the documentation provided by the Applicant in order to determine the possibility of Flufenacet and its identified major degradation products of reaching drinking water abstraction plants and estimation of their fate during the various stages of the process,
- b) analysis of the structural formula of Flufenacet in order to examine the possibility of the formation of the unwanted/toxic by-products of the water abstraction processes, in particular disinfection using halogenated (chlorinated) compounds and UV light; the analysis was focused on the halogenated by-products, such as haloacetic acids, and nitrosamines;
- c) analysis of the identified publications in order to determine the potential of generating nitrosamines from Flufenacet and/or its degradation products present in the substrate after filtration;
- d) characterisation, on the basis of the available literature data, of the processes leading to the effective elimination of Flufenacet from the treated substrate during the abstraction of drinking water;
- e) characterisation, on the basis of the available literature data, the impact of the degradation products of Flufenacet on the process and the risk they may pose to the consumers.

The analysis of the data available in the documentation submitted by the Applicant showed that Flufenacet is not mobile in soil, with average $K_{fOC} = 245$ mL/g. That in turn may indicate that when reaching the drinking water abstraction plants in substrate – surface water, it should be effectively eliminated at early stages – bank filtration, filtration on sand and gravel filters and finally on GAC (Granular Activated Carbon) filters. Similar statement can be made in case of wastewater treatment plants, where it is expected that the compound should be efficiently removed at early stages – during mechanical and chemical treatment (filtration, sedimentation using coagulants and/or flocculants, e. t. c.). Therefore, it can be estimated that in wastewater treatment plants only small fraction of the initial amount of Flufenacet present in the “substrate” would reach the biological stage of the process. The problem of the impact on biological treatment of wastewater is dealt with in more detailed way in section B.9. – Ecotoxicology of this Renewal Assessment Report, therefore it is recommended to consult the relevant point in that section. However, the literature search performed by the RMS enabled the identification of at least one publication examining the impact of Flufenacet on the performance of typical, small biological wastewater treatment installation, designed to deal with wastewater generated on the farm and containing the residues of Plant Protection Products. That publication will be summarised further down this part of the Report.

Flufenacet was demonstrated to be not prone to abiotic hydrolysis and direct photolysis. Therefore it may be stated that at later stages of the process of abstraction of drinking water – the disinfection of the product using UV light, it is not expected that any potentially harmful transformation products, if Flufenacet is present at that stage, may be formed.

The indirect photolysis is not expected to be of any relevance at this stage, as the compounds considered to be photosensitizers shall be removed from the processed substrate at earlier stages of the whole process.

As the trace amounts of Flufenacet may still be present in the treated substrate – water processed with aim to obtain drinking water, after filtration, it is necessary to assess would it pose any threat to the consumer, via formation of unwanted/toxic by-products of chemical disinfection through chlorination or ozonation. As such may be considered various nitrosamines or low-weight haloorganic compounds. On the basis of the data presented by the Applicant such assessment was not possible. As a result it had to be based fully on the structural examination of Flufenacet and available literature data. That assessment is presented further down this chapter.

Finally, it shall be indicated that the results of both model exposure assessment and the lysimeter studies showed that Flufenacet is not expected to leach to the groundwater compartment in any significant amounts and

hence pose a risk to that compartment. As a result, it will not be a compound of concern in case drinking water is abstracted from that source.

As a result of the examination of fate and behaviour of Flufenacet in soil and aquatic environment seven degradation products were identified that were classified as major in soil, in water or in both components. These are:

- FOE Oxalate, observed forming in soil and aquatic environment, but only in soil classified as a major degradation/transformation product;
- FOE Sulfonic acid observed forming in soil and aquatic environment, but only in soil classified as a major degradation/transformation product;
- FOE Methylsulfone observed forming in soil and aquatic environment, but only in soil classified as a major degradation/transformation product;
- FOE Methylsulfide observed forming only in the aquatic environment and there classified as a major degradation/transformation product;
- FOE Thiadone observed forming in soil and aquatic environment, and in both environmental compartments classified as a major degradation/transformation product;
- FOE 5043-Trifluoroethanesulfonic acid (FOE TFESA) observed forming only in soil and there classified as a major degradation/transformation product; it was not observed in the aquatic environment in any amounts probably because the relevant experiments using the appropriately labelled active substance (C5 in the thiadiazole moiety) were not performed (as a result its formation in water cannot be ruled out);
- Trifluoroacetic acid (TFA) observed forming only in soil and there classified as a major degradation/transformation product; it was not observed in the aquatic environment in any amounts probably because the relevant experiments using the appropriately labelled active substance (C5 in the thiadiazole moiety) were not performed (as a result its formation in water cannot be ruled out);

The examination of the data available in the documentation provided by the Applicant showed that:

- FOE Oxalate was demonstrated to be very mobile in soil, with average $K_{fOC} = 10.60$ mL/g, therefore it would probably not be efficiently removed from the substrate – raw water, during the filtration stage of the drinking water abstraction procedure; it may also be a compound of concern, as testify the results of the GW model exposure assessment, in case drinking water is abstracted from groundwater resources;
- FOE Sulfonic acid was demonstrated to be very mobile in soil, with average $K_{fOC} = 11.10$ mL/g, therefore it would probably not be efficiently removed from the substrate – raw water, during the filtration stage of the drinking water abstraction procedure; it will also be a compound of concern, as testify the results of the GW model exposure assessment and lysimeter studies, in case drinking water is abstracted from groundwater resources;
- FOE Methylsulfone was demonstrated to be moderately mobile in soil, with average $K_{fOC} = 61.03$ mL/g, therefore it would probably be only partly removed from the substrate – raw water, during the filtration stage of the drinking water abstraction procedure during filtration; it may also be a compound of concern, as testify the results of the GW model exposure assessment, in case drinking water is abstracted from groundwater resources (although the associated risk is in this case lower than that estimated for FOE Oxalate);
- FOE Methylsulfide was estimated to be strongly sorbed onto organic carbon – the calculated $K_{OC} = 598.0$ mL/g, therefore, if present in raw processed water abstracted for drinking water, it should be efficiently removed from the treated substrate during filtration; the problem of risk related to its presence in groundwater as a source of drinking water is not relevant as this is an aquatic degradation/transformation product, hence not expected to occur in any amounts in Groundwater recharge;
- FOE Thiadone Methylsulfone was demonstrated to be moderately mobile in soil, with average $K_{fOC} = 42.10$ mL/g, therefore it would probably be only partly removed from the substrate – raw water, during the filtration stage of the drinking water abstraction procedure; the compound was demonstrated to be not expected to leach to GW compartment, hence the problem of risk related to its presence in groundwater as a source of drinking water is not relevant;
- FOE TFESA was demonstrated to be very mobile in soil, with average $K_{fOC} = 0.0$ mL/g, therefore it would not be efficiently removed from the substrate – raw water, during the filtration stage of the drinking water abstraction procedure; it may also be a compound of concern, as testify the results of the GW model exposure assessment, in case drinking water is abstracted from groundwater resources;

- TFA was demonstrated to be very mobile in soil, with average $K_{FOC} = 0.0$ mL/g, therefore it would not be efficiently removed from the substrate – raw water, during the filtration stage of the drinking water abstraction procedure; it may also be a compound of concern, as testify the results of the GW model exposure assessment, in case drinking water is abstracted from groundwater resources;

The abiotic hydrolysis and direct and indirect photolysis as degradation mechanisms in aquatic environment were examined by the Applicant only for FOE Thiadone. The compound was demonstrated not to be prone to either abiotic hydrolysis or direct photolysis in water. It may be therefore stated, as it was in case of Flufenacet, that at later stages of the process of abstraction of drinking water – the disinfection of the product using UV light, it is not expected that any potentially harmful transformation products, if FOE Thiadone is present at that stage, may be formed. The analysis of the possible formation of any unwanted/toxic by-products of disinfection by chlorination or ozonation has to be based, due to the lack of any experimental data or other assessment provided by the Applicant, on the results of the literature search carried out by the RMS.

As a next step, because it could not be ruled out that Flufenacet may reach later stages of substrate-processing during abstraction of drinking water, the structural formula of that compound was inspected in search of potentially alarming structures, that theoretically may lead to the formation of unwanted/toxic by-products.

Three such groups were identified. They are indicated below on the figure B.8.2.6._CA-1 by circling them red and marking with letters **a**, **b** and **c**.

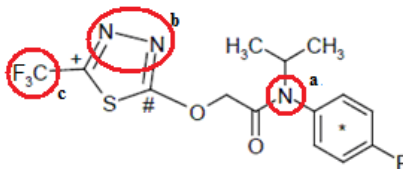


Figure B.8.2.6._CA-1: The structural formula of Flufenacet with the potentially alarming structures it contains marked by red circles and indicator letters **a**, **b** or **c** (the structural formula copied from the documentation submitted by the Applicant).

The groups marked **a** and **b** contain nitrogen atoms so may possibly be precursors of nitrosoamines. The group **c** – trifluoromethyl, was selected because it was demonstrated to form, during the breakdown of the thiadiazole moiety, trifluoroacetic acid. It may also be a component of other haloorganic compounds formed from either Flufenacet or FOE Thiadone during the breakdown of these molecules

To estimate the would be fate of the potentially alarming group marked **b** present in both Flufenacet and FOE Thiadone RMS consulted the following publication:

- Bond T., Tempelton M. R., Graham N. “Precursors of nitrogenous disinfection byproducts in drinking water – A Critical review and analysis.”; Journal of Hazardous Materials 2012, **235-236**, 1 – 16.

The data presented in that paper do not indicate that the group of concern may yield in any compound considered to be unwanted in the terminal product of drinking water abstraction, such as nitrosoamines, haloacetonitriles, cyanogen halides or halonitromethanes. RMS therefore decided not to continue the examination for that group.

The F₃C- group in Flufenacet and FOE Thiadone is known to be transformed into trifluoroacetic acid in soil. Similar process may occur in natural waters as well. Therefore it cannot be excluded (and the literature data which will be presented further down this chapter suggest that such process indeed will occur) that the compound will be formed from Flufenacet or FOE Thiadone during the drinking water abstraction. To estimate its toxic potential RMS consulted the following publications:

- Boorman G. A., Dellarco V., Dunnick J. K., Chapin R. E., Hunter S., Hauchman F., Gardner H., Cox M., Sills R. C., “Drinking Water Disinfection Byproducts: Review and Approach to Toxicity Evaluation.”; Environmental Health Perspectives, 1999, **107 Supplement 1**, 207 – 217;

- Richardson S. D., Postigo C., “Drinking Water Disinfection By-products” in Barcelo D. (ed.) “Emerging Organic Contaminants and Human Health”, “Handbook of Environmental Chemistry”, 2012, Springer Verlag, 93 – 138;
- Toxicological data sheet for TFA published on TOXNET – Toxicology Data Network, site of US NIH National Library of Medicine; available on-line at <http://toxnet.nlm.nih.gov/index.html> as a record CASRN: 76-05-1;

TFA was not listed in any of the publications cited above as a potential by-product of drinking water disinfection. Additionally it was not considered, if present in water very diluted and totally dissociated, to pose any serious risk to human health.

It shall also be indicated that TFA, being quite widely used compound, may be present in drinking water from other sources than Flufenacet and the contribution of either Flufenacet or/FOE Thiadone to the presence of that compound in drinking water may not be substantial in comparison to other sources.

As a result, RMS decided that that group as well, as well as TFA formed from Flufenacet in soil/natural water bodies, may not be a compound of special concern with regard to drinking water abstraction procedures.

The third group, marked **a** structurally, abstracted from the surrounding groups, is a ternary amino- group and as such may be a precursor of nitrosamines. Therefore RMS consulted several publications characterizing the formation of that group of compounds, i. e. :

- Boorman G. A., Dellarco V., Dunnick J. K., Chapin R. E., Hunter S., Hauchman F., Gardner H., Cox M., Sills R. C., “Drinking Water Disinfection Byproducts: Review and Approach to Toxicity Evaluation.”; Environmental Health Perspectives, 1999, **107 Supplement 1**, 207 – 217;
- Richardson S. D., Postigo C., “Drinking Water Disinfection By-products” in Barcelo D. (ed.) “Emerging Organic Contaminants and Human Health”, “Handbook of Environmental Chemistry”, 2012, Springer Verlag, 93 – 138;
- Le Roux J., Gallard H., Croué J.-P., “Chloramination of nitrogenous contaminants (pharmaceuticals and pesticides): NDMA and halogenated DBPs formation.”; Water Research, 2011, **45**, 3164 – 3174;
- Krasner S. W., Mitch W. A., McCurry D. L., Hanigan D., Westerhoff P., “Formation, precursors, control and occurrence of nitrosoamines in drinking water: a review.”; Water Research, 2013, **47**, 4433 – 4450;
- Kim J., Clevenger T. E., “Prediction of *N*-nitrosodimethylamine (NDMA) formation as a disinfection by-product.”; Journal of Hazardous Materials, 20007, **145**, 270 – 276;
- Nawrocki J., Andrzejewski P., “Nitrosoamines and water.”; Journal of Hazardous Materials 2011, **189**, 1 – 18;
- Bond T., Tempelton M. R., Graham N. “Precursors of nitrogenous disinfection byproducts in drinking water – A Critical review and analysis.”; Journal of Hazardous Materials 2012, **235-236**, 1 – 16;
- Mitch W. A., Sedlak D. L., “Factors controlling nitrosamine formation during wastewater chlorination.”; Water Science and Technology: Water Supply, 2002, **2** (3), 191 – 198;
- Rostkowska K., Zwierz K., Róžański A., Moniuszko-Jakoniuk J., Roszczenko A., „Formation and Metabolism of *N*-Nitrosamines.”; Polish Journal of Environmental Studiwm, 1998, **7** (6), 321 – 325;
- Anon.: “Report on Carcinogens, Thirteen Edition; *N*-Nitrosamines: 15 Listing.”; NIH National Toxicology Program, Department of Health and Human Services; document available on-line on: <http://ntp.niehs.nih.gov/go/roc13>

Analysis of these documents showed that theoretically the group may be a precursor of nitrosamines containing aromatic group as one of functional groups. However, no similar structure could be found listed in the NIH-NIEHS report listing 15 priority nitrosamines. Also no analogues could be found in other publications. In publication by Le Roux et al (2011) a formation of NDMA from a similar structure – diuron, was examined. It was indicated that the presence of the carbonyl group – C=O in the immediate vicinity of both amino groups – terminal and linked to the dichlorophenyl ring significantly limited the formation of nitrosamines. Additionally, the reaction occurred for rather terminal group than that in the aliphatic chain. Finally, the “middle” amino-group was a secondary amine.

It shall be also indicated that in case of Flufenacet and all its degradation products containing the group of concern – FOE Oxalate, FOE Sulfonic acid, FOE Methylsulfone and FOE Methylsulfide, the group of concern, due to its surrounding, is in fact an amido- group, therefore less prone to form nitrosamines.

As a result, RMS is of the opinion that in spite of containing three N-atoms, and one of them in configuration of ternary amino- group, Flufenacet may not be considered as a would-be precursor of nitrosamines.

As a next step the effectiveness of the removal of Flufenacet from raw water treated to produce the drinking water was evaluated on the basis of the available scientific literature.

One of the key publications on which that assessment was based was the DEFRA report “Understanding the changes in pesticide usage to inform water company risk assessment”, issued in 2013 as a final report of the DEFRA Project WT1264 (reference: anon., “*Final Report of Project WT1246- Understanding changes in pesticide usage to inform water company risk assessment.*”, DEFRA 2013, available: <http://dwi.defra.gov.uk/research/completed-research/2000todate.htm>.)

The aims of that project were following:

- to characterize the current, for the period of the study, usage of Plant Protection products in England and Wales and observed recent trends in that area;
- to characterize the regulatory changes in that area, their potential impact and its time frame;
- developments of the scenarios estimating the impact characterised in the point above;
- estimation, on the basis of known properties and use patterns, the likelihood of the presence of the given Plant Protection Product (active substance) in substrate for drinking water abstraction (ground water or surface water) in concentration above the regulatory trigger value – 0.1 µg/L;
- assessment of the would-be effectiveness of the removal of the substances identified at the above step, from the processed raw water in the commonly used drinking water abstraction procedures.

Flufenacet was identified as one of active substances that were newly introduced within the period of 20 years preceeding the issuing of that report. The use of which rapidly increased. It was declared to be introduced in the UK – England and Wales (as the report specifically refers to these parts of the United Kingdom) in 2002 as a replacement for isoproturon to control black-grass in cereals. Its annual use reported in the document was 99 tonnes in 2006, 150 tonnes in 2008 and 244 tonnes in 2010, showing a general increase in use.

More detailed examination showed that in the year 2010, in case of cereals, the total area treated with flufenacet was 1236000 ha, the total amount used was 231000 kg and the application rate 0.187 kg/ha. Similar analysis performed for the use on maize showed that for 2010 the total area treated with that compound was 25082 ha, the total amount used in maize was 7818 kg and the application rate 0.312 kg/ha.

In the table presenting the potential impact on sources of drinking water Flufenacet was estimated to pose medium risk related to leaching, low risk related to runoff and high risk related to the drainflow. In that assessment the ADI = 0.005 mg/kg BW was also reported.

In the part of the report characterizing the regulatory changes in the pesticide use pattern Flufenacet is indicated as being one of the alternative compounds, together with diflufenican and prosulfocarb, for pendimethalin.

Characterising a risk posed to the water resources the authors once again indicated Flufenacet as a compound being the alternative for Pendimethalin – the active substance included into the group of high risk, Group 2 because of failing PBT criteria, and for Flumioxazin – the active substance included into the same group because of failing R2 criteria.

The next step – estimation of the would-be risk posed to the resources of drinking water, was performed using the numerical modelling, by calculating the PEC values. In case of the surface waters the calculations were performed using a modified ADAS implementation of SWAT model. In case of similar calculations for groundwater compartment the adapted MACRO model was used.

The classification of risk was based on the comparison of the obtained values with the so called “drinking water prescribed concentration or value (PVC) – 0.1 µg/L. The following four classes were identified:

- at risk – **AR**, with calculated PEC > 5 µg/L;
- possibly at risk – **PAR**, for 5 µg/L > PEC > 0.1 µg/L;
- possibly not at risk – **PNAR**, for 0.1 µg/L > PEC > 0.002 µg/L, and
- not at risk – **NAR**, with PEC < 0.002 µg/L.

Flufenacet was evaluated under the Scenario 4 for both surface water and ground water.

The assumptions used in calculations were following:

- for the **Baseline approach** the total weight of flufenacet applied was 299.4 tonnes, total area treated was 1233000 ha and the application rate was 0.24 kg/ha;
- for the **Scenario 4 approach** the total weight of flufenacet applied was 409.7 tonnes, total area treated was 1693000 ha and the application rate was 0.24 kg/ha;
- the differences between the two approaches were following: change in total weight applied (Scenario 4: Baseline) 36.9, change in total area treated (Scenario 4: Baseline) 37.3%, the application rate did not change;
- the characterised risk related to: leaching was **medium**, runoff was **low**, drainflow was **high**.

In case of the estimation of the surface water drinking water protected areas the results obtained for **Baseline** approach was following:

- 1.0% of such areas were classified as **AR**,
- 78.7% of such areas were classified as **PAR**,
- 19.1% of such areas were classified as **PNAR**,
- 1.2% of such areas were classified as **NAR**.

When **Scenario 4** approach these values looked as follows:

- 0.0% of the surface water drinking water protected areas were classified as **AR**;
- 85.7% of the surface water drinking water protected areas were classified as **PAR**;
- 13.2% of the surface water drinking water protected areas were classified as **PNAR**;
- 1.1% of the surface water drinking water protected areas were classified as **NAR**;

When referred to the individual Water Company Areas (WAC) the results of the estimation for Flufenacet looks as follows:

- for **Anglian WAC** and assessment with **Baseline** approach the surface water drinking water protected areas classified as: **AR** accounted for 1.0%, as **PAR** accounted for 10.8%, as **PNAR** accounted for 0.0% and as **NAR** accounted for 0.0%; for the assessment with **Scenario 4** approach these numbers were: 0.0% for **AR**, 11.8% for **PAR**, 0.0% for **PNAR** and 0.0% for **NAR**;
- for **Northumbrian WAC** and assessment with **Baseline** approach the surface water drinking water protected areas classified as: **AR** accounted for 0.0%, as **PAR** accounted for 3.4%, as **PNAR** accounted for 1.6% and as **NAR** accounted for 0.0%; for the assessment with **Scenario 4** approach these numbers were: 0.0% for **AR**, 3.5% for **PAR**, 1.5% for **PNAR** and 0.0% for **NAR**;
- for **Severn Trent WAC** and assessment with **Baseline** approach the surface water drinking water protected areas classified as: **AR** accounted for 0.0%, as **PAR** accounted for 19.2%, as **PNAR** accounted for 0.6% and as **NAR** accounted for 0.2%; for the assessment with **Scenario 4** approach these numbers were: 0.0% for **AR**, 19.7% for **PAR**, 0.1% for **PNAR** and 0.2% for **NAR**;
- for **South West WAC** and assessment with **Baseline** approach the surface water drinking water protected areas classified as: **AR** accounted for 0.0%, as **PAR** accounted for 2.3%, as **PNAR** accounted for 1.0% and as **NAR** accounted for 0.0%; for the assessment with **Scenario 4** approach these numbers were: 0.0% for **AR**, 2.8% for **PAR**, 0.5% for **PNAR** and 0.0% for **NAR**;
- for **Southern WAC** and assessment with **Baseline** approach the surface water drinking water protected areas classified as: **AR** accounted for 0.0%, as **PAR** accounted for 5.2%, as **PNAR** accounted for 0.0% and as **NAR** accounted for 0.0%; for the assessment with **Scenario 4** approach these numbers were: 0.0% for **AR**, 5.2% for **PAR**, 0.0% for **PNAR** and 0.0% for **NAR**;
- for **Thames WAC** and assessment with **Baseline** approach the surface water drinking water protected areas classified as: **AR** accounted for 0.0%, as **PAR** accounted for 22.6%, as **PNAR** accounted for 0.0% and as **NAR** accounted for 0.0%; for the assessment with **Scenario 4** approach these numbers were: 0.0% for **AR**, 22.65% for **PAR**, 0.0% for **PNAR** and 0.0% for **NAR**;
- for **UU WAC** and assessment with **Baseline** approach the surface water drinking water protected areas classified as: **AR** accounted for 0.0%, as **PAR** accounted for 0.5%, as **PNAR** accounted for 4.2% and as **NAR** accounted for 0.4%; for the assessment with **Scenario 4** approach these numbers were: 0.0% for **AR**, 2.6% for **PAR**, 2.1% for **PNAR** and 0.4% for **NAR**;
- for **Wales WAC** and assessment with **Baseline** approach the surface water drinking water protected areas classified as: **AR** accounted for 0.0%, as **PAR** accounted for 3.6%, as **PNAR** accounted for 10.6% and as **NAR** accounted for 0.6%; for the assessment with **Scenario 4** approach these numbers were: 0.0% for **AR**, 6.4% for **PAR**, 7.8% for **PNAR** and 0.5% for **NAR**;
- for **Wessex WAC** and assessment with **Baseline** approach the surface water drinking water protected areas classified as: **AR** accounted for 0.0%, as **PAR** accounted for 4.6%, as **PNAR** accounted for 0.0% and as **NAR** accounted for 0.0%; for the assessment with **Scenario 4** approach these numbers were: 0.0% for **AR**, 4.6% for **PAR**, 0.0% for **PNAR** and 0.0% for **NAR**;
- for **Yorkshire WAC** and assessment with **Baseline** approach the surface water drinking water protected areas classified as: **AR** accounted for 0.0%, as **PAR** accounted for 6.5%, as **PNAR** accounted for 1.1% and as **NAR** accounted for 0.0%; for the assessment with **Scenario 4** approach these numbers were: 0.0% for **AR**, 6.5% for **PAR**, 1.1% for **PNAR** and 0.0% for **NAR**;

In case of the estimation of the groundwater source protected zones the results obtained for **Baseline** approach was following:

- 0.0% of such areas were classified as **AR**,
- 0.0% of such areas were classified as **PAR**,
- 61.3% of such areas were classified as **PNAR**,
- 38.7% (19.0 in number) of such areas were classified as **NAR**.

When **Scenario 4 approach** these values looked as follows:

- 0.0% of the Groundwater source protected areas were classified as **AR**;
- 0.0% of the Groundwater source protected areas were classified as **PAR**;
- 60.6% of the Groundwater source protected areas were classified as **PNAR**;
- 39.2% of the Groundwater source protected areas were classified as **NAR**;

The results of the model estimation may indicate that while for the drinking water abstracted from the groundwater resources in the UK Flufenacet may pose no serious threat, it may become a compound of concern when in case of drinking water abstracted from the surface water resources.

As a next step of the assessment, the effectiveness of various methods of removal of micropollutants from drinking water were assessed. Initially, the assessment covered the following methods:

- adsorption on Granular Activated Carbon (GAC),
- adsorption on Powdered Activated Carbon (PAC),
- removal by ozone/GAC adsorption,
- removal by UV irradiation,
- removal by advanced oxidation,
- removal by nanofiltration/reverse osmosis.

All these methods were characterised and performance of one of them – adsorption on GAC, was characterised and evaluated for its performance in a more detailed way being relatively commonly used.

In case of Flufenacet it was stated that there was no known experimental data on the effectiveness of the removal of that compound from water. Therefore the whole assessment was based on the comparative analysis using Metazachlor as a reference compound. Metazachlor was selected because it belonged to the same family of anilide herbicides and displayed some structural similarities to Flufenacet. It was demonstrated to be very well removed by GAC. The comparison resulted in stating that Flufenacet displayed, in addition to higher molecular weight (363.33 g/mol vs. 277.75 g/mol for Metazachlor), lower solubility in water (56 mg/L vs. 450 mg/L) and higher affinity to organic substances expressed in terms of log K_{OW} (3.2 vs. 2.49). That, according to the authors of the report suggested that Flufenacet as well would be very well removed from treated water by GAC.

That conclusion was presented at the end of the summarized report, with suggestion however that the performance of GAC in the removal of the plant protection products subjected to the examination should be conformed experimentally.

Another identified by the RMS publication providing, this time based on the experimental data, the information on the removal efficiency of Flufenacet from raw water during its processing for drinking water was following:

Verstraeten I. M., Thurman E. M., Lindsey M. E., Lee E. C., Smith R. D., “Changes in concentrations of triazine and acetamide herbicides by bank filtration, ozonation and chlorination in a public water supply.”, *Journal of Hydrology*, 2002, **266**, 190 – 208

The aim of that study was to examine the changes in the concentration of several triazine and acetamide herbicides in the processed substrate at various stages of production of drinking water in drinking water abstraction plants. The analysed compounds were: atrazine and its degradation products, cyanazine and its degradation products, propazine, simazine, alachlor and its degradation products, acetochlor and its degradation products, metolachlor and its degradation products, dimethenamid and flufenacet.

The test facility was municipal drinking water treatment plant of the City of Lincoln, Nebraska, USA, abstracting water from the Platte River and groundwater wells.

The analytical period covered three years – from June 1997 to 1999. The analysed water samples were: raw riverine water, water samples from the collector wells, effluent after the bank filtration, post-ozonation effluent, post-chlorination and filtration effluent, treated drinking water (final product) and groundwater. The samples were taken during the study period in months April – June of each year, indicated as a typical period of the

spring runoff. That period was selected because then the concentrations of herbicides in the river significantly impacted the quality of surface water, groundwater and drinking water.

Characterising the test facility the authors of the publication stated that it contained a well field consisting of 38 wells, of which two were horizontal, collector wells with daily capacity of 25 m³ each, and remaining 36 were vertical wells with a daily capacity of up to 1 m³ each. The filling of the wells were layers of alluvial sand, gravel, silt and clay, having a total thickness of 27 m.

The riverine water was transported to them by means of bank filtration over the distance of 25 metres, with a mean estimated residence time of 6 days. The bank-filtered water was transported from collector wells to the treatment plant for subsequent treatment within 20-60 minutes. The subsequent stages of water treatment were: ozonation, filtration, chlorination, fluoridation, ammonization and residence in reservoir.

Characterising the plant the authors of the paper stated that it had a capacity of 190 m³/day and that more than 90% of treated water was a riverine water.

The concentrations of Flufenacet as a compound of interest at each step of the treatment process were determined only in 1999. The reason for that was not given, but as the paper bears the reference to the earlier publication, presenting the analysis of the concentrations of various pesticides in water from municipal collector wells, it may be assumed that Flufenacet in significant amounts was started to be detected from that year onwards (N.b. that may be confirmed by the results presented in the reports of USDA, summarized in the chapter dealing with the results of the monitoring studies, showing that Flufenacet started to be extensively used on the Great Plains about that period, with its peak occurring around the year 2002).

The analytical method used for the identification and quantitation of Flufenacet was that developed within the USDA by Kish et al. (2000), and it consisted of GC/MS analysis preceded by SPE. The LOQ for that method was 0.05 µg/L – a half of the regulatory drinking water limit set for the individual active substances of the plant protection products.

The concentrations of Flufenacet determined at each stage of the examination of treated water were:

- 0.19 µg/L for raw riverine water;
- 0.07 µg/L for the bank-filtered water,
- 0.07 – 0.08 µg/L for water collected from the collector wells,
- 0.05 µg/L for the post-ozonation effluent,
- < 0.05 µg/L for the post-chlorination and filtration effluent,
- 0.05 µg/L for the final product – treated drinking water.

The concentrations of Flufenacet in groundwater were not measured. The results indicate that Flufenacet was efficiently removed from the treated water during filtration, its concentration being reduced by 58%. However, there is no information about its degradation products, such as FOE Oxalate, FOE Sulfonic acid or FOE Thiadone, which may be formed during the bank filtration as a result of the degradation of Flufenacet. At the same time, in the paper, which examined also the fate of the analogues of FOE Oxalate and FOE Sulfonic acid – OXA and ESA degradation products of other acetamide plant protection products, namely of Alachlor, Acetochlor and Metolachlor, it was stated that not only these compounds may be partly removed during filtration, in amounts up to ~40% but efficiently removed, with 79%-effectiveness, during ozonation stage. It was stated that the process results in formation of alcohols, carbonyls, carboxylic acids (by cleavage of the double bonds), opening of aromatic rings and removal or oxidation of alkyl groups. Similar processes, with regard to the mechanisms and overall effectiveness, may take place also for the relevant degradation products of Flufenacet reaching that stage of water treatment.

The good insight into the possible efficiency of the removal of Flufenacet and its degradation products at later stages of treatment during the process of drinking water abstraction provides the following paper:

Sakkas V. A., Calza P., Vlachou A. D., Medana C., Minero C., Albanis T., “Photocatalytic transformation of flufenacet over TiO₂ aqueous suspension: Identification of intermediates and the mechanisms involved.”, *Applied Catalysis B: Environmental*, 2011, **110**, 238 – 250;

The paper provides the detailed characterisation of the mechanisms involved in photooxidation of Flufenacet in water carried out over the TiO₂ as a catalyst.

The aim of the experiment was to assess the efficiency of the removal of Flufenacet from the processed drinking water through its photochemical degradation in presence of TiO₂ as a catalyst. That was done by the means of:

- a) optimization of the process through the examination of the simultaneous effect of varying concentrations of TiO₂ and H₂O₂, and changes in pH on the efficiency of degradation;

- b) determination of transformation pathways through identification of the transformation products;
- c) examination of temporal evolution of final products of mineralization;
- d) assessment of the changes in the toxicity of treated water in function of the exposure to the reacting agents, by carrying out the luminescence bioassays using *Vibrio fischeri*

The test compound was “cold” (not radiolabelled) Flufenacet, having a chemical purity of >99%, supplied by Riedel-de H  en company. Other reagents used in the study were: analytical-grade pure 30% H₂O₂ – the oxidising agent, and TiO₂ powder (Degussa P25) used as photocatalyst.

The experiment aimed on the determination of the kinetics of degradation of Flufenacet – efficiency of the process, was carried out at combination of the following initial conditions:

- pH of the aqueous solution was 4.5, 7.0 or 9.5, with single samples having pH = 2.8 or pH = 11.2;
- concentration of the photocatalyst – TiO₂ in the solution was 250 mg/L, 500 mg/L or 750 mg/L, with single samples containing 80 mg/L or 920 mg/L of TiO₂;
- concentration of H₂O₂ in solution (in moles/L) was 0.013M, 0.026M or 0.039 M, with with single samples having concentration of H₂O₂ 0.004M or 0.048M;
- the volume of the solution was 50 mL, the concentration of the test compound in it was not specified, but it may be assumed that, to limit the number of variables it had to be constant (possibly 15 mg/L as in the second experiment);
- after introduction of the photocatalyst – TiO₂, the test solutions were pre-equilibrated in the darkness for 60 minutes before being irradiated (that was done to reach the adsorption equilibrium on the surface of semiconductor);
- irradiation was performed using Sunset CPS+ apparatus equipped with 1500-W xenon lamp and set of filters cutting off the radiation wavelengths $\lambda < 290$ nm, the temperature of irradiated samples was maintained at the level $T < 20^{\circ}\text{C}$;
- the estimation of the efficiency of the process of degradation of Flufenacet was performed in samples taken after 30 minutes of irradiation;
- liquid samples, before being analysed were filtered through 0.45 μm PVDF Millipore membrane filters to remove the suspended TiO₂.

To determine the mechanisms of photocatalytical degradation of Flufenacet in water and its kinetics second experiment was performed. Its major features were following:

- volume of the samples: 5 mL;
- concentration of the test item – Flufenacet: 15 mg/L;
- concentration of the photocatalyst – TiO₂: 200 mg/L;
- the experiment was performed in air-saturated conditions;
- the irradiation was carried out using a lamp having energy emission intensity of 40W/m² and maximum emission at $\lambda = 360$ nm;
- The temperature during irradiation reached $T = 38 \pm 2^{\circ}\text{C}$.

Samples for the content of Flufenacet and identification and quantitation of its transformation products were analysed using the following analytical methods:

- HPLC-MS – the primary identification method for the phototransformation products of Flufenacet;
- HPLC with the UV detection;
- Ion chromatography – method used for quantitation of some terminal products of photocatalytic degradation of Flufenacet, such as fluoride, sulphate, nitrite and nitrate ions;
- TOC analysis;

The toxicity of the samples, obtained at different time points in the experiment aimed on the elucidation of the transformation pathways of Flufenacet during its photooxidative decomposition, was examined using Microtox Model 500 Toxicity analyser. It was based on the determination of the ability of the given sample to inhibit the natural bioluminescence of the marine bacterium *Vibrio fischeri*.

In the preliminary experiments, lasting 2 hours, it was demonstrated that Flufenacet was not prone to either hydrolysis or direct photolysis and it was negligibly adsorbed onto TiO₂. As a result it was stated that these processes will have no influence on the results of the whole experiment.

The efficiency of the process was optimised using the determined % disappearance of Flufenacet from samples after 30-minutes lasting irradiation. The results are presented below in the table B.8.2.6._CA-1. They indicate generally high efficiency of the process, with the level of degradation $\geq 70\%$ of the initial amount of Flufenacet within relatively short exposure time. The efficiency of the process depended on all three variables, although not to the same extent. It was noticed that the increase of the concentration of H₂O₂ would have an

inhibitory effect. Also initial pH of the solution was demonstrated to have a substantial effect, related also to the catalyst properties. The process reached its optimum at $\text{pH} \approx 7$, which is estimated to be natural pH of the riverine water. Finally, it was demonstrated that the efficiency of the removal increased with the increasing concentration of TiO_2 , reaching the optimum at 500 mg/L, to stabilise or even decrease afterwards.

These results created the basis for further examination of the process for its kinetic performance and transformation patterns – the optimised conditions for that experiment have been presented above.

Table B.8.2.6._CA-1 The results of the experiment aimed on the optimisation of the process of photocatalytical degradation of Flufenacet over TiO_2 .

Experiment No	Experimental conditions			Degradation of Flufenacet [%]	
	Concentration of H_2O_2 [mole/L]	Concentration of TiO_2 [mg/L]	pH	predicted	observed
1	0.013	250	4.5	93.39	94.53
2	0.013	750	4.5	94.89	95.30
3	0.013	250	9.5	89.07	94.40
4	0.013	750	9.5	98.41	97.00
5	0.039	250	4.5	87.78	90.55
6	0.039	750	4.5	91.97	92.10
7	0.039	250	9.5	70.75	71.70
8	0.039	750	9.5	82.78	83.03
9	0.026	500	7.0	88.93	88.76
10	0.026	500	7.0	88.93	88.99
11	0.026	80	7.0	73.94	70.92
12	0.026	960	7.0	85.31	86.43
13	0.026	500	2.8	100.88	98.96
14	0.026	500	11.2	89.52	89.53
15	0.004	500	7.0	100.04	99.83
16	0.048	500	7.0	82.20	80.50

The examination of the transformation pattern showed that three possible mechanism are involved. First of them is an initial hydroxylation of either in fluorophenyl ring, isopropyl group or of the C atom standing next to the bridging O in the alkyl group. Second postulated mechanism is defluorination of the fluorophenyl ring and third N-delakylation of the molecule. These processes resulted in formation of 32 intermediate compounds (TP). The authors stated that the decomposition of Flufenacet was very quick, with $t_{1/2} = 5$ minutes. The compound totally disappeared from the solution within 60 minutes of irradiation and almost all of its identified TP within two hours from the initiation of the process. It was also stated that the proposed tentative reaction pathway displayed similarities to that determined in the environment, with the cleavage of the bridging C-O bond within the N-alkyl chain observed. Thiadiazole moiety was subjected to the ring cleavage, while N-alkylic chain and phenyl moiety were involved in hydroxylation and demethylation.

The analysis of the toxicity of the solution showed that at least some of TPs formed within the first 60 minutes of the process displayed higher toxicity than the active substance – while the initial inhibition of the luminescence of *Vibrio fischeri*, attributed to Flufenacet, was 32% and decreased slightly within first 5 minutes of the experiment, it significantly increased afterwards to reach the maximum 66%-level around its 30th minute. It decreased afterwards, first slowly (55% inhibition around 45th minute since the beginning of irradiation), to reach the level comparable to that obtained for the active substance at minute 60th and then dropping to the level of 5% around 120th minute of the whole experiment. That may indicate that by that time all toxic byproducts would be effectively eliminated from the treated substrate (treated water). However, although Flufenacet and its toxic phototransformation products disappeared within 120 minutes of the process, during that time only 60% mineralisation with regard to organic carbon and 40% mineralisation with regard to organic nitrogen was observed. It was estimated that to obtain the complete mineralisation of organic carbon, the required residence time would be 24 hours. After that period only 65% of N present in the molecule was recovered, what was attributed to the loss of it related to its partial photoconversion to N_2 . Of the recovered 65% of N, 25% was in form of ammonium ions and 40% as nitrite/nitrate.

Only 25% of Fluorine was recovered, but that in turn was attributed to the fact that the process of the transformation of $-\text{CF}_3$ was not sufficiently covered.

In conclusion the authors stated that the method has a great potential with regard to the removal of Flufenacet from water abstracted for drinking water, as a low-cost, environmental friendly and sustainable treatment technology.

Nowadays this, still considered novel, method of removal of micropollutants from treated drinking water is one of well-known and commonly applied method within the set of methods known under the common name “advanced oxidation process” or AOP. Its general characteristic may be found in many publications, such as:

Manoj A. Lazar, Shaji Varghese, Santosh S. Nair “Photocatalytic Water Treatment by Titanium Dioxide: Recent Updates.”, *Catalyst*, 2012, **2**, 572 – 601.

The already performed analysis for Flufenacet showed that also its degradation products should be efficiently removed from treated water during drinking water abstraction procedures. RMS however decided to further conform that using the available literature data.

The data on the removal efficiency of FOE Oxalate and FOE Thiadone from the substrate treated to obtain drinking water were found in the following publication:

Sinclair C., van Beinum W., Adams C., Bevan R., Levy L., Parsons S., Goslan E., Baumann G., “A Desk Study on Pesticide Metabolites, Degradation and Reaction Products to Inform the Inspectorate’s Position on Monitoring Requirements. Final Report for Drinking Water Inspectorate.”; The Food and Environment Research Agency (FERA), Sand Hutton, York, UK, FERA Project S3VB, DEFRA Project WT1221, DWI Project 70/2/232, February 2010, report available on-line on DEFRA web-site.

The study had following aims:

- to review and collate the available information on the degradation and transformation products of the Plant Protection Products used in the UK at the time of issuing of the Report;
- to identify the degradation and transformation products that may exhibit pesticidal activity and/or additional toxicological concerns;
- for the degradation products identified at previous step to estimate the likely concentrations in drinking water;
- to estimate, for the degradation products of concern, the would-be risk to human health;
- to estimate the likelihood and the extent of their reaction with ozone and/or chlorine during water treatment and the possibility of the formation of toxic compounds;
- to prepare the recommendations with regard to the updating of the relevant guidances in force at the period of the issuing of the report.

The review and collation of the available information on the degradation and transformation products, further called metabolites of the Plant Protection Products (further called active substances) in use in the UK at time of the performance of the research, resulted in the identification of 523 soil metabolites, originating from 185 active substances. For 485 of them (92.7% of the initial number) it was possible to identify 2-dimensional structural representation – their structural formulas. These data were next used to estimate the mammalian toxicity of the so pre-selected compounds using two modelling tools – DEREK and TOPKAT. The knowledge of the structural formulas of the metabolites of concern was also used to estimate their potential pesticidal activity in relation to their precursor – parent pesticides, through examination of the presence of toxicophores.

That complex analysis resulted in selection of 53 compounds for further investigation. Among them were two major soil degradation products of Flufenacet – FOE Oxalate and FOE Thiadone.

The next step of the examination was the estimation of the likely concentrations of the selected 53 degradation products in substrate and final product of drinking water abstraction processes.

That examination was carried out using three existing surface water abstraction catchments in England, two selected because of being identified as high-risk catchment for pesticide contamination, while the third one because of the availability of the data from monitoring of metabolites of atrazine. The identity of these catchments for the purpose of the study was not revealed, instead they were referred to in the study, and characterised, as Catchments A, B and C.

It was stated that the major migration route of the degradation products from the treated fields to the to the surface water bodies was a discharge from a drainage system. It was also assumed that, due to the shorter pathway, the concentrations in surface water following drainage would be higher than those in groundwater. As a result, the first step of the estimation was the calculation of the predicted concentrations in the drainflow, using the methodology adapted from the study undertaken on behalf of Pesticide Safety Directorate, into the controlling factors for pesticide losses via drainflow.

The whole estimation of the likely concentrations of the compounds of concern in drinking water consisted of the following three steps:

- 1) estimation of the concentrations in drainage water;

- 2) estimations of the concentrations in the downstream surface water
- 3) estimations of concentrations in finished drinking water.

In case of the third step, the performance of the treatment processes in removal of each investigated compound from treated water was evaluated. The processes taken into consideration were:

- coagulation;
- removal by activated carbon, granular (GAC) or powdered (PAC),
- ozonation,
- chlorination.

The estimation was performed for two types of treatment procedure:

- **conventional treatment**, comprising (in order of appearance) coagulation-flocculation, removal by PAC, chlorination; filtration was not included as it was not expected to result in any further removal;
- **advanced treatment**, comprising (in order of appearance) coagulation-flocculation, ozonation, removal by PAC and chlorination.

The estimation of the performance of each process was based on the examination of the known substance properties. For coagulation-flocculation/filtration it was based on the examination of how the given molecule is charged. The key parameter used in the estimation of the efficiency of removal by PAC was the log K_{OW} estimated or measured for the given molecule at pH = 7. In case of ozonation and chlorination QSPR (quantitative structure-property relationship) models were used and the molecules were converted from 2-D (planar) to 3-D (spatial) representation. The calculations were performed using the equations developed by Lei and Snyder.

The so estimated levels of removal of FOE Oxalate and FOE Thiadone are presented below in the table B.8.2.6._CA-2.

Table B.8.2.6._CA-2: The estimated levels of removal of FOE Oxalate and FOE Thiadone during drinking water treatment.

Removed compound	Conventional treatment - % removed in:				Advanced treatment - % removed in				
	Coagulation	PAC	Chlorination	Total	Coagulation	Ozonation	PAC	Chlorination	Total
FOE Oxalate	25	50	53.1	82.4	25	59	50	53.1	92.8
FOE Thiadone	0	50	6.5	53.3	0	50	50	6.5	76.6

It shall be indicated however that both FOE Oxalate and FOE Thiadone were classified, as a result of further examination, as “**Metabolites with unknown detoxification due to the lack of information on reactive sites or toxic moieties**”.

The determination of risk to human health, based on the calculation of the worst-case intake of metabolites from drinking water for each catchment, returned the results which, for FOE Oxalate and FOE Thiadone, are provided below in table B.8.2.6._CA-3. The conservative estimate assumed no removal of the compounds of concern from drinking water (consumption of raw water), while the refined estimate took into account the level of their removal during conventional and advanced treatments. The results were provided individually for each analysed catchment.

Table B.8.2.6._CA-3: The results of the estimation of the worst-case intake of FOE Oxalate and FOE Thiadone presented in the report.

Catchment	Compound	Estimated worst-case intake – percentage of ADI for:			
		Adult		Toddler	
		Conservative estimate	Refined estimate	Conservative estimate	Refined estimate
Catchment A	FOE Oxalate	0.09 – 0.21	<0.01	0.29 – 0.81	<0.01
	FOE Thiadone	0.08 – 0.17	<0.01	0.37 – 0.75	<0.01
Catchment B	FOE Oxalate	0.17 – 0.41	<0.01	0.176 – 1.86	<0.01
	FOE Thiadone	0.16 – 0.32	0.01	0.73 – 1.46	<0.01
Catchment C	FOE Oxalate	<0.01 – 0.01	<0.01	0.01 – 0.04	<0.01
	FOE Thiadone	<0.01 – 0.01	<0.01	0.01 – 0.03	<0.01

Both compounds were considered, as a result of the estimation presented in the table above, to be of no concern, because predicted for them daily total intake from drinking water was <10% ADI.

The analysis was performed only for these two degradation products. Neither FOE Sulfonic acid, formed in amounts comparable to those determined for FOE Oxalate and displaying similar to it mobility in soil but higher persistence, nor FOE Methylsulfone, another important soil degradation product of Flufenacet having a structure similar to that of FOE Oxalate, were taken into account. It shall be noted however that, because of the structural similarities the three metabolites display, the efficiency of their removal in either conventional or advanced treatment may be on the comparable level. Similar conclusion can be drawn also regarding FOE Methylsulfide.

Selected degradation/transformation products of Flufenacet – FOE Sulfonic acid, FOE Oxalate, FOE Methylsulfone, FOE Thioglycolate sulfoxide and FOE Thiadone, have calculated risk indexes that may be used in creation of prioritisation schemes for drinking water supplies. These were provided in the supplementary data (available on-line) to the following publication:

Sinclair C. J., Boxall A. B. A., Parsons S. A., Thomas M. R., “Prioritization of Pesticide Environmental Transformation Products in Drinking Water Supplies.”, *Environmental Science and Technology*, 2006, **40** (23), 7283 – 7289;

The paper presented prioritization approach for identifying the most important, from the point of view of consumers risk, degradation/transformation products of pesticides. That approach was developed as a result of the workshop organized in Prague, Czech Republic, on the 5th of June 2004. To prioritise the transformation products their risk index should be calculated.

The proposed calculation methodology consisted of the following stage:

- **Stage 1:** calculation of the exposure index **E** for the given transformation product, comprising the following factors: index **A** characterising the amount of the given metabolite released into the environmental compartment of concern, index **F** that characterises the mobility of the given compound in the environment and index **P** that characterises its persistence in the environment (soil and water compartments); to calculate that index the following final equation is recommended to be used: $E = A \cdot F \cdot P$
- **Stage 2:** determination of the toxicological effects – the factor declared to be most useful here, for drinking water, was **ADI** – Acceptable Daily Intake.
- **Stage 3:** at that stage is performed risk characterisation and ranking; the analysis performed at two previous stages and obtained factors are used to calculate a risk index – **RI**, using the following equation: $RI = E/ADI$; it was stated that the higher was the RI value, the greater was the potential risk posed by the given metabolite to drinking water supplies within the defined system.

Characterising the approach the authors indicated that in many instances not all data required for determination of **E** factor (these are: maximum formation fraction for the given compound within the compartment of interest – *f*, *K_d*, *DT₅₀ SOIL* and *DT₅₀ WATER*) are available and, in case of their lack these shall be replaced by their default counterparts. Based on the data availability the degradation products were divided into five general data classes:

- A, with no default values required,
- B, with 1 default value required,
- C, with 2 default values required,
- D, with 3 default values required,
- E, with 4 default values required.

Class B was additionally divided into three subgroups:

- B_f in which a default for formation is used;
- B_m in which the default for mobility is required;
- B_p in which the default for persistence is used.

Two examples were provided to illustrate such approach – the priority list for the UK and priority list for California.

All ranked degradation products of Flufenacet were included into the background information used to create the priority list for the UK.

FOE Sulfonic acid and FOE Oxalate were included into class D with regard to the availability of the data for them, while FOE Methylsulfone, FOE Thiadone and FOE Thioglycolate sulfoxide to class E.

The risk index values calculated for them were:

- for FOE Sulfonic acid RI = 0.31247;
- for FOE Oxalate RI = 0.21737;
- for FOE Methylsulfone RI = 0.13586;
- for FOE Thioglycolate sulfone RI = 0.13586;
- for FOE Thiadone RI = 0.13586

RMS also briefly examined the available literature in search of the data informing about the would be impact of the residues of Flufenacet – the active substance or/and its identified major degradation products on wastewater treatment procedures.

Two such publications were identified.

First of them:

Hollender J., Zimmermann S. G., Koepke S., Krauss M., McArdell C. S., Ort C., Singer H., von Gunten U., Siegrist H., „Elimination of Organic Micropollutants in a Municipal Wastewater Treatment Plant Upgraded with a Full-Scale Post-Ozonation Followed by Sand Filtration.”, *Environmental Science and Technology*, 2009, **43** (20), 7862 – 7869.

examined the efficiency of additional step in wastewater treatment – post-ozonation (ozonation after biological purification of wastewater) followed by sand filtration, in elimination of some persistent organic micropollutants. The examination was performed on existing and fully operational Municipal Wastewater Treatment Plant located in Switzerland (WWTP Wüeri in Regensdorf, Switzerland), characterised as receiving typical Swiss municipal wastewater. The aim was to examine the efficiency of the elimination of some 220 organic micropollutants from the secondary effluent (after biological stage of wastewater treatment process), among them Flufenacet and its two degradation products – FOE Sulfonic acid and FOE Oxalate, listed in supplementary material as compounds of the targeted screening of the secondary effluent and ozonation effluent. For these compounds the Limit of Quantification (LOQ) was set to 15 ng/L for Flufenacet (not reported in the paper, but determined when contacting one of the authors), 13 ng/L for FOE Sulfonic acid and 23 ng/L for FOE Oxalate. These compounds were however not listed as those detected in any examined effluent, so it may be assumed that if present in the wastewater stream incoming to the WWPT, they were efficiently removed at earlier stages. That cannot be confirmed, as the paper provides no information with regard to the content of these compounds in raw wastewater or in the effluent entering the biological treatment step. At the same time it shall be indicated that such situation is probable in light of the results of the monitoring of the residues of Flufenacet in surface water bodies of five Swiss catchments, presented in the paper summarised in this Renewal Assessment Report in the document Vol. 3_CA – B.8. under the point B.8.5 (paper by [Moschet et al.; 2014]).

Another publication:

Dealtry S., Holmsgaard P. N., Dunon V., Jechalke S., Ding G-C. Krögerrecklenfort E., Heuer H., Hansen L. H., Springael D., Zühlke S., Sørensen S., Smalla K., „Shifts in abundance and Diversity of Mobile Genetic Elements after the Introduction of Diverse Pesticides into an On-Farm Biopurification System over the Course of a Year.”, *Applied and Environmental Microbiology*, 2014, **80** (13), 4012 – 4020.

presented the results of the performance of the typical on-farm Biopurification system (BPS) in controlling the environmental pollution caused by release of water containing Plant Protection Products. That was done by the means of examining the concentrations of various active substances of PPPs in BPS and their changes during the year, as well as diversity and abundance of microorganisms carrying MGEs – mobile genetic elements harboring genes involved in degradation of xenobiotic compounds. One of such group of MGEs were IncP-1 plasmids.

The examination was performed on a BPS in Kortrijk, Belgium, containing a biomix composed of coco chips, straw, manure and field soil, filtering wastewater containing different plant protection products from spillage and collected during cleaning the spraying equipment. Flufenacet was one of the compounds that was detected in wastewater reaching the BPS and then detected there. Although its amounts reaching the installation were not reported in the paper, it provided the results of its quantification in the BPS's filling material during the experiment: in March, when it was measured in concentration 150 ng/g, July – 5062 ng/g and September – 4804 ng/g. Other active substances detected in BPS were Azoxystrobin (23 – 38 ng/g), Bentazone (46060 – 55795 ng/g), Diflufenican (671 – 1647 ng/g), Duiro (80 – 111 ng/g), Epoxiconazole (612 – 936 ng/g), Ethofumesate (91 – 119 ng/g), Fenpropimorph (< 4 – 6 ng/g), Fluroxypyr (90 – 1251 ng/g), Metamitron (39 – 63 ng/g), Metribuzine (141 – 2065 ng/g), Propiconazole (46 – 168 ng/g), S-metolachlor (2958 – 11806 ng/g), Tebuconazole (796 – 941 ng/g) and Terbutylazine (694 – 8579 ng/g). The concentration profile of these compounds was positively correlated with the increase in abundance of bacteria carrying the IncP-1β plasmids, indicating their important role in degradation of Plant Protection Products. Also was observed high diversity of

different IncP-1 groups in BPS bacterial communities, similar to that observed in sewage sludge. That may indicate that Flufenacet present in mixture with other active substances and in relatively high amounts would probably not have a significant impact on the performance of wastewater treatment processes in such installations.

Conclusions:

On the basis of the presented above evaluation it can be stated that neither Flufenacet nor any of its identified major degradation products are expected to pose any serious threat or have any significant impact on the water treatment processes aimed on the abstraction of drinking water or purification of wastewater.

B.8.3 - Fate and behaviour in air

As the first step in the assessment of the fate and behaviour of Flufenacet in the air compartment RMS analysed the basic data on the volatility potential of that active compound and its major degradation products in order to identify the substances of concern for the atmosphere. The basic data on the volatility potential of Flufenacet and its major degradation products are presented below in the table B.8.3._CA-1. The data were taken from the section B.2 (AS) for Flufenacet, unless it was clearly stated that they were derived from other sources.

Table B.8.3._CA-1: The key physico-chemical properties of Flufenacet and its major degradation products relevant for the determination of the fate and behaviour in the atmosphere.

Parameter	Compound ¹⁾							
	FOE 5043	FOE Oxalate	FOE S. A.	FOE Methylsulfone	FOE Methylsulfide	FOE Thiadone	FOE TFESA	TFA ²⁾
Molecular weight [g/mol]	363.4	225.2	275.3	257.3	241.0	170.1	164.1	114.02
Vapour pressure V_p [Pa] at $T = 20^\circ\text{C}$	9 E-5 ³⁾	4.5 E-7	1.35 E-7 ⁶⁾	8.6 E-4	8.06 E-3 ¹⁰⁾	2.05	<1.0 E-8	<1.0 E-6
Solubility in water, S_{aq} [mg/L] at $T = 20^\circ\text{C}$	pH 5	56 ⁴⁾	> 1.2 E5	5.5 E4 ⁷⁾	4.1 E3 ⁹⁾	2.0 E3 ¹¹⁾	95.5 E3 ¹³⁾	>1.6 E5
	pH 7	56	> 1.2 E5	5.5 E4 ⁷⁾	4.1 E3 ⁹⁾	2.0 E3 ¹¹⁾	> 1.0 E5	>1.6 E5
	pH 9	53	>1.2 E5	5.5 E4 ⁷⁾	4.1 E3 ⁹⁾	2.0 E3 ¹¹⁾	> 1.0 E5	>1.6 E5
Henry's law constant, H, [Pa*m³/mol] at $T = 20^\circ\text{C}$	pH 5	1.2 E-3 ⁵⁾	<8.4 E-10	n. a. ⁸⁾	n. a. ⁸⁾	1.72 E-2 ¹²⁾	0.012 ¹⁴⁾	<1.2 E-11
	pH 7	1.3 E-3 ⁵⁾	<6.8 E-10	n. a. ⁸⁾	5.7 E-5	1.72 E-2 ¹²⁾	n. a. ⁸⁾	<1.2 E-11
	pH 9	1.1 E-3 ⁵⁾	<6.8 E-10	n. a. ⁸⁾	n. a. ⁸⁾	1.72 E-2 ¹²⁾	n. a. ⁸⁾	<1.2 E-11

Footnotes to the table:

- 1) The following code-names were used to denominate the substances: FOE 5043 for Flufenacet, FOE S. A. for FOE Sulfonic acid, FOE TFESA for FOE Trifluoroethanesulfonic acid and TFA for Trifluoroacetic acid;
- 2) **In aqueous solution TFA, being a very strong acid with $\text{pK}_a = 1.6$, is fully dissociated, therefore the values are provided for trifluoroacetate and the test substance used to determine them was TFA-Na salt;**
- 3) In section B.2 it was stated that Flufenacet isomerised by evaporation forming a mixture containing 10% of Flufenacet and 90% of its *N*-isomer; as a result, the value is that characteristic for *N*-isomer of Flufenacet;
- 4) The value determined at pH = 4;
- 5) The values determined for *N*-isomer of Flufenacet, using the solubility values determined for that compound;
- 6) The measured value not provided; instead the Applicant presented the value determined theoretically, using QSAR method, and for $T = 25^\circ\text{C}$; RMS subsequently converted that value to presented here value for $T = 20^\circ\text{C}$ using appropriate Van't Hoff equation (presented in the "Manual for FOCUS TOXSWA version 2.2.1", Alterra Report No. 586, Wageningen, 2006);
- 7) The value determined in unbuffered solution and representative for the whole environmentally relevant pH range, since it was experimentally demonstrated that water solubility of FOE S. A. is not pH-dependent;
- 8) Value not available;
- 9) The value determined in pH = 7 buffer solution, but considered representative for the whole environmentally relevant pH range, since it was experimentally demonstrated that water solubility of FOE Methylsulfone is not pH-dependent;
- 10) The theoretical value determined by the RMS using QSAR methods – it was calculated using Modified Grain method for $T = 25^\circ\text{C}$; for more details please refer to the data presented in the table B.8.8-a.3_CA-4 under the point B.8.8.-A.3 – Appendix 3, of this Renewal Assessment Report;
- 11) The value determined in pH = 6.1 buffer solution, but considered representative for the whole environmentally relevant pH range, since it was experimentally demonstrated that water solubility of FOE Methylsulfide is not pH-dependent;
- 12) The theoretical value determined by the RMS using QSAR methods – it was calculated using Modified Grain method for $T = 25^\circ\text{C}$; for more details please refer to the data presented in the table B.8.8-a.3_CA-4 under the point B.8.8.-A.3 – Appendix 3, of this Renewal Assessment Report;
- 13) The value determined at pH = 5.77;
- 14) The value determined at pH < 5.

The further analysis was carried out using the vapour pressure classification presented in the Guidance document "Pesticides in Air: Considerations for Exposure Assessment" – Report of the FOCUS Working Group on Pesticides in Air (FOCUS; 2008)]. That document provides the proposal for the classification of the given substance with regard to its volatility on the basis of its vapour pressure – table 2.7-1. The table is reproduced below on figure B.8.3.-CA-1.

Table 2.7-1: Vapour pressure classifications

Volatility of compounds	Vapour Pressure in Pa		
	Seiber, Woodrow, 1983 Unsworth <i>et al.</i> , 1999	Koerdel <i>et al.</i> , 1999	EPPO
Volatile	$> 10^{-1}$	$> 10^{-3}$	Soil : $> 10^{-1}$ Plants : 10^{-3}
Medium volatile	between 10^{-1} and 10^{-5}	between 5×10^{-3} and 10^{-6}	Soil : between 10^{-1} and 10^{-3} Plants : between 10^{-3} and 10^{-5}
Low or non volatile	$< 10^{-3}$	$< 10^{-6}$	Soil : $< 10^{-3}$ Plants : $< 10^{-5}$

Figure B.8.3._CA-1: The classification of the volatility of the compounds on the basis of their vapour pressure – the table copied from the FOCUS report “Pesticides in Air: Considerations for Exposure Assessment”.

According to that Guidance document the trigger values indicating the need to establish whether the substance has the potential to reach the air are:

- $V_p \geq 10^{-4}$ Pa at $T = 20^\circ\text{C}$ for volatilisation from soil, and
- $V_p \geq 10^{-5}$ Pa at $T = 20^\circ\text{C}$ for volatilisation from plants.

Using these criteria RMS identified the following compounds as those of potential concern:

- Flufenacet, being medium volatile according to the classification presented above on figure B.8.3._CA-1 and having a potential to reach air via volatilisation from plants;
- FOE Methylsulfone, being medium volatile according to the classification presented above on figure B.8.3._CA-1 and having a potential to reach air via volatilisation from soil and plants;
- FOE Methylsulfide, being medium volatile according to the classification presented above on figure B.8.3._CA-1 and having a potential to reach air via volatilisation from soil and plants; it shall be indicated however that for that compound the assessment is based on theoretically determined values;
- FOE Thiadone, being volatile according to the classification presented above on figure B.8.3._CA-1 and having a potential to reach air via volatilisation from soil and plants.

RMS also decided to take into consideration TFA. Although the experimental values presented in the table B.8.3._CA-1 do not indicate that it is a compound of concern, they were derived for trifluoroacetate. The examination of the available open-source data showed that the non-dissociated acid displayed high volatility potential resulting from its high vapour pressure – 11 kPa at $T = 20^\circ\text{C}$ (source: Pubchem – open chemistry database, url: <https://pubchem.ncbi.nlm.nih.gov>). For that reason RMS decided to evaluate its fate and behaviour in the atmosphere as well. **At the same time it shall be indicated that the $pK_a = 1.6$ value determined for TFA in aqueous solutions clearly indicate that when formed from Flufenacet either in soil or surface water compartments the compound, being entirely dissociated would display very limited volatility and hence risk to atmosphere, unless the environment becomes very acidic. Therefore the whole assessment for that compound is presented mainly for completeness.**

The whole evaluation is presented below, under the relevant data points.

B.8.3.1. – Route and rate of degradation in air

In order to address this data requirement the Applicant submitted two study reports, also evaluated for the purpose of the previous authorisation of Flufenacet in the EU, examining the fate and behaviour of Flufenacet in the air compartment. They are summarised below as *Study 1* and *Study 2*.

It was also stated that three degradation products of Flufenacet – FOE Methylsulfone, FOE Methylsulfide and FOE Thiadone would require further assessment, being either semi-volatile or volatile compounds and therefore posing a potential threat to the atmosphere. Additionally RMS decided to include into the assessment another degradation product of Flufenacet – TFA, also displaying high volatility when not dissociated. For that reason RMS calculated their atmospheric half-lives using AOPWin modelling tool. The calculations are summarised under this point, individually for each compound, as *Studies 3 - 6*. In case of TFA the further assessment is based on the literature data.

Study 1:

Report: Hellpointner E., (1995): “Determination of the Volatilisation Behavior of FOE 5043 (60WG) in a Field Trial.”; Bayer AG, Crop Protection-Development, Institute for Metabolism Research and Residue Analysis, D-51368 Leverkusen, Germany (performing laboratory) for Bayer Corporation, Agriculture Division, P. O. Box 4913, Kansas City, MO 64120, USA; Bayer Report No. 107281 (PF-4091); 12 September 1995; study reference number M-002237-01-2.

Guidelines: The study was performed to comply with the following Guidelines:

- US. EPA Guidelines for Pesticide Registration, Subdivision N, Section 163-3, Field Volatility;
- BBA Guidelines for Testing of Plant Protection Products in Registration Procedure, Part IV, 6-1 (July 1990) entitled “Determination of the volatilization and the fate of plant protectants in the air”.

GLP: Yes;

RMS comments: The study had been evaluated for the previous authorisation of Flufenacet in the EU, by its inclusion into the Annex I of the Directive 91/414/EEC. Its summary can be found under the point B.7.7.1., in section B.7 of the Annex B to the Monograph prepared by the RMS – France, for Flufenacet. Evaluated for the purpose of the present assessment it was found acceptable and is summarised below.

Summary:

The aim of the study was to determine the level of volatilisation of Flufenacet from the soil surface under the field conditions. The experiment was performed in accordance with the BBA Test Guideline IV, 6-1 using one test soil, in three separate trials.

In order to carry out as complete as possible quantitative analysis, including the determination of the non-volatile degradation products as well as the residues of the active substance being bound to soil and/or plant matrices, the experiment was performed with the radiolabelled compound, having a specific activity of 65 kBq/mg (1.756 $\mu\text{Ci}/\text{mg}$) and radiochemical purity of > 99% (determined by HPLC and TLC). The compound was uniformly labelled in fluorophenyl ring. Its structural formula, together with the radiolabelling position indicated by an asterisk, is presented below on figure B.8.3.1._CA-1.

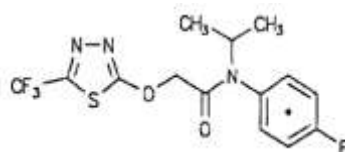


Figure B.8.3.1._CA-1: The structural formula of the test compound – [Phenyl-U-¹⁴C] Flufenacet, with radiolabelling positions is indicated by an asterisk;
(copied from the study report).

In the experiment it was used as a formulated product – FOE 5043 60 WP, prepared according to the recipe for the formulation FOE 5043 60 WG (for purpose of the present experiment the preparation of the formulation was terminated before the last stage – preparation of the wettable granules – WG). The content of the active substance in that formulation was 60% or 600 g/kg.

Due to the fact that when the experiment was carried out it was not permitted to use the radioactive isotopes in field trials (for reasons of radiation protection and health physics), each trial was performed in a plant container arrangement, presented below on figure B.8.3.1._CA-2.

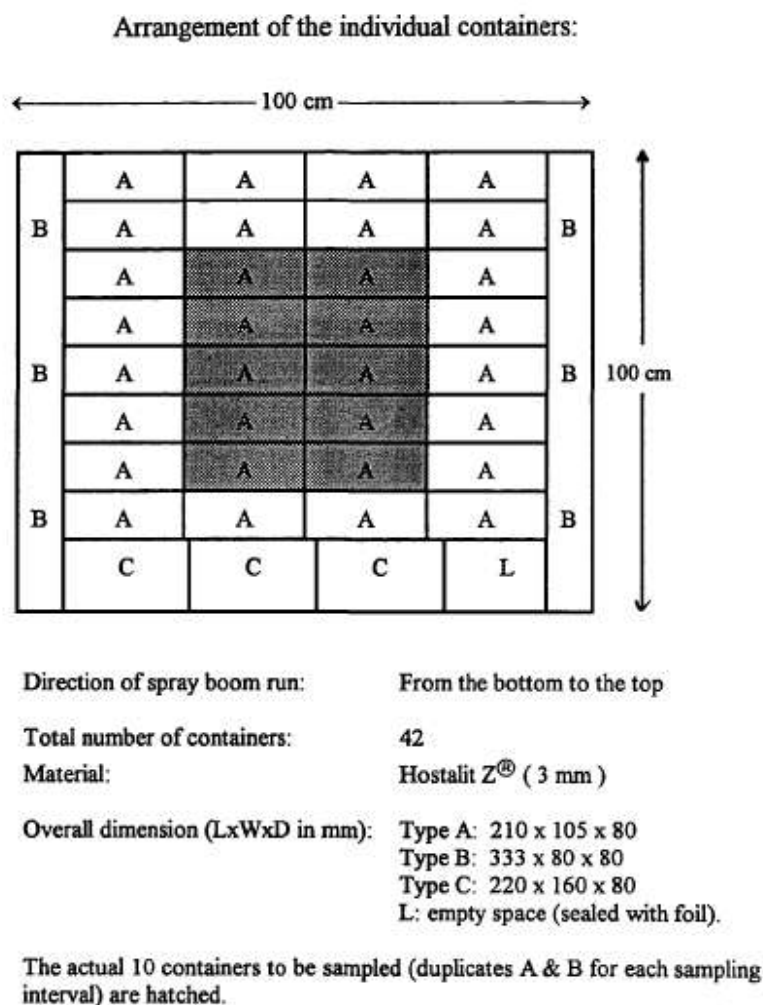


Figure B.8.3.1._CA-2: The scheme of the container arrangement used in the experiment; for explanations please refer to the text below (the scheme copied from the study report).

The whole setup consisted of 42 PVC vessels, of which 10 central, marked A and shaded gray on the scheme above, made the sampling area. They were surrounded by other 32 vessels simulating a close field situation to minimise the marginal effect. The vessels were fixed on a pallet and the whole set surrounded with a steel collar before being transferred to the test site.

Each vessel was filled with the test soil characterised below in the table B.8.3.1._CA-1.

Table B.8.3.1._CA-1: The characteristic of the test soil used in the experiment.

Parameter	Soil:
Soil origin	<i>Langenfeld, Rheinland, Germany</i>
Soil type USDA (as reported in the study)	Loamy sand
Soil type USDA (calculated by RMS)	US Loamy sand
Particle size distribution	Sand [%]
	77.3
	Silt [%]
	17.5
	Clay [%]
	5.2
pH (measured in CaCl ₂)	5.9
Organic matter content (OM) [%]	2.37
Organic carbon content (C _{org}) [%]	1.38
Cation Exchange Capacity – CEC [mEq/100g]	5.00
Bulk density [g/cm ³]	2.57
Maximum Water Holding Capacity [g/100 soil, dry weight]	29.41
Available nutrients	Dithionite sol. Fe [mg/kg d. w.]
	3550
	CaCO ₃ [%]
	<0.1
	N [mg/kg soil, d. w.]
	90
	total P [mg/kg soil, d. w.]
	670

The test formulation was applied to the bare surface of the test soil as a spray liquid, using automated application device consisting of a mobile steel frame with a vertically adjustable platform containing the arrangement of the spray nozzles attached to it. The spray boom contained 3 nozzles, each 50-cm apart from the others. During application it was moved at the constant speed 6 km/h, covering the spraying distance of 100 cm plus 10-cm distances for acceleration and stopping (120 cm in total). The spray liquid, prepared by dissolving the appropriate amount of the test formulation in 200 mL of the Milli-Q water, was administered from a tank, in which it was constantly mixed using magnetic stirrer, at a constant rate, using pressurised air. The amount of the application solution in the tank of the application device was 150 mL.

The application rate was calculated using the following assumptions:

- the formulation was intended to be used as a pre-emergence herbicide in maize;
- the application rate was in range 375 – 750 g Flufenacet/ha, depending on the soil characteristic, and OC content in particular.

Using the soil characteristic presented below in the table B.8.3.1._CA-1 it was determined to be 600 g Flufenacet/ha, corresponding to 1000 g formulation/ha, administered as a spray liquid at rate 340 L/ha.

The test compound was applied to the bare soil surface, being in a stage “shortly after seedbed preparation”, three times during the experiment: on 25th May 1994 at 10:00 am CET – 1st trial, on 26th May 1994 at 10:40 am CET – 2nd trial, and on 30th May 1994 at 10:00 am CET – 3rd trial. The characterisation of the spray liquid used in each trial is presented in the table B.8.3.1._CA-2.

Table B.8.3.1._CA-2: The characteristic of the application solution used in each trial.

Trial No.	Application time	Preparation of the spray liquid		Characteristic of the spray liquid		
		Amount of WP formulation [mg]	Amount of Milli-Q water [mL]	Activity [kBq/mL]	Concentration of Flufenacet [mg/mL]	Content of Flufenacet in solution [mg]
1	25/05/1994/10:00	592.3	200	111.98	1.723	344.60
2	26/05/1994/10:40	588.1	200	110.10	1.694	338.80
3	30/05/1994/10:00	459.3	150	118.74	1.827	274.05

The pallets containing the treated vessels were placed on the trial site immediately after treatment and exposed to the field conditions for up to 24 hours..

Each trial lasted for 24 hours after application of the test compound. At pre-designated time points – shortly after application (0-hours sample), 1 hour, 3 hours, 6 hours and 24 hours after application two containers from the sampling area (see figure B.8.3.1._CA-2) were removed from the set and immediately processed. That was done in the following way: the top 2-3 cm layer of soil was collected using a spoon and extracted with two 300-mL portions of MeOH. The extracts were combined, filtered through paper filters and analysed for radioactivity

content and nature. The surfaces of the rims of containers were cleaned with soft wipe paper, extracted then with MeOH. The extracts were analysed for radioactivity content by LSC.

The soil samples after extraction were analysed for radioactivity content. For that purpose the whole samples were air-dried, homogenised by grinding them and their subsamples combusted. The $^{14}\text{CO}_2$ formed during combustion was absorbed in Oxysolv C 400.

In a similar way were processed the residues contained on the paper filters and those used to clean the rims of the test vessels.

The whole processing procedure was performed immediately after sampling of the test vessels in order to minimise volatilisation effects during sampling and processing.

All samples were analysed for the radioactivity content by LSC, using Rackbeta 1219 Spectral, LS6000LL or LS6500 liquid scintillation counter.

Additionally organic extracts were analysed by TLC. The analysis was performed on silica gel 60 F₂₅₄, 20 x 20 cm., 0.25-mm thick TLC plates. The plates were developed in $\text{CHCl}_3/\text{CH}_3\text{COOC}_2\text{H}_5$ 3:1 solvent system. The detection was carried out using Bio-Imaging Analyser BAS 2000.

Additionally the HPLC method was used to check the radiochemical purity of the active substance in the formulation as well as its purity and content in the application solution.

During the whole experiment for each trial the weather data were continuously monitored. That was done within the 3 metres from the container arrangement at the soil level and at the level of 2 metres above the ground. The parameters recorded at the soil level (~0.5 m. above the ground) were:

- air temperature;
- air humidity;
- wind velocity (~1m. apart from the containers).

The parameters recorded at the level of 2 m. above the ground were:

- prevailing wind direction;
- wind velocity;
- duration of sunshine;
- intensity of sunshine.

Additional weather data were obtained either from the weather station located at the trial site (precipitation) or from the weather bulletins presented by local media (Kölner-Stadtanzeiger).

Results and their discussion:

The key results of the determination of the weather conditions during each trial are presented below in the table B.8.3.1_CA-3. The detailed results of that determination, recorded for each trial, are presented in a graphical form on figures B.8.3.1_CA-3 – B.8.3.1_CA-5.

Table B.8.3.1_CA-3: The weather conditions recorded for each trial.

Weather parameter		Results obtained for the trial (trial number / duration period):		
		No. 1/ 25 – 26. 05. 1994	No.2/ 26 – 27. 05. 1994	No 3/ 30 – 31. 05. 1994
Sunshine	Duration [h]	0 ¹⁾	0 ¹⁾	10.67
	Energy [kJ/cm ³]	0 ²⁾	0 ²⁾	25.513
Precipitation [mm]		6.2 ³⁾	0.0 ³⁾	0.03)
Air temperature [°C]	Minimum	10.5	8.3	5.6
	Maximum	16.0	14.2	16.7
Relative air humidity [%]	Minimum	83.7	65.0	38.8
	Maximum	97.9	96.5	98.0
Wind speed at 0.5 m above the ground [m/s.]	Minimum	0.0	0.3	0.0
	Maximum	1.7	2.3	1.5
	Mean	0.6	1.0	0.6
Wind speed at 2.0 m above the ground [m/s.]	Minimum	0.0	0.0	0.0
	Maximum	2.1	1.9	1.3
	Mean	0.7	0.8	0.5

Footnotes to the table:

- 1) During that period, according to the weather data provide in the study report the sky on the area where the experiment was performed was partly or totally clouded;
- 2) The value was lower than the detection limit of the sensor;
- 3) In the study report it was stated that to protect the containers from the rainfall during the night or when the rain was forecasted a stainless steel roof was installed 1 metre above the soil surface.

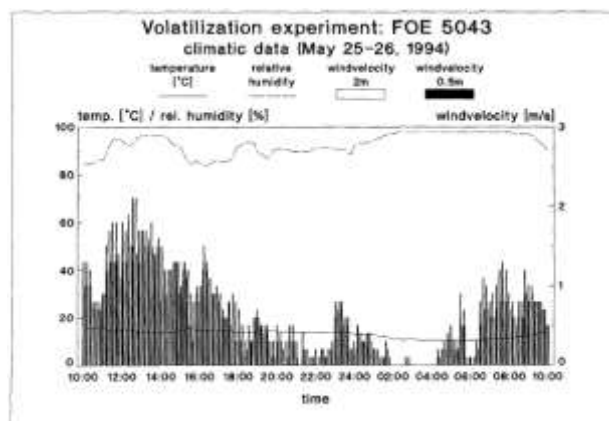


Figure B.8.3.1_CA-3: The detailed weather conditions – temperature, relative humidity and the windspeed, recorded for the trial No. 1 (copied from the study report).

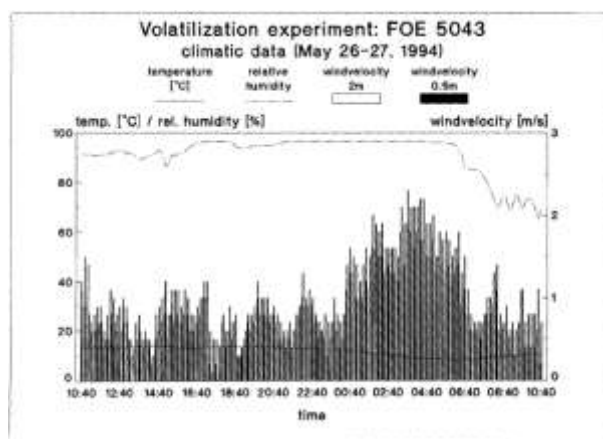


Figure B.8.3.1_CA-4: The detailed weather conditions – temperature, relative humidity and the windspeed, recorded for the trial No. 2 (copied from the study report).

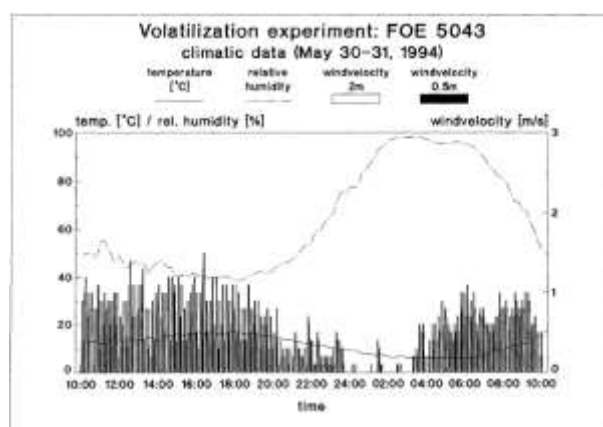


Figure B.8.3.1_CA-5: The detailed weather conditions – temperature, relative humidity and the windspeed, recorded for the trial No. 3 (copied from the study report).

The data concerning the application rates used in each trial are presented below in the table B.8.3.1._CA-4. The values are the averages of the two replicates.

Table B.8.3.1._CA-4: The data on the application rate of the test compound for each trial.

Trial No.	Radioactivity in application solution [kBq/mL]	Data on application			Radioactivity recovered immediately after application (0 hours after application)		
		Volume of the application solution sprayed [mL/m ²]	Amount of the test compound applied		from soil in [% AR]	from rims of the test vessels in [% AR]	Total radioactivity recovered in [% AR]
			in [mg/m ²]	in [g/ha]			
1	112.0	31.8	54.8	548	92.7	7.3	100.0
2	110.1	34.8	59.0	590	94.3	5.7	100.0
3	118.7	37.1	67.7	677	92.7	7.3	100.0
Mean	113.6	34.6	60.5	605	93.2	6.8	100.0

The results showed relatively good reproducibility of the application in all three trials, with $\geq 93\%$ of the applied radioactivity reaching the soil surface.

The results of the quantification of radioactivity in each trial in function of time are presented below in the table B.8.3.1._CA-5. The results are the mean of the two replicates. The radioactivity characterised in the table as “not recovered” was attributed to be lost due to the volatilisation. That term was applied also to the part of radioactivity bound to the soil particles and removed with them from the sampling area as a result of the wind erosion.

Table B.8.3.1._CA-5: The distribution of the radioactivity in the test systems during each trial as a function of time.

Trial No.	Radioactivity in the test system		The exposure time under field conditions				
			0 hours	1 hour	3 hours	6 hours	24 hours
1	Recovered [%AR]	in soil, extracted	72.10	64.46	67.60	63.73	60.40
		in soil, as NER fraction	26.91	19.06	16.97	23.58	26.30
		remainder	0.99	0.96	1.11	1.00	0.92
		Total recovered	100.00	84.48	85.68	88.31	87.62
	Not recovered (lost) [%AR]		0.00	15.52	14.32	11.69	12.38
2	Recovered [%AR]	in soil, extracted	64.70	58.61	50.82	42.34	42.51
		in soil, as NER fraction	34.30	29.39	23.71	28.74	27.58
		remainder	1.01	0.88	0.84	0.67	0.74
		Total recovered	100.01	88.88	75.37	71.75	70.83
	Not recovered (lost) [%AR]		0.00	11.12	24.63	28.25	29.17
3	Recovered [%AR]	in soil, extracted	72.16	66.10	65.02	58.25	57.59
		in soil, as NER fraction	26.81	25.25	28.41	33.77	33.88
		remainder	1.03	0.74	0.66	0.57	0.53
		Total recovered	100.00	92.09	94.09	92.55	92.10
	Not recovered (lost) [%AR]		0.00	7.91	5.92	7.45	7.90
Mean	Recovered [%AR]	in soil, extracted	69.65	63.06	61.14	54.77	53.53
		in soil, as NER fraction	29.34	24.57	23.03	28.70	29.26
		remainder	1.01	0.86	0.87	0.73	0.53
		Total recovered	100.00	88.49	85.04	84.20	83.52
	Not recovered (lost) [%AR]		0.00	11.51	14.96	15.80	16.48

The results showed that, depending on the trial, 70.83 – 92.10% AR, remained in the test system after 24 hours. The amount of radioactivity lost from the system after 24 hours was in range 7.90 – 29.17% AR, being highest – 29.17% AR, in the trial No. 2 and lowest – 7.90 % AR, in the trial No. 3. On average the amount of radioactivity recovered from soil, as extractable residues and the remainder fraction, was 83.52% AR while the amount lost from the test system after 24 hours due to volatilisation was 16.48% AR.

The results obtained in the trials No. 1. and No. 3 were considered by the Applicant to be similar, with the volatilisation on the level of 12.38% of the applied dose after 24 hours in the trial No. 1 and 7.90% of the applied dose in the trial No. 3. In case of the trial No. 3, the level of volatilisation was significantly higher – 29.17% of the applied dose after 24 hours. That phenomenon cannot however be explained by unfavourable weather

conditions, what indicated the Applicant. According to the Applicant, the analysis of the kinetics of volatilisation showed that it was the fastest during the 1st hour after application and after that time it slowed down. RMS however noticed that in case of the trial No. 2 the significant losses due to volatilisation occurred not within the 1st hour of the experiment, but within its first three hours, after what the process slowed down.

It shall be also indicated that while in case of the trials No. 2 and No. 3 a clear trend was observed – substantial initial volatilisation after first 1-3 hours and after that period the amount of radioactivity lost from the system remained on relatively stable level, in case of the trial No. 1 significant fluctuations were observed – the amount of radioactivity not recovered in samples taken 1 and 3 hours after treatment were higher than the levels of lost radioactivity recorded at later time points. The Applicant did not provide a satisfactory explanation of that phenomenon.

The radioactivity recovered from the test vessels was predominantly in the extractable fraction, although its significant portion – 16.97 – 26.91% AR in case of trial No. 1, 23.71 – 34.30% AR in case of the trial No. 2 and 25.25 – 33.88% AR in case of the trial No. 3, formed a non-extractable fraction. The level of that NER fraction in each trial was relatively stable throughout the whole exposure period. The explanation of that phenomenon was not provided, but in RMS's opinion that may be related to the extraction procedure, very mild one, which was not developed with aim to do the proper profiling of Flufenacet and its degradation and/or transformation products in the test soil.

It cannot be also excluded, because only the top 2 – 3-cm layer of the soil in each sampled vessel was analysed, that the losses may partly be attributed to the migration below that layer, although that process does not seem to be very significant, taking into account the study duration and the fact that the container arrangements were protected from the precipitation.

The further qualitative examination of the radioactivity extracted from soil, performed by means of TLC, showed that it consisted predominantly, if not solely, of Flufenacet. The exemplary TLC chromatograms, conforming that statement, are presented below on figure B.8.3.1._CA-6.

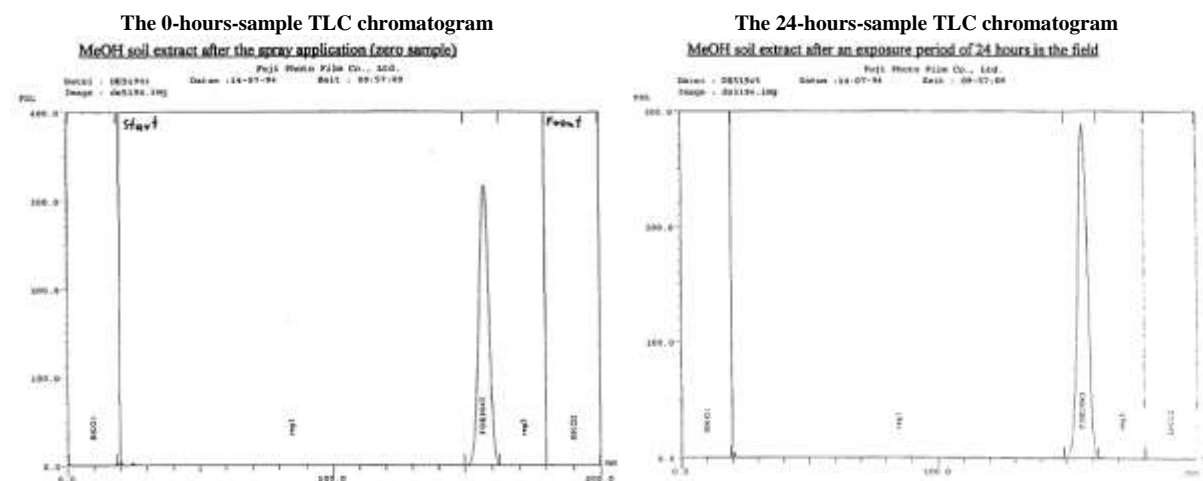
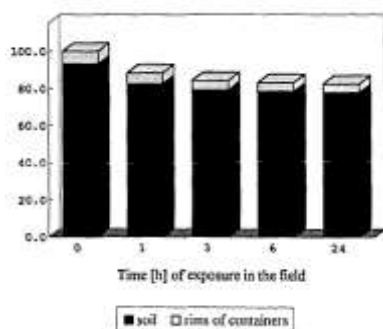


Figure B.8.3.1._CA-6: The graphical results of the qualitative examination of the soil extracts – the exemplary TLC chromatograms (copied from the study report).

The graphical analysis of the averaged results obtained in the study – the mean results of the three trials, are presented below on figure B.8.3.1._CA-7. The left-hand graph shows the recovery levels of radioactivity from soil and rims of containers in function of time and the right-hand graph the trend line for the total radioactivity recovery in the function of time. When reversed, that line would represent the trend line for volatilisation from soil.

The recoveries of radioactivity from the test vessels in function of time



The trend line showing the trend in change of the recovery level over the period of 24 hours

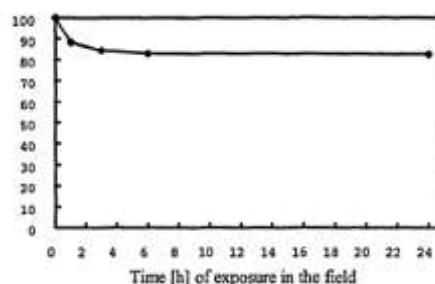


Figure B.8.3.1._CA-7: The graphical results of the experiment (copied from the study report).

Conclusions of the study:

The results of the experiment showed that the level of volatilisation of the residues of Flufenacet (active substance and its degradation products) from the bare soil surface within 24 hours after application of that compound would be on average 16.5% of the applied dose, ranging from ~8% to ~29% of the applied amount. The process was demonstrated to be most intensive within first one to three hours after application. After that time volatilisation was low or even negligible.

On that basis it was stated that volatilisation of Flufenacet would be low and therefore the compound is expected to pose a low to negligible threat to the atmosphere, as well as is not expected to cause a secondary pollution due to the wet or dry deposition from air.

Study 2:

Report: Hellpointner E., (1995): "Calculation of the Chemical Lifetime of Thiaflumide (FOE 5043) I the Troposphere."; Bayer AG, Crop Protection-Development, Institute for Metabolism Research and Residue Analysis, D-51368 Leverkusen, Germany; Report No. PF-4069 (HPO-123); 07 July 1995; study reference number M-002236-01-1.

Guidelines: The study was performed to comply with the following Guidelines:

- BBA Guidelines for Testing of Plant Protection Products in Registration Procedure, Part IV, 6-1 (July 1990) entitled "Determination of the volatilization and the fate of plant protectants in the air".

GLP: No, not required – model calculations;

RMS comments: The study had been evaluated for the previous authorisation of Flufenacet in the EU, by its inclusion into the Annex I of the Directive 91/414/EEC. Its summary can be found under the point B.7.7.2., in section B.7 of the Annex B to the Monograph prepared by the RMS – France, for Flufenacet. Evaluated for the purpose of the present assessment it was found acceptable and is summarised below.

Summary:

The aim of the study was to determine the half-life of Flufenacet in air when subjected to the reaction of photochemical degradation in presence of the $\bullet\text{OH}$ radicals. The assessment was performed using the calculation procedure developed by Atkinson. The calculations were carried out using AOPWin ver. 1.55a tool. They were performed for 12-hours long day and assuming the concentration of the $\bullet\text{OH}$ radicals equal to $1.5 \text{ E}6$ [radicals/ cm^3]. The results of the calculations – the report generated by the modelling tool, are presented below on figure B.8.3.1._CA-8. On their basis it was stated that the calculated by AOPWin overall rate constant was $27.2547 \text{ E-12} [\text{cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}]$. The calculated on that basis for Flufenacet in air, assuming 12-hours

lasting day and the concentration of the •OH radicals of $1.5 \text{ E}6 \text{ [radicals/cm}^3\text{]}$, $t_{1/2} = 4.7 \text{ hours}$, what corresponded to the chemical lifetime of Flufenacet in air $\text{DT}_{50} = 6.8 \text{ hours}$. On that basis it may be stated that Flufenacet will not be persistent in air, with $\text{DT}_{50} < 2 \text{ days}$.

```

SMILES : n1c(C(F)(F)(F))sc(OCC(-O)N(C(C)(C))c2ccc(F)cc2)n1
CHEM : FOE 5043
MOL FOR: C14 H13 F4 N3 O2 S1
MOL WT : 363.33

----- SUMMARY: HYDROXYL RADICALS -----
**Hydrogen Abstraction      = 11.9425 E-12 cm3/molecule-sec
**Reaction with N, S and -OH = 11.8000 E-12 cm3/molecule-sec
Addition to Triple Bonds    = 0.0000 E-12 cm3/molecule-sec
Addition to Olefinic Bonds  = 0.0000 E-12 cm3/molecule-sec
**Addition to Aromatic Rings = 3.5122 E-12 cm3/molecule-sec
Addition to Fused Rings     = 0.0000 E-12 cm3/molecule-sec

=> OVERALL OH Rate Constant = 27.2547 E-12 cm3/molecule-sec
=> HALF-LIFE                = 0.392 Days (12-hr day; 1.5E6 OH/cm3)
=> HALF-LIFE                = 4.709 Hrs
** Designates Estimation(s) Using ASSUMED Value(s)

----- SUMMARY: OZONE REACTION -----
***** NO OZONE REACTION ESTIMATION *****
(ONLY Olefins and Acetylenes are Estimated)
Experimental Database: NO Structure Matches

-----
Hydrogen Abstraction Calculation: (ASSUMED Values designated by: **)
Kaac      = 0.838 F(-C(=O)-)F(-O-)-0.838(0.760)(6.100)= 3.885
Ktert     = 1.83 F(-CH3)F(-CH3)F(-N-C(=O)-) = 1.83(1.000)(1.000)(4.200) = 7.686
Kprim     = 0.144 F(>CH-) = 0.144(1.290) = 0.186
Kprim     = 0.144 F(>CH-) = 0.144(1.290) = 0.186
H Abstraction TOTAL = 11.942 E-12 cm3/molecule-sec

Reaction Rates With Nitrogen, Sulfur and -OH: (ASSUMED Values designated by: **)
K(-NC(=O)- **) = 11.800 E-12 cm3/molecule-sec

OH Addition to Aromatic Rings Calculation: (ASSUMED Values designated by: **)
Most negative Es+ = 0.000
Log Kar = -12.1549 - 1.35(Es+) cm3/molecule-sec, where -12.1549 is the estimated parent value for
thiadiazole or thiazotriazole Ring #1 Kar = 0.700 E-12 cm3/molecule-sec
Es+ = sp+(-N= **) + sm+(-F) + = 0.502
Es+ = sm+(-N= **) + sp+(-F) + = -0.103
Es+ = sm+(-N= **) + sp+(-F) + = -0.103
Es+ = sp+(-N= **) + sm+(-F) + = 0.502
Most negative Es+ = -0.103
Log Kar = -11.69 - 1.35(Es+) cm3/molecule-sec, Ring #2 Kar = 2.8122 E-12 cm3/molecule-sec
TOTAL Kar = 3.5122 E-12 cm3/molecule-sec

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Figure B.8.3.1._CA-8: The report of the calculations generated by the modelling tool – AOPWin ver. 1.55a (copied from the study report).

Conclusions of the study:

The model assessment of the persistence of Flufenacet in air showed that the compound would be short-living in that compartment, with the half-life, calculated assuming 12-hours lasting day and the concentration of the •OH radicals of $1.5 \text{ E}6 \text{ [radicals/cm}^3\text{]}$, $t_{1/2} = 4.7 \text{ hours}$, what corresponded to the chemical lifetime of Flufenacet in air $\text{DT}_{50} = 6.8 \text{ hours}$. That value is significantly shorter than the $\text{DT}_{50} = 2 \text{ days}$, what indicates that Flufenacet, even in case of reaching the atmosphere in significant amounts, would pose a serious threat to that compartment. It would also not be prone to medium- or long-range transport in that compartment and therefore it would not pose a threat of secondary pollution resulting from the wet and dry deposition from the atmosphere.

The next four summaries present the results of the determination of the persistence in air of the four major degradation products of Flufenacet identified, on the basis of the analysis of their physico-chemical properties, as semivolatile or volatile and for that reason posing a potential threat to the air compartment – FOE Methylsulfone (semi-volatile compound), FOE Methylsulfide (semi-volatile compound) FOE Thiadone (volatile compound and Trifluoroacetic acid (TFA) – highly volatile compound when not dissociated (that is based on the reported in the literature for that compound $V_p = 0.1446 \text{ atm}$. corresponding to $V_p = 14651.595 \text{ Pa}$). The results of that

assessment, performed using the approach developed by Atkinson, are presented individually for each compound in *Studies 3 – 6*.

Study 3:

Report: RMS (2016): “The determination of the persistence in air of FOE Methylsulfone – the major soil degradation product of Flufenacet, using Atkinson’s method and EPISuite modelling tool”; RMS’s internal report;

Guidelines: not applicable.

GLP: No, not applicable (modelling exercise);

RMS comments: not applicable

Summary:

The aim of the study was to determine the half-life of FOE Methylsulfone – the major soil degradation product of Flufenacet, in air when subjected to the reaction of photochemical degradation in presence of the •OH radicals. The assessment was performed using the calculation procedure developed by Atkinson and the AOPWin ver. 1.92, a part of EPISuite 4.1 modelling tool.

The estimation was performed for the following SMILES code created for FOE Methylsulfone:

c1c(F)ccc(N(C(C)(C))C(=O)CS(=O)(=O)C)c1

The calculations were performed for 12-hours long day and assuming the concentration of the •OH radicals equal to 1.5 E6 [radicals/cm³]. The results of the calculations – the report generated by the modelling tool, are presented below on figure B.8.3.1._CA-9.

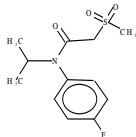
<p>Simulated compound: FOE Methylsulfone</p>	<p>Structural formula:</p> 
<p>Obtained results:</p> <p>SMILES : <chem>c1c(F)ccc(N(C(C)(C))C(=O)CS(=O)(=O)C)c1</chem> CHEM : MOL FOR: C12 H16 F1 N1 O3 S1 MOL WT : 273.32</p> <p>----- SUMMARY (AOP v1.92): HYDROXYL RADICALS (25 deg C) -----</p> <p>**Hydrogen Abstraction = 14.8133 E-12 cm3/molecule-sec Reaction with N, S and -OH = 0.0000 E-12 cm3/molecule-sec Addition to Triple Bonds = 0.0000 E-12 cm3/molecule-sec Addition to Olefinic Bonds = 0.0000 E-12 cm3/molecule-sec **Addition to Aromatic Rings = 4.1910 E-12 cm3/molecule-sec Addition to Fused Rings = 0.0000 E-12 cm3/molecule-sec</p> <p>OVERALL OH Rate Constant = 19.0043 E-12 cm3/molecule-sec HALF-LIFE = 0.563 Days (12-hr day; 1.5E6 OH/cm3) HALF-LIFE = 6.754 Hrs</p> <p>..... ** Designates Estimation(s) Using ASSUMED Value(s) ----- SUMMARY (AOP v1.91): OZONE REACTION (25 deg C) -----</p> <p>***** NO OZONE REACTION ESTIMATION ***** (ONLY Olefins and Acetylenes are Estimated)</p> <p>Experimental Database: NO Structure Matches</p>	

Figure B.8.3.1._CA-9: The report of the calculations generated by the modelling tool – AOPWin ver. 1.92.

On their basis it was stated that the calculated by AOPWin overall rate constant was 19.0043 E-12 [cm³ • molecule⁻¹ • s⁻¹]. The calculated on that basis for FOE Methylsulfone in air, assuming

12-hours lasting day and the concentration of the $\bullet\text{OH}$ radicals of $1.5 \text{ E6} [\text{radicals}/\text{cm}^3]$, $t_{1/2} = \mathbf{6.754 \text{ hours}}$, what corresponded to the chemical lifetime of Flufenacet in air $\mathbf{DT_{50} = 0.563 \text{ days}}$. On that basis it may be stated that FOE Methylsulfone will not be persistent in air, with $\text{DT}_{50} < 2 \text{ days}$.

Conclusions of the study:

The model assessment of the persistence of FOE Methylsulfone in air showed that the compound would be short-living in that compartment, with the half-life, calculated assuming 12-hours lasting day and the concentration of the $\bullet\text{OH}$ radicals of $1.5 \text{ E6} [\text{radicals}/\text{cm}^3]$, $t_{1/2} = \mathbf{6.754 \text{ hours}}$, what corresponded to the chemical lifetime of FOE Methylsulfone in air $\mathbf{DT_{50} = 0.563 \text{ days}}$. That value is significantly shorter than the $\text{DT}_{50} = 2 \text{ days}$, what indicates that FOE Methylsulfone, even in case of reaching the atmosphere in significant amounts, would pose a serious threat to that compartment. It would also not be prone to medium- or long-range transport in that compartment and therefore it would not pose a threat of secondary pollution resulting from the wet and dry deposition from the atmosphere.

Study 4:

Report: RMS (2016): “The determination of the persistence in air of FOE Methylsulfide – the major aquatic degradation product of Flufenacet, using Atkinson’s method and EPISuite modelling tool”; RMS’s internal report;

Guidelines: not applicable.

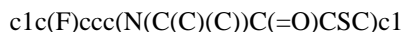
GLP: No, not applicable (modelling exercise);

RMS comments: not applicable

Summary:

The aim of the study was to determine the half-life of FOE Methylsulfide – the major aquatic degradation product of Flufenacet, in air when subjected to the reaction of photochemical degradation in presence of the $\bullet\text{OH}$ radicals. The assessment was performed using the calculation procedure developed by Atkinson and the AOPWin ver. 1.92, a part of EPISuite 4.1 modelling tool.

The estimation was performed for the following SMILES code created for FOE Methylsulfide:



The calculations were performed for 12-hours long day and assuming the concentration of the $\bullet\text{OH}$ radicals equal to $1.5 \text{ E6} [\text{radicals}/\text{cm}^3]$. The results of the calculations – the report generated by the modelling tool, are presented below on figure B.8.3.1._CA-10.

On their basis it was stated that the calculated by AOPWin overall rate constant was $\mathbf{20.7043 \text{ E-12} [\text{cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}]}$. The calculated on that basis for FOE Methylsulfide in air, assuming 12-hours lasting day and the concentration of the $\bullet\text{OH}$ radicals of $1.5 \text{ E6} [\text{radicals}/\text{cm}^3]$, $t_{1/2} = \mathbf{6.199 \text{ hours}}$, what corresponded to the chemical lifetime of FOE Methylsulfide in air $\mathbf{DT_{50} = 0.517 \text{ days}}$. On that basis it may be stated that FOE Methylsulfide will not be persistent in air, with $\text{DT}_{50} < 2 \text{ days}$.

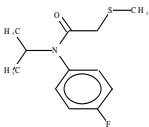
<p>Simulated compound: FOE Methylsulfidee</p>	<p>Structural formula:</p> 
<p>Obtained results:</p> <p>SMILES : <chem>c1c(F)ccc(N(C(C)(C))C(=O)CSC)c1</chem> CHEM : MOL FOR: C12 H16 F1 N1 O1 S1 MOL WT : 241.33</p> <p>----- SUMMARY (AOP v1.92): HYDROXYL RADICALS (25 deg C) -----</p> <p>Hydrogen Abstraction = 14.8133 E-12 cm3/molecule-sec Reaction with N, S and -OH = 1.7000 E-12 cm3/molecule-sec Addition to Triple Bonds = 0.0000 E-12 cm3/molecule-sec Addition to Olefinic Bonds = 0.0000 E-12 cm3/molecule-sec **Addition to Aromatic Rings = 4.1910 E-12 cm3/molecule-sec Addition to Fused Rings = 0.0000 E-12 cm3/molecule-sec</p> <p>OVERALL OH Rate Constant = 20.7043 E-12 cm3/molecule-sec HALF-LIFE = 0.517 Days (12-hr day; 1.5E6 OH/cm3) HALF-LIFE = 6.199 Hrs</p> <p>..... ** Designates Estimation(s) Using ASSUMED Value(s) ----- SUMMARY (AOP v1.91): OZONE REACTION (25 deg C) -----</p> <p>***** NO OZONE REACTION ESTIMATION ***** (ONLY Olefins and Acetylenes are Estimated)</p> <p>NOTE: Reaction with Nitrate Radicals May Be Important!</p> <p>Experimental Database: NO Structure Matches</p>	

Figure B.8.3.1._CA-10: The report of the calculations generated by the modelling tool – AOPWin ver. 1.92.

Conclusions of the study:

The model assessment of the persistence of FOE Methylsulfide in air showed that the compound would be short-living in that compartment, with the half-life, calculated assuming 12-hours lasting day and the concentration of the •OH radicals of 1.5 E6 [radicals/cm³], $t_{1/2}$ = **6.199 hours**, what corresponded to the chemical lifetime of FOE Methylsulfide in air **DT₅₀ = 0.517 days**. That value is significantly shorter than the DT₅₀ = 2 days, what indicates that FOE Methylsulfide, even in case of reaching the atmosphere in significant amounts, would pose a serious threat to that compartment. It would also not be prone to medium- or long-range transport in that compartment and therefore it would not pose a threat of secondary pollution resulting from the wet and dry deposition from the atmosphere.

Study 5:

Report: RMS (2016): “The determination of the persistence in air of FOE Thiadone – the major soil and aquatic degradation product of Flufenacet, using Atkinson’s method and EPISuite modelling tool”; RMS’s internal report;

Guidelines: not applicable.

GLP: No, not applicable (modelling exercise);

RMS comments: not applicable

Summary:

The aim of the study was to determine the half-life of FOE Thiadone – the major soil and aquatic degradation product of Flufenacet, in air when subjected to the reaction of photochemical degradation in presence of the •OH

radicals. The assessment was performed using the calculation procedure developed by Atkinson and the AOPWin ver. 1.92, a part of EPISuite 4.1 modelling tool.

The estimation was performed for the following SMILES codes created for FOE Thiadone:



The calculations were performed for 12-hours long day and assuming the concentration of the •OH radicals equal to 1.5 E6 [radicals/cm³]. The results of the calculations – the report generated by the modelling tool, are presented below on figure B.8.3.1._CA-11.

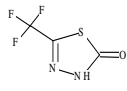
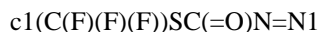
<p>Simulated compound: FOE Thiadone</p>	<p>Structural formula:</p> 
<p>Obtained results:</p> <p>SMILES : <chem>O=C1NN=C(C(F)(F)(F))S1</chem> CHEM : MOL FOR: C3 H1 F3 N2 O1 S1 MOL WT : 170.11</p> <p>----- SUMMARY (AOP v1.92): HYDROXYL RADICALS (25 deg C) -----</p> <p>Hydrogen Abstraction = 0.0000 E-12 cm3/molecule-sec Reaction with N, S and -OH = 0.0000 E-12 cm3/molecule-sec Addition to Triple Bonds = 0.0000 E-12 cm3/molecule-sec Addition to Olefinic Bonds = 0.0000 E-12 cm3/molecule-sec Addition to Aromatic Rings = 0.0000 E-12 cm3/molecule-sec Addition to Fused Rings = 0.0000 E-12 cm3/molecule-sec</p> <p>OVERALL OH Rate Constant = 0.000000 E-12 cm3/molecule-sec HALF-LIFE = -----</p> <p>----- SUMMARY (AOP v1.91): OZONE REACTION (25 deg C) -----</p> <p>***** NO OZONE REACTION ESTIMATION ***** (ONLY Olefins and Acetylenes are Estimated)</p> <p>Experimental Database: NO Structure Matches</p>	

Figure B.8.3.1._CA-11: The report of the calculations generated by the modelling tool – AOPWin ver. 1.92.

For that structure AOPWin modelling tool was not able to calculate the overall rate constant for reaction with hydroxyl radicals, hence the half-life of FOE Thiadone in air. That may indicate that FOE Thiadone when reaching the air compartment will not undergo the photochemical oxidative degradation in air.

Additional estimation was performed for a very similar structure, with the relocated double bond. That estimation was performed for the following SMILES code, representing FOE Thiadone:



The calculations were performed for 12-hours long day and assuming the concentration of the •OH radicals equal to 1.5 E6 [radicals/cm³]. The results of the calculations – the report generated by the modelling tool, are presented below on figure B.8.3.1._CA-12.

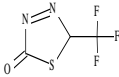
Simulated compound: FOE Thiadone	Structural formula: 
<p>Obtained results:</p> <p>SMILES : C1(C(F)(F)(F))SC(=O)N=N1 CHEM : MOL FOR: C3 H1 F3 N2 O1 S1 MOL WT : 170.11 ----- SUMMARY (AOP v1.92): HYDROXYL RADICALS (25 deg C) ----- **Hydrogen Abstraction = 0.3614 E-12 cm³/molecule-sec Reaction with N, S and -OH = 0.0000 E-12 cm³/molecule-sec Addition to Triple Bonds = 0.0000 E-12 cm³/molecule-sec Addition to Olefinic Bonds = 0.0000 E-12 cm³/molecule-sec Addition to Aromatic Rings = 0.0000 E-12 cm³/molecule-sec Addition to Fused Rings = 0.0000 E-12 cm³/molecule-sec OVERALL OH Rate Constant = 0.3614 E-12 cm³/molecule-sec HALF-LIFE = 29.594 Days (12-hr day; 1.5E6 OH/cm³) ** Designates Estimation(s) Using ASSUMED Value(s) ----- SUMMARY (AOP v1.91): OZONE REACTION (25 deg C) ----- ***** NO OZONE REACTION ESTIMATION ***** (ONLY Olefins and Acetylenes are Estimated)</p> <p>Experimental Database: NO Structure Matches</p>	

Figure B.8.3.1._CA-12: The report of the calculations generated by the modelling tool – AOPWin ver. 1.92.

On their basis it was stated that the calculated by AOPWin overall rate constant was **0.3614 E-12 [cm³ • molecule⁻¹ • s⁻¹]**. The calculated on that basis for FOE Thiadone in air, assuming 12-hours lasting day and the concentration of the •OH radicals of 1.5 E6 [radicals/cm³], **DT₅₀ = 29.594 days**. On that basis it may be stated that FOE Thiadone will be persistent in air, with DT₅₀ > 2 days.

Conclusions of the study:

The model assessment of the persistence of FOE Thiadone in air showed that the compound would be very persistent in air. For the structural formula exactly matching that of FOE Thiadone the results indicated that no reaction with •OH radicals occurred. For the structure that was slightly altered by comparison to that of FOE Thiadone – the double bond was repositioned from C=N to N=N, that reaction was demonstrated to be very slow with the half-life, calculated assuming 12-hours lasting day and the concentration of the •OH radicals of 1.5 E6 [radicals/cm³], **DT₅₀ = 29.594 days**. That value is significantly longer than the DT₅₀ = 2 days. The results therefore indicate that FOE Thiadone in case of reaching the atmosphere in significant amounts, would pose a serious threat to that compartment. It would be prone to medium- or long-range transport in that compartment and therefore it may pose a threat of secondary pollution resulting from the wet and dry deposition from the atmosphere.

Study 6:

Report: RMS (2016): “The determination of the persistence in air of TFA (Trifluoroacetic acid) – the major secondary soil degradation product of Flufenacet, using Atkinson’s method and EPISuite modelling tool”; RMS’s internal report;

Guidelines: not applicable.

GLP: No, not applicable (modelling exercise);

RMS comments: not applicable

Summary:

The aim of the study was to determine the half-life of Trifluoroacetic acid (TFA) – the major soil degradation product of Flufenacet, in air when subjected to the reaction of photochemical degradation in presence of the •OH radicals. The assessment was performed using the calculation procedure developed by Atkinson and the AOPWin ver. 1.92, a part of EPISuite 4.1 modelling tool.

The estimation was performed for the following SMILES code created for TFA:



The calculations were performed for 12-hours long day and assuming the concentration of the •OH radicals equal to 1.5 E6 [radicals/cm³]. The results of the calculations – the report generated by the modelling tool, are presented below on figure B.8.3.1._CA-13.

On their basis it was stated that the calculated by AOPWin overall rate constant was **0.5200 E-12 [cm³ • molecule⁻¹ • s⁻¹]**. The calculated on that basis for TFA in air, assuming 12-hours lasting day and the concentration of the •OH radicals of 1.5 E6 [radicals/cm³], **DT₅₀ = 20.569 days**. On that basis it may be stated that TFA will be persistent in air, with DT₅₀ > 2 days.

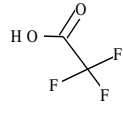
<p>Simulated compound: TFA</p>	<p>Structural formula:</p> 
<p>Obtained results:</p> <p>SMILES : OC(=O)C(F)(F)F CHEM : Trifluoroacetic acid MOL FOR: C2 H1 F3 O2 MOL WT : 114.02</p> <p>----- SUMMARY (AOP v1.92): HYDROXYL RADICALS (25 deg C) -----</p> <p>Hydrogen Abstraction = 0.0000 E-12 cm3/molecule-sec Reaction with N, S and -OH = 0.5200 E-12 cm3/molecule-sec Addition to Triple Bonds = 0.0000 E-12 cm3/molecule-sec Addition to Olefinic Bonds = 0.0000 E-12 cm3/molecule-sec Addition to Aromatic Rings = 0.0000 E-12 cm3/molecule-sec Addition to Fused Rings = 0.0000 E-12 cm3/molecule-sec</p> <p>OVERALL OH Rate Constant = 0.5200 E-12 cm3/molecule-sec HALF-LIFE = 20.569 Days (12-hr day; 1.5E6 OH/cm3)</p> <p>----- SUMMARY (AOP v1.91): OZONE REACTION (25 deg C) -----</p> <p>***** NO OZONE REACTION ESTIMATION ***** (ONLY Olefins and Acetylenes are Estimated)</p> <p>Experimental Database Structure Match: Chem Name : Trifluoroacetic acid CAS Number: 000599-00-8 Exper OH rate constant : 0.12 E-12 cm3/molecule-sec Exper OH Reference: CARR,S ET AL. (1994) Exper Ozone rate constant: --- cm3/molecule-sec Exper NO3 rate constant : --- cm3/molecule-sec</p>	

Figure B.8.3.1._CA-13: The report of the calculations generated by the modelling tool – AOPWin ver. 1.92.

The additional calculations were also performed for the dissociated form of TFA – Trifluoroacetate in form of its sodium salt, using the same assumptions and the same modelling tool. The results of those calculations are presented below on figure B.8.3.1._CA-14. It shall be indicated that for that compound the modelling tool was not able to calculate the overall rate constant for the reaction with the •OH radicals and hence the half-life values for that compound.

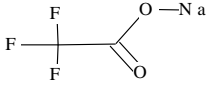
<p>Simulated compound: TFA-Na</p>	<p>Structural formula:</p>  <p style="text-align: right; font-size: small;">TRIFLUOROACETIC ACID SODIUM SALT</p>
<p>Obtained results:</p> <p>SMILES : O([Na])C(=O)C(F)(F)F CHEM : TRIFLUOROACETIC ACID SODIUM SALT MOL FOR: C2 F3 O2 NaI MOL WT : 136.01</p> <p>----- SUMMARY (AOP v1.92): HYDROXYL RADICALS (25 deg C) -----</p> <p>Hydrogen Abstraction = 0.0000 E-12 cm³/molecule-sec Reaction with N, S and -OH = 0.0000 E-12 cm³/molecule-sec Addition to Triple Bonds = 0.0000 E-12 cm³/molecule-sec Addition to Olefinic Bonds = 0.0000 E-12 cm³/molecule-sec Addition to Aromatic Rings = 0.0000 E-12 cm³/molecule-sec Addition to Fused Rings = 0.0000 E-12 cm³/molecule-sec</p> <p>OVERALL OH Rate Constant = 0.000000 E-12 cm³/molecule-sec HALF-LIFE = -----</p> <p>----- SUMMARY (AOP v1.91): OZONE REACTION (25 deg C) -----</p> <p>***** NO OZONE REACTION ESTIMATION ***** (ONLY Olefins and Acetylenes are Estimated)</p> <p>Experimental Database: NO Structure Matches</p>	

Figure B.8.3.1._CA-14: The report of the calculations generated by the modelling tool – AOPWin ver. 1.92.

The results presented above for the acetate clearly indicate that that compound will not undergo degradative any reaction with the •OH radicals, so it would not degrade in the air compartment. It shall be indicated however that trifluoroacetate, unlike its not dissociated counterpart, displays very low vapour pressure so it is not volatile.

Conclusions of the study:

The model assessment of the persistence of TFA in air showed that the compound would be persistent in air, with the half-life, calculated assuming 12-hours lasting day and the concentration of the •OH radicals of 1.5 E6 [radicals/cm³], **DT₅₀ = 20.569 days**. That value is significantly longer than the DT₅₀ = 2 days, what indicates that TFA in case of reaching the atmosphere in significant amounts, would pose a serious threat to that compartment. It may also be prone to medium- or long-range transport in that compartment and therefore it may pose a threat of secondary pollution resulting from the wet and dry deposition from the atmosphere.

The results of the estimation of the persistence in air of the degradation products of Flufenacet that may pose a threat to the atmosphere due to their volatility (being either semivolatile compounds – FOE Methylsulfide and FOE Methylsulfone, or volatile compounds – FOE Thiadone and Trifluoroacetic acid, according to the values of their saturated vapour pressure) showed that neither FOE Methylsulfide nor FOE Methylsulfone, in case they migrate to the atmosphere in substantial amounts, would pose any threat to that compartment due to their low persistence in air.

In case of FOE Thiadone and TFA their high volatility, combined with the determined high persistence in air indicated that the further determination of their fate and behaviour in that environmental compartment was necessary.

In case of FOE Thiadone the Applicant did not submit any data to address that issue. Also the literature search performed by the RMS has not resulted in identification of any papers dealing with the problem.

It shall however be indicated that FOE Thiadone was observed in soil in amounts not surpassing 10%. It was also demonstrated to be quickly degraded in that compartment. Additionally the results of the studies aimed on the examination of soil photolysis of FOE Thiadone showed that the compound would be mineralised to much greater extent that it would evaporate from soil surface (in irradiated samples within 14 days of the experiment only ~5% of the radioactivity applied was recovered as VOC fraction, in the dark control samples that amount was only ~2.5%). Also in the experiments with radiolabelled FOE Thiadone aimed on the determination of its persistence in aerobic soil under laboratory conditions the levels of radioactivity recovered as VOC fraction was low: 2 – 4%AR at the study's end (10 – 14 days after the experiment was initiated) with no more than 5% of the initial amount of FOE Thiadone remaining in soil. **That may indicate, assuming that the VOC fraction is entirely FOE Thiadone, that despite its high vapour pressure the compound would not migrate to atmosphere from soil in amounts that may pose any substantial threat to that compartment. Also not relevant may be considered the volatilisation from plants as the route of exposure, because that compound would probably not be formed as a transformation product of Flufenacet on plant surfaces.**

The only potential route of exposure of air is volatilisation from SW bodies, where FOE Thiadone was demonstrated to be formed as a major degradation product, but at present there is no clear methodology to assess that issue.

In case of TFA the Applicant as well did not submit any relevant data. **However in the documentation submitted for the evaluation it was stated several times that the TFA formed as a degradation product of Flufenacet will be present as Trifluoroacetate – the dissociated form displaying very low volatility potential and as such not posing any substantial risk to the atmosphere. RMS agrees with that statement.**

The literature search performed by the RMS resulted in identification of several scientific papers addressing the issue of behaviour of TFA in the atmosphere, four of which dealt specifically with persistence, transformation mechanisms and mechanisms of elimination of TFA in/from air.

They are summarised below.

The persistence of TFA in atmosphere, by theoretical estimation of its transformation rate constant in reaction with the hydroxyl radicals, was examined in the following study by [Oeberg; 2005]:

Oeberg. T. "A QSAR for the hydroxyl radical reaction rate constant: validation, domain of application, and prediction."; Atmospheric Environment 2005, **39** (12), 2189 – 2200.

In this paper was presented the methodology of determining the theoretical rate constants for the reaction of 743 chemical compounds characterised by names, chemical structures (SMILES codes) and physical properties in the PhysPropDatabase, found among ~25000 listed there. The compounds were selected on the basis of the experimentally determined rate constants for the reaction with the •OH radicals at temperature range 295 – 300 K (corresponds to T = 22 – 27°C). They were used to calibrate and validate developed empirical QSAR model.

The approach was alternative to that developed by Atkinson and used by AOPWin software developed by US EPA, the limitations of which were briefly characterised.

As a next step the set of following molecular descriptors was generated:

- Constitutional descriptors,
- Topological descriptors,
- Walk and path counts,
- Connectivity indices,
- Information indices,
- 2D autocorrelations,
- Edge adjacency indices,
- BCUT descriptors,
- Topological charge indices,

- Eigenvalue-centered fragments,
- Functional group counts,
- Atom-centered fragments.

Most of them were taken from the available literature data.

The correct interpretation of the SMILES codes was validated by comparison of the molecular weights calculated and reported in the data bases.

The analysis of the data and modelling were carried out using ANOVA method (analysis of variance) partial least squares regression method (PLSR). The approach was fully characterised in the paper. The model was fully validated and compared with other approaches used in that area.

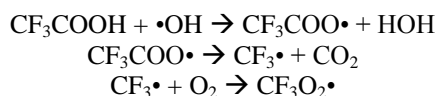
Finally, the list of 152 compounds that are high production volume chemicals (HPVC) with the rate constants of their reaction with the $\bullet\text{OH}$ radicals – k_{OH} and the half-lives in the troposphere. One of the compounds on that list was TFA for which $k_{\text{OH}} = 5.4 \text{ E-14 } [\text{cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}]$ and the half-life 148 days. That value was determined using, most probably, the concentration of the $\bullet\text{OH}$ radicals of $1.0 \text{ E6 } [\text{molecule}/\text{cm}^3]$, but the length of the day was not provided. It shall be indicated that although that value may be considered only supplementary in the current assessment, it confirms the fact that TFA is persistent in the air compartment.

The kinetic of the reaction of TFA with the $\bullet\text{OH}$ radicals was experimentally examined and the results of that examination presented in the following publication:

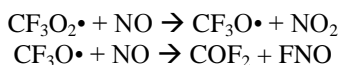
Hurley M. D., Sulbaek Andersen, M. P., Wallington T. J., Ellis D. A., Martin J. W., Mabury S. A., *“Atmospheric Chemistry of Perfluorinated Carboxylic Acids: Reaction with OH Radicals and Atmospheric Lifetimes.”*; Journal of Physical Chemistry, A, 2004, **108** (4), 615 – 620.

The general aim of that study was to determine the kinetics of the reaction of a series of perfluorinated aliphatic carboxylic acids, having a general formula $(\text{F}_3\text{C})_n\text{COOH}$ and containing 1 – 4 $-\text{CF}_3$ groups in the molecule, with the $\bullet\text{OH}$ radicals in 700 Torr and at $T = 296 \pm 2 \text{ K}$ ($\sim 23^\circ\text{C}$). These compounds is an emerging group of pollutants requiring thorough examination for their sources in the atmosphere as well as transformation pathways they are following in that compartment.

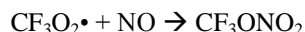
In case of TFA the $\bullet\text{OH}$ -initiated transformation is expected to proceed via the following steps:



The next step was the two-step reaction with the NO molecules leading to the formation of COF_2 and FNO molecules as final transformation products of the photooxidative degradation of TFA. The reactions involved in that process were following:



It was stated that the reaction of $\text{CF}_3\text{O}_2\bullet$ with NO may follow different pattern, which is shown below:



That process however was demonstrated to be a side-reaction, in which only 1.67% of the available $\text{CF}_3\text{O}_2\bullet$ radicals are involved.

The experimental rate constant of the photooxidative degradation of TFA initiated by the $\bullet\text{OH}$ radicals was determined as a relative value, using two reference compounds – C_2H_2 and C_2H_4 .

The initial concentration of CF_3COOH was in range 8-363 mTorr, those of the reference compounds – C_2H_2 and C_2H_4 , 2-10 mTorr, of CH_3ONO and NO (the compounds involved in the atmosphere in process of generating of the $\bullet\text{OH}$ radicals in presence of UV radiation) – 100-232 mTorr and 10-25 mTorr respectively. The reactions were examined in 700 mTorr of air diluent.

It was stated that the factor limiting the rate of photooxidative degradation of TFA, as well as other perfluorinated aliphatic carboxylic acid was their dimerisation, the reaction which is shown below on figure B.8.3.1._CA-14.

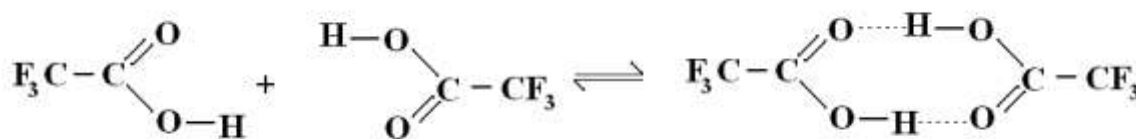
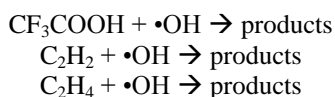


Figure B.8.3.1_CA-15: The reaction of the dimerisation of TFA (after [Hurley *et. al.*; 2004]).

In case of TFA the vapour-phase dimerisation constant was determined to be $K_d = 0.32 \pm 0.03$ [Torr⁻¹] at $T = 298\text{K}$ (corresponding to $\sim 25^\circ\text{C}$). The value was shown to be in good agreement with the results of other studies in the same area.

The rate constant for the reaction of CF_3COOH with the $\bullet\text{OH}$ radicals was determined as relative value to that for the analogous reactions for C_2H_2 and C_2H_4 , assuming the following reactions:



The so determined rate constants were:

$$\begin{aligned}k &= (8.70 \pm 1.44) \text{ E-14 } [\text{cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}], \text{ when relative to the reaction for } \text{C}_2\text{H}_2, \\ k &= (1.00 \pm 0.11) \text{ E-13 } [\text{cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}], \text{ when relative to the reaction for } \text{C}_2\text{H}_4,\end{aligned}$$

When averaged rate constant for the reaction of CF_3COOH with the $\bullet\text{OH}$ radicals was:

$$k = (9.35 \pm 2.08) \text{ E-14 } [\text{cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}]$$

The authors of the publication noted that the determined value was in quite good agreement with results of the other studies. It was also stated that the fact of dimerisation of TFA may not be a factor strongly limiting the reaction – it was suggested that the dimer may be reactive to some degree.

The estimated in that study atmospheric half-life of TFA was approx. 230 days. It was determined using the known atmospheric half-life of CH_3CCl_3 equal to 5.99 years and its rate constant for reaction with $\bullet\text{OH}$ radicals $k = 1.00 \text{ E-14 } [\text{cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}]$.

It was stated that that value was not very sensitive for temperature change, therefore the value determined for $T = 296 \text{ K}$ is also representative for $T = 272 \text{ K}$ – the temperature optimal for such scaling analysis.

The value of atmospheric half-life were indicated to be a global average due to the fact that the concentrations of $\bullet\text{OH}$ radicals vary significantly depending on the location and season.

Finally, the calculated half-life was compared with the rate constants of other processes leading to the removal of TFA from the atmosphere.

In case of TFA, its removal from the atmosphere was estimated to occur at the similar rate as that determined for HNO , with the half-life for the wet deposition equal to 9 days and that for dry deposition of 10-30 days. That makes the reaction of TFA with $\bullet\text{OH}$ radicals of minor importance as the process of the loss of that compound from the air compartment.

The problem of the partition of TFA into water as a mechanism of its removal from the atmosphere was examined in several publications. Probably one of the earliest, basic studies, to which the references were made in numerous publication, including that summarised above, was the following paper:

Bowden D. J., Clegg S. L., Brimblecombe P. “*The Henry’s law constant of Trifluoroacetic acid and its partitioning into liquid water in the atmosphere.*”; *Chemosphere*, 1996, **32** (2), 405 – 420.

The aim of that study was to experimentally determine the Henry’s law constant for Trifluoroacetic acid and on that basis examine the implications for the partitioning of that compound and its removal from the atmosphere.

In the paper the degradation of HCFCs, such as CHCl_2CF_3 , CHClFCF_3 and CH_2FCF_3 , is indicated as one of the main sources of TFA in the air compartment. Additionally other potential sources of that compound, such as degradation of CF_3CHBrCl via CF_3COCl as intermediate, were also named.

The determination of the Henry's law constant for TFA was a multi-stage procedure. Its first step was the determination of the dissociation constant K_a for that compound at $T = 298.15 \text{ K}$ on the basis of the available data. By averaging the results of the several previous studies the authors of the summarised publication derived the $\text{p}K_a = 0.47 \pm 0.1 [\text{mol}/\text{dm}^3]$.

As a next step the equilibrium partial pressure of TFA – $p\text{CF}_3\text{COOH}$ over aqueous solution, in which the known amount of that compound was dissolved, was determined. That was done using the following method:

TFA was removed from above the solution with known concentration of that compound dissolved using the stream of N_2 . The compound present in the gas stream was absorbed in 10 cm^3 of 1.0 M KCl_{aq} solution (unbuffered), the pH of which was then determined. The change of pH of the solution was recorded and related to the amount of TFA in the gas stream.

In order to overcome a problem of strong dissociation of TFA, resulting from its low $\text{p}K_a$ value, strong acid – HBr , was added to the solution to suppress the dissociation of CF_3COOH in it. The amounts of that compound used in the experiment were in range $0.25 - 6.0 \text{ mol/kg}$.

Finally, as a reference, the partial pressures of pure HCl , compound of well known Henry's law constant, over its aqueous solutions were measured.

The measurements of the partial vapour pressure of CF_3COOH over its aqueous solution were performed at three different temperatures: $T = 5^\circ\text{C}$, $T = 25^\circ\text{C}$ and $T = 35^\circ\text{C}$, using three initial concentrations of that compound dissolved – $m\text{CF}_3\text{COOH}_{(\text{T})}$: 0.05 mol/kg (used only for the experiments at $T = 25^\circ\text{C}$ and $T = 35^\circ\text{C}$), 0.15 mol/kg and 0.25 mol/kg .

These values were subsequently used to determine the thermodynamic Henry's law constant – K_H , defined by the following equation:

$$K_H = m\text{CF}_3\text{COOH} \cdot \gamma\text{CF}_3\text{COOH} / f\text{CF}_3\text{COOH}$$

where:

K_H is thermodynamic Henry's law constant,

$m\text{CF}_3\text{COOH}$ is molality of undissociated TFA

$\gamma\text{CF}_3\text{COOH}$ is activity coefficient of undissociated TFA

$f\text{CF}_3\text{COOH}$ is fugacity of TFA, being the equivalent of its partial vapour pressure

When transformed to take into account the total amount of the CF_3COOH dissolved – $m\text{CF}_3\text{COOH}_{(\text{T})}$, the equation takes the following form:

$$p\text{CF}_3\text{COOH} = m\text{CF}_3\text{COOH} \cdot \gamma\text{CF}_3\text{COOH} / [(1 + K_a/m\text{H}^+) \cdot K_H]$$

where:

$p\text{CF}_3\text{COOH}$ is partial vapour pressure of TFA,

$m\text{CF}_3\text{COOH}_{(\text{T})}$ is the total amount of TFA dissolved,

$\gamma\text{CF}_3\text{COOH}$ is activity coefficient of TFA,

K_H is thermodynamic Henry's law constant,

K_a is dissociation constant of TFA.

That equation was used to calculate the K_H value at $T = 298.15 \text{ K}$. Additionally the change of the enthalpy – $\Delta_r H^0$, at the same temperature was calculated. The results are presented below:

$$K_H = 8.95 \text{ E}3 \pm 0.1 \text{ E}3 [\text{mol/kg} \cdot \text{atm}]$$

$$\Delta_r H^0 = -77.6 \pm 0.42 [\text{kJ/mol}]$$

Analysing the obtained results and their implications for the fate and behaviour of TFA in the air compartment the authors made the following statements:

- the Henry's law constant for TFA was similar to the values obtained for CH_3COOH and HCOOH , but its lower dissociation constant results in greater solubility in water; as a result TFA will entirely partition to cloud and fog water, where the liquid water content is $0.05 - 1 \text{ g/m}^3$, and the pH, of which is low;
- more complex would be the situation in case of the atmospheric aerosols displaying the water content of $1\text{E}-5 - 1\text{E}-4 \text{ g/m}^3$; there the partition would depend on the composition of aerosol and the temperature;

- as a result the removal of TFA from atmosphere was expected to occur primarily by means of wet deposition and to much lesser extent by dry deposition.

The problem was also examined, and the results of that examination presented in the following publication:

Kutsuna S., Hori H., "Experimental determination of Henry's law constants of trifluoroacetic acid at 278-298 K."; Atmospheric Environment, 2008, **42** (7), 1399 – 1412.

The aim of the study was to determine the Henry's law constant for Trifluoroacetic acid and the temperature-dependence of that thermodynamical constant. The obtained results were compared with those obtained in the summarised above study by [Bowden *et al.*; 1996].

To do that the partial vapour pressures of TFA over the aqueous solutions having the initial content of that compound in range 0.008 – 0.35 mol/dm³, were determined at three different temperatures – 278.15 K (5°C), 288.15 K (15°C) and 298.15 K (25°C). Additionally the same parameter was determined in solutions containing 0.008 – 0.1 mol/dm³ of TFA and 0.1 – 0.4 mol/dm³ H₂SO₄ at the same temperature range.

The experiment was performed by passing the N₂ stream through the column filled with the aqueous solution of TFA or TFA + H₂SO₄ mixture. The gaseous TFA was captured in two traps filled with 20 mL of 0.1M NaOH. The concentration of TFA in traps, as trifluoroacetate ions, in those solutions, was determined by ion exclusion chromatography. It was subsequently used to calculate the partial vapour pressure values for TFA. The N₂ used to purge the volatilised TFA from the test system was administered at a rate 0.55- 0.57 dm³/min. The concentrations of the not dissociated TFA and trifluoroacetate ions remaining in the solutions were determined by means of IR analysis.

The determined values of the Henry's law constant – K_H , were following:

- at T = 278.15 K, $K_H = 15600 \pm 2800$ [mol/dm³ · atm];
- at T = 288.15 K, $K_H = 9300 \pm 1400$ [mol/dm³ · atm];
- at T = 298.15 K, $K_H = 5800 \pm 700$ [mol/dm³ · atm];

For the T = 298.15 K the corresponding solvation enthalpy for gas-to-water transfer, assuming $K_H = 5780 \pm 30$ [mol/dm³ · atm], was $\Delta H_{\text{sol}} = -34.2 \pm 0.2$ kJ/mol. It was calculated using the van't Hoff equation relating the K_H to the temperature.

It was noticed that the determined in this experiment K_H value for the $\text{pK}_a = 0.47$ was 0.65 of the value reported by [Bowden *et al.*; 1996], but equal to that determined in another study with lower $\text{pK}_a = 0.20$.

As a result it was stated that although the obtained K_H value was very similar to that obtained by [Bowden *et al.*; 1996], the results may indicate that the CF₃COOH may be transported from water at low pH to atmosphere with much less difficulty than previously estimated. Also noticed was low dependence of K_H value on temperature, but the fully satisfying explanation of that fact was not provided.

RMS conclusions:

The presented above results of the determination of the fate and behaviour of TFA in air, based on the literature studies, clearly demonstrate high persistence of that compound in the atmosphere with the DT₅₀ values for the process of photooxidative degradation initiated by the •OH radicals as high as 230 days. The only relevant mechanism of elimination of TFA from that compartment would therefore be, predominantly, wet deposition – with rain or fog with estimated DT₅₀ = approx. 9 days, and, to some extent also by dry deposition, with estimated DT₅₀ = 10-30 days. The identified products of photooxidative degradation of TFA in air initiated by the •OH radicals are COF₂ and FNO. It was also indicated that the dimerisation of TFA may be the factor limiting the rate of degradation of that compound in air in the process of photooxidative degradation initiated by the •OH radicals.

The determination of the Henry's law constant for TFA demonstrated that the compound displayed high affinity towards water, therefore atmospheric water, either in form of clouds or as fog, may be an effective sink for that compound. At the same time however it was postulated that the evaporation of TFA from water phase to air cannot be totally excluded and the process can occur more easily than previously expected.

Conclusions of the assessment:

The examination of the fate and behaviour of Flufenacet in air showed that that compound displayed some tendency for migration to the atmosphere, with the determined average level of volatilisation from soil surface equal to 16.5% of the applied dose (with range of 7.9 – 29.2%), but was not expected to be persistent in that compartment – the determined for the process of the photooxidative degradation initiated by the •OH radicals **DT₅₀ = 6.8 hours**. That value, being significantly shorter than the DT₅₀ = 2 days, indicates that Flufenacet, even in case of reaching the atmosphere in significant amounts, would not pose a serious threat to that compartment. It

would also not be prone to medium- or long-range transport in that compartment and therefore it would not pose a threat of secondary pollution resulting from the wet and dry deposition from the atmosphere.

Of seven major soil, aquatic or soil and aquatic major degradation products of Flufenacet, four were identified as posing potential threat to the atmosphere, being volatile or semivolatile – FOE Methylsulfone, FOE Methylsulfide, FOE Thiadone and Trifluoroacetic acid – TFA. For them was performed the additional estimation of their persistence in air, by determining the DT_{50} values for the process of the photooxidative degradation initiated by the $\bullet OH$ radicals. The calculated for FOE Methylsulfide and FOE Methylsulfone DT_{50} values for that process were **0.517 days** and **0.563 days** respectively, what clearly indicates that even in case of reaching the atmosphere in significant amounts, these compounds would not pose a serious threat to that compartment. They would also not be prone to medium- or long-range transport in that compartment and therefore it would not pose a threat of secondary pollution resulting from the wet and dry deposition from the atmosphere.

The model assessment of the persistence of FOE Thiadone in air showed that the compound would be very persistent in air. For the structural formula exactly matching that of FOE Thiadone the results indicated that no reaction with $\bullet OH$ radicals occurred. For the structure that was slightly altered by comparison to that of FOE Thiadone – the double bond was repositioned from $C=N$ to $N=N$, that reaction was demonstrated to be very slow with the half-life, calculated assuming 12-hours lasting day and the concentration of the $\bullet OH$ radicals of $1.5 E6$ [radicals/cm³], $DT_{50} = 29,594$ days. That value is significantly longer than the $DT_{50} = 2$ days. The results therefore indicate that FOE Thiadone, in case of reaching the atmosphere in significant amounts, would pose a serious threat to that compartment. It would be prone to medium- or long-range transport in that compartment and therefore it may pose a threat of secondary pollution resulting from the wet and dry deposition from the atmosphere.

For that compound RMS was not able to identify any literature data dealing with its the fate and behaviour in air. It shall however be indicated that FOE Thiadone was observed in soil in amounts not surpassing 10%. It was also demonstrated to be quickly degraded in that compartment. Additionally the results of the studies aimed on the examination of soil photolysis of FOE Thiadone showed that the compound would be mineralised to much greater extent that it would evaporate from soil surface (in irradiated samples within 14 days of the experiment only ~5% of the radioactivity applied was recovered as VOC fraction, in the dark control samples that amount was only ~2.5%). Also in the experiments with radiolabelled FOE Thiadone aimed on the determination of its persistence in aerobic soil under laboratory conditions the levels of radioactivity recovered as VOC fraction was low: 2 – 4%AR at the study's end (10 – 14 days after the experiment was initiated) with no more than 5% of the initial amount of FOE Thiadone remaining in soil. That may indicate, assuming that the VOC fraction is entirely FOE Thiadone, that despite its high vapour pressure the compound would not migrate to atmosphere from soil in amounts that may pose any threat to that compartment. Also not relevant may be considered the volatilisation from plants as the route of exposure, because that compound would probably not be formed as a transformation product of Flufenacet on plant surfaces.

The only potential route of exposure of air is volatilisation from SW bodies, where FOE Thiadone was demonstrated to be formed as a major degradation product, but at present there is no clear methodology to assess that issue.

The model assessment of the persistence of TFA in air showed that the compound would be persistent in air, with the half-life, calculated assuming 12-hours lasting day and the concentration of the $\bullet OH$ radicals of $1.5 E6$ [radicals/cm³], $DT_{50} = 20,569$ days. That value is significantly longer than the $DT_{50} = 2$ days, what indicates that TFA in case of reaching the atmosphere in significant amounts, would pose a serious threat to that compartment. It may also be prone to medium- or long-range transport in that compartment and therefore it may pose a threat of secondary pollution resulting from the wet and dry deposition from the atmosphere.

The Applicant did not submit any relevant data enabling the elucidation of the fate and behaviour of TFA in the air compartment. However in the documentation submitted for the evaluation it was stated several times that the TFA formed as a degradation product of Flufenacet will be present as Trifluoroacetate – the dissociated form displaying very low volatility potential and as such not posing any substantial risk to the atmosphere.

The literature search performed by the RMS resulted in identification of several scientific papers addressing the issue of behaviour of TFA in the atmosphere, four of which specifically dealt with persistence, transformation mechanisms and mechanisms of elimination of TFA in/from air. On their basis it was possible to state that TFA clearly demonstrated high persistence in the atmosphere with the DT_{50} values for the process of photooxidative degradation initiated by the $\bullet OH$ radicals as high as 230 days. The only relevant mechanism of elimination of TFA from that compartment would therefore be, predominantly, wet deposition – with rain or fog with estimated $DT_{50} = \sim 9$ days, and, to some extent also by dry deposition, with estimated $DT_{50} = 10-30$ days. The identified products of photooxidative degradation of TFA in air initiated by the $\bullet OH$ radicals are COF_2 and FNO. It was also indicate that the dimerisation of TFA may be the factor limiting the rate of degrdation of that compound in air in the process of photooxidative degradation initiated by the $\bullet OH$ radicals.

The determination of the Henry's law constant for TFA demonstrated that the compound displayed high affinity towards water, therefore atmospheric water, either in form of clouds or as fog, may be an effective sink for that compound. At the same time however it was postulated that the evaporation of TFA from water phase to air cannot be totally excluded and the process can occur more easily than previously expected.

B.8.3.2. – Transport via air

In the document MCA, Section 7 for Flufenacet, under the point 7.3.2. the Applicant indicated one study report as addressing the problem of volatilisation of Flufenacet from soil surface and hence its transport through air. That study is the study by [Hellpointner; 1995], already summarised in this Renewal Assessment Report under the previous data point – B.8.3.1., as *Study 1*. It showed that under the standard German conditions when applied to the bare soil as pre-emergent herbicide in maize (in late May) the volatilisation of Flufenacet from soil would not be substantial. The average level of volatilisation from soil, including the process of wind erosion of soil particles with the compound, or its transformation products, adsorbed onto them, within 24 hour following application was 16.5%, with range (for three trials) of 7.9 – 29.2%.

Flufenacet was demonstrated to be short living in air, with the DT_{50} = 4.7 hours in the process of photochemical oxidative degradation in air.

On that basis it can be stated that the compound will not be prone to the medium-and long-range transport. However, the level of volatilisation does not exclude that the short-range transport effect may be observed. To assess the problem RMS examined the available literature data. One publication, summarised below, was identified presenting the results of the examination of effects of the transport in air.

In the following paper:

Vogel J. R., Majewski M. S., Capel P. D., "*Pesticides in Rain in Four Agricultural Watersheds in the United States.*"; Journal of Environmental Quality, 2008, **37**, 1101 – 1115.

were presented the results of the determination of the content of 42 selected active substances of the plant protection product – 18 herbicides, 21 insecticides and 3 fungicides, as well as their 40 degradation products, in rainfall samples collected at four agricultural locations across the USA in years 2003 and 2004. The samples were collected during the crops growth season.

The samples were collected on single sampling locations in small, well defined, intensively agriculturally used watersheds in Maryland, Indiana, Nebraska and California, chosen to meet the criteria of the US National atmospheric Deposition Programme.

The full characteristic of the sampling locations as well as the criteria for selecting the compounds of interest were provided in the paper:

Capel P. D., McCarthy K. A., Barbash J. E., "*National, Holistic, Watershed-Scale Approach to Understand the Sources, Transport, and Fate of Agricultural Chemicals.*"; Journal of Environmental Quality, 2008, **37**, 983 – 993 (contains extended supplement available on-line on the journal editor's web-site).

which RMS decided not to summarise, but which was cross-referenced in the study summarised here.

On the basis of the data provided in the cross-referenced study by [Capel et al.; 2008] it was possible to identify the sampling locations as following:

- for California: lower Merced River basin with the Mustang Creek catchment as a sub-location where the sampling sites for precipitation were located;
- for Maryland: Morgan creek catchment;
- for Indiana: Sugar Creek catchment, including the Leary Weber Ditch Basin;
- for Nebraska: Maple River catchment.

The primary crops identified on each sampling location were following:

- for California: almond groves (45%), Vineyards (12%) and maize (16%);
- for Maryland: maize, soybean small grain crops (60%), pastures (13%), orchards and nurseries (1.5%);
- for Indiana: soybean (50%) and maize (50%);
- for Nebraska: soybean (50%) and maize (50%)

In case of locations in Maryland, Indiana and Nebraska rain samples were collected and analysed as weekly samples during the growth season – from April/May till the end of September. In case of location in California the precipitation samples were collected and analysed on the event basis, because of the infrequent rainfall on the area, from November until March.

The samples were collected during two consecutive years – 2003 and 2004.

In case of Flufenacet, for which the laboratory reporting limit was set to 0.02 µg/L, 52 samples were analysed for its content. The compound was not detected in any of the samples collected in 2003 and in 4% of those collected in 2004. The total percentage of detection for the period 2003 – 2004 was 4% of the collected samples.

The detailed results for each location showed that Flufenacet was detected only in samples collected in Nebraska. It was found in the 11% of the 18 samples subjected to the analysis for the content of that compound (2 in total) with the maximum concentration of 0.05 µg/L recorded on the 4th of May 2004. The median concentration reported in the study was <0.02 µg/L and the wet deposition, estimated on the basis of the obtained results, was 3.09 µg/m² with maximum occurring on the 4th May 2004.

In none of the other examined locations Flufenacet was reported to be found in rainwater samples. It has to be indicated, that other herbicides being the target compounds in that study were detected more frequently and in much higher amounts, although their estimated use pattern was comparable to that of Flufenacet.

These results may indicate that Flufenacet, even in case of reaching the air compartment will not be subjected to the medium-and long distance transport, but rather deposited locally, at the site of use. The aeric mean deposition determined in that study (for not précised application rates) was not significant, by comparison to e. g. that determined in the SW modelling exposure assessment at Step 3 for the use of that compound in Autumn on Winter cereals at application rate 240 g/ha – 0.05 – 0.46 mg/m².

Therefore it may be stated that even when reaching the air compartment in substantial amounts Flufenacet would not be transported in air far from the application sites and pose a significant threat to adjacent areas by wet or dry deposition.

Of the four degradation products identified as semi-volatile or volatile, therefore potentially causing a threat to the atmosphere – FOE Methylsulfide, FOE Methylsulfone, FOE Thiadone and TFA (Trifluoroacetic acid), two – FOE Methylsulfide and FOE Methylsulfone were demonstrated to be short-living in air, therefore not prone to transport via air. The remaining two – FOE Thiadone and TFA were demonstrated not only to be highly volatile, but also persistent in air, with DT₅₀ values for the process of photochemical oxidative degradation in air of 29.6 days and 20.6 days respectively. Therefore in case they reach air compartment in significant amounts their medium- and long-range transport in that compartment is very probable. As a result that issue should be further examined. The Applicant provided no data on the issue of the transport of FOE Thiadone and TFA in air.

In case of FOE Thiadone RMS was also not able to identify any literature data dealing with the transport of that compound in air. It shall however be indicated that FOE Thiadone was observed in soil in amounts not surpassing 10%. It was also demonstrated to be quickly degraded in that compartment. Additionally the results of the studies aimed on the examination of soil photolysis of FOE Thiadone showed that the compound would be mineralised to much greater extent than it would evaporate from soil surface (in irradiated samples within 14 days of the experiment only ~5% of the radioactivity applied was recovered as VOC fraction, in the dark control samples that amount was only ~2.5%). Also in the experiments with radiolabelled FOE Thiadone aimed on the determination of its persistence in aerobic soil under laboratory conditions the levels of radioactivity recovered as VOC fraction was low: 2 – 4%AR at the study's end (10 – 14 days after the experiment was initiated) with no more than 5% of the initial amount of FOE Thiadone remaining in soil. That may indicate, assuming that the VOC fraction is entirely FOE Thiadone, that despite its high vapour pressure the compound would not migrate to atmosphere from soil in amounts that may pose any threat to that compartment. Also not relevant may be considered the volatilisation from plants as the route of exposure, because that compound would probably not be formed as a transformation product of Flufenacet on plant surfaces.

The only potential route of exposure of air is volatilisation from SW bodies, where FOE Thiadone was demonstrated to be formed as a major degradation product, but at present there is no clear methodology to assess that issue.

As a result, on the basis of the weight of evidence it may be stated that the migration of FOE Thiadone to the air is not expected to be a significant process and therefore the transport of that compound via air, despite its high vapour pressure and significant persistence in that compartment air, would not be an issue of concern. It shall be also indicated that FOE Thiadone is very soluble in water, what may indicate that even reaching atmosphere it will partition to water phase and probably quickly removed from there with rain.

In case of TFA the literature data indicate that the presence of that compound is associated with the phototransformation of haloalkanes and emission from installations where it is used. The physicochemical properties of that acid, and in particular its low pK_a value (≤ 1.0) clearly indicate that when formed in soil or SW compartment it will be present there in form of Trifluoroacetate, which has very low vapour pressure and hence TFA formed in these compartments from Flufenacet would not contribute to the overall content of TFA in the atmosphere. That statement was confirmed by the open-source literature data (for more details please see the text further down this section).

The literature search performed by the RMS showed that there are numerous publications examining the sources of TFA in that compartment as well as its impact on the atmosphere. From that number RMS selected several exemplary papers addressing the problem. They are summarised below.

The following paper:

Solomon K. R., Tang X., Wilson S. R., “*Changes in tropospheric composition and air quality due to stratospheric ozone depletion and climate change.*”; Photochemical and Photobiological Sciences, 2007 **6** (3), 301 – 310.

presented the impact of the various man-made chemicals on the atmosphere and implications of that for human health and global climate. A large section of that paper is focused on the impact of perfluorinated substances on the air compartment in terms of ozone depletion and global warming.

It was stated that long- and short chain HCFCs (hydrochlorofluorocarbons) are unlikely to form short-chain perfluorinated carboxyl acids, such as TFA. However, other polyfluorinated hydrocarbons, such as halothane, isoflurane, HCFC123, HCFC-124, HFC-134a and HFC-143a were indicated to be transformed entirely to TFA. Therefore with increasing emissions of the listed above compounds to the atmosphere, the concentrations of TFA in that compartment are expected to increase as well. At the time of issuing the publication the amounts of TFA in rainwater were in range <0.5 – 350 ng/L, depending on location and distance of the sampling point from the emission sources of its precursors, or TFA itself.

According to the estimates presented in that paper the total conversion of HFCs (hydrofluorocarbons) and HCFCs to TFA in the atmosphere may result in production of 22,00,000 tonnes of TFA, for which the final sink are oceans and landlocked lakes.

It was stated that the predominant sources of TFA in fresh surface water are anthropogenic, with concentrations in flowing SW bodies reaching the max. level of 350 ng/L, but higher in some landlocked lakes – up to 40000 ng/L.

In oceans the concentrations of TFA are close or equal to 200 ng/L, but unlike in fresh water SW bodies the compound is considered to come partly from the natural sources.

The authors pointed out that even for the estimated amount of TFA produced in the atmosphere from HFCs and HCFCs the increase of its concentrations in oceans as the terminal sink would be small – 0.016 ng/L. Even the consideration of other potential anthropogenic sources of TFA, that increase was estimated to be negligible.

It was also stated that TFA displayed very low toxicity to aquatic organisms, therefore no additional environmental risk resulting from the observed loadings to fresh- and saltwater dwellers was expected to be observed.

In the publication :

Römpf A., Klemm O., Fricke W., Hartmut F., „*Haloacetates in Fog and Rain.*“; Environmental Science and Technology, 2001, **35** (7), 1294 – 1298.

were presented the results of the determination of concentrations of various haloacetates, including TFA, in fog and rain samples collected in Northeastern Bavaria with estimation of the possible sources of those compounds in atmospheric water.

The analysis of the possible sources of atmospheric TFA, based on the determination of frequency of its appearance in samples and its concentrations in comparison to the concentrations of other compounds, showed that the compound came from various anthropogenic sources. That was stated on the basis of the fact that TFA was detected in all examined samples at relatively constant level of 0.43 – 0.65 µg/L and were strongly correlated with the atmospheric concentrations of SO_4^{2-} and NO_3^- (99%), the ions known to be emitted, or formed from the precursors emitted, predominantly by power plants, industrial facilities and motor vehicles. The fog/rain concentration ratio of TFA was on average 6.6 with range 0.2 – 18.

The problem of formation of TFA in the air compartment from HCFCs in the atmosphere and the impact on that process on the environment, as well as the impact of the emissions to the atmosphere of the HCFCs, such as HFO-1234yf, on the environment was characterised in the following paper by Henne and co-workers:

Henne, S.; Shallcross, D. E.; Reimann, S.; Xiao, P.; Boulos, S.; Gerecke, A. C.; Brunner, D.; “*Environmental impacts of HFO-1234yf and other HFOs.*”; Moving Towards Sustainability, ASHRAE/NIST Refrigerants Conference, Gaithersburg, MD, United States, Oct. 29-30, 2012 (2012), 13/1-13/13.

It focused on the formation of TFA from HCFCs in air and implications of that process for the environment. Although the main compound of concern was HFO-1234yf also the fate of other HFOs in air and their contribution to the formation of TFA in atmosphere was examined. HFO-1234yf was indicated as a compound having the highest transformation potential to TFA – 100%. Additionally, due to its relatively short DT_{50} in comparison to some other HFOs having similar transformation potential to TFA, such as HFC-134 (weeks v/s

years), the depositions of TFA formed from HFO-1234yf were estimated to be more localized than those from other HFOs.

The paper also provided the concentrations of TFA in rainwater samples collected in Switzerland in 2011 in course of the air-pollution monitoring programme carried out in that country in comparison to the results obtained in the years preceeding that period in various European and non-European countries.

It contained also the model estimations of the concentrations of TFA in air and the levels of wet deposition resulting from the estimated emission levels of HFO-1234yf.

Finally, in the paper:

Jordan A., Frank H., *“Trifluoroacetate in the Environment. Evidence for Sources Other Than HFC/HCFs.”*; Environmental Science and Technology, 1999, **33** (4), 522 – 527.

in a comprehensive way are presented all sources of TFA in atmosphere and their contribution to the pollution of the environment with that compound. The authors indicated that the HFCs and HCFCs, such as HFC-134a, HCFC-123 or HCFC-124 may be considered as main sources of TFA in the atmosphere. However, the other potential sources are also listed. Among them are fluorinated inhalation anesthetics – halothane (CF₃CHClBr), desflurane (CF₃CHFOCHF₂) and isoflurane (CF₃CHClOCHF₂), the emissions of TFA from industrial processes, such as electrolytic aluminium production, production and use of perfluorinated polymers and the active substances of the plant protection products containing trifluoromethyl groups, with trifluralin given as an example of such compound. It was stated that although volatilisation of such compounds and their transformation in atmosphere is possible, not expected is the process of their degradation leading to the formation of TFA. Additionally it was stated that although TFA may be formed from such compounds in processes of their degradation in soil, that process is not conceivable to be the relevant source of atmospheric TFA. That statement may be extended also to Flufenacet.

Therefore on the basis of the presented above literature data it may be stated that TFA in atmosphere comes from sources other than the use of the plant protection products such as Flufenacet and that the importance of these sources in the global pollution by TFA is much greater. The results also show that at present TFA in the atmosphere does not pose a serious threat to that compartment, being neither ozone-depleting compound nor greenhouse gas, or to other environmental compartments, such as SW water bodies (fresh and saltwater ones) which it may enter through wet or, predominantly, dry deposition from the atmosphere, because of its experimentally demonstrated low toxicity, in dissociated form (acetate), to the living organisms.

B.8.3.3. – Local and global effects

In the document MCA, Section 7 for Flufenacet, under the point 7.3.3. the Applicant made the following statement to address this issue: *“Local and global effects of flufenacet were not considered since its half-life in air is ≤ 2 days.”*

The RMS considers that statement acceptable and no additional data with regard to Flufenacet to cover that issue were required.

Also for none of the major identified degradation products of Flufenacet such assessment was not necessary, as showed the analysis of the available data for them performed under the preceeding data points.

B.8.3.4. – Summary: fate and behaviour in air

As the first step in the assessment of the fate and behaviour of Flufenacet in the air compartment RMS analysed the basic data on the volatility potential of that active compound and its major degradation products in order to identify the substances of concern for the atmosphere. The basic data on the volatility potential of Flufenacet and its major degradation products are presented below in the table B.8.3.4._CA-1. The data were taken from the section B.2 (AS) for Flufenacet, unless it was clearly stated that they were derived from other sources.

Table B.8.3.4._CA-1: The key physico-chemical properties of Flufenacet and its major degradation products relevant for the determination of the fate and behaviour in the atmosphere.

Parameter		Compound ¹⁾							
		FOE 5043	FOE Oxalate	FOE S. A.	FOE Methylsulfone	FOE Methylsulfide	FOE Thiadone	FOE TFESA	TFA ²⁾
Molecular weight [g/mol]		363.4	225.2	275.3	257.3	241.0	170.1	164.1	114.02
Vapour pressure V_p [Pa] at $T = 20^{\circ}\text{C}$		9 E-5 ³⁾	4.5 E-7	1.35 E-7 ⁶⁾	8.6 E-4	8.06 E-3 ¹⁰⁾	2.05	<1.0 E-8	<1.0 E-6
Solubility in water, S_{aq} , [mg/L] at $T = 20^{\circ}\text{C}$	pH 5	56 ⁴⁾	> 1.2 E5	5.5 E4 ⁷⁾	4.1 E3 ⁹⁾	2.0 E3 ¹¹⁾	95.5 E3 ¹³⁾	>1.6 E5	>5.0 E5
	pH 7	56	> 1.2 E5	5.5 E4 ⁷⁾	4.1 E3 ⁹⁾	2.0 E3 ¹¹⁾	> 1.0 E5	>1.6 E5	>5.0 E5
	pH 9	53	>1.2 E5	5.5 E4 ⁷⁾	4.1 E3 ⁹⁾	2.0 E3 ¹¹⁾	> 1.0 E5	>1.6 E5	>5.0 E5
Henry's law constant, H , [Pa*m ³ /mol] at $T = 20^{\circ}\text{C}$	pH 5	1.2 E-3 ⁵⁾	<8.4 E-10	n. a. ⁸⁾	n. a. ⁸⁾	1.72 E-2 ¹²⁾	0.012 ¹⁴⁾	<1.2 E-11	<2.7 E-10
	pH 7	1.3 E-3 ⁵⁾	<6.8 E-10	n. a. ⁸⁾	5.7 E-5	1.72 E-2 ¹²⁾	n. a. ⁸⁾	<1.2 E-11	<2.7 E-10
	pH 9	1.1 E-3 ⁵⁾	<6.8 E-10	n. a. ⁸⁾	n. a. ⁸⁾	1.72 E-2 ¹²⁾	n. a. ⁸⁾	<1.2 E-11	<2.7 E-10

Footnotes to the table:

- 1) The following code-names were used to denominate the substances: FOE 5043 for Flufenacet, FOE S. A. for FOE Sulfonic acid, FOE TFESA for FOE Trifluoroethanesulfonic acid and TFA for Trifluoroacetic acid;
- 2) **In aqueous solution TFA, being a very strong acid with $pK_a = 1.6$, is fully dissociated, therefore the values are provided for trifluoroacetate and the test substance used to determine them was TFA-Na salt;**
- 3) In section B.2 it was stated that Flufenacet isomerised by evaporation forming a mixture containing 10% of Flufenacet and 90% of its *N*-isomer; as a result, the value is that characteristic for *N*-isomer of Flufenacet;
- 4) The value determined at pH = 4;
- 5) The values determined for *N*-isomer of Flufenacet, using the solubility values determined for that compound;
- 6) The measured value not provided; instead the Applicant presented the value determined theoretically, using QSAR method, and for $T = 25^\circ\text{C}$; RMS subsequently converted that value to presented here value for $T = 20^\circ\text{C}$ using appropriate Van't Hoff equation (presented in the "Manual for FOCUS TOXSWA version 2.2.1", Alterra Report No. 586, Wageningen, 2006);
- 7) The value determined in unbuffered solution and representative for the whole environmentally relevant pH range, since it was experimentally demonstrated that water solubility of FOE S. A. is not pH-dependent;
- 8) Value not available;
- 9) The value determined in pH = 7 buffer solution, but considered representative for the whole environmentally relevant pH range, since it was experimentally demonstrated that water solubility of FOE Methylsulfone is not pH-dependent;
- 10) The theoretical value determined by the RMS using QSAR methods – it was calculated using Modified Grain method for $T = 25^\circ\text{C}$; for more details please refer to the data presented in the table B.8.8-a.3._CA-4 under the point B.8.8.-A.3 – Appendix 3, of this Renewal Assessment Report;
- 11) The value determined in pH = 6.1 buffer solution, but considered representative for the whole environmentally relevant pH range, since it was experimentally demonstrated that water solubility of FOE Methylsulfide is not pH-dependent;
- 12) The theoretical value determined by the RMS using QSAR methods – it was calculated using Modified Grain method for $T = 25^\circ\text{C}$; for more details please refer to the data presented in the table B.8.8-a.3._CA-4 under the point B.8.8.-A.3 – Appendix 3, of this Renewal Assessment Report;
- 13) The value determined at pH = 5.77;
- 14) Value determined at pH < 5.

The further analysis was carried out using the vapour pressure classification presented in the Guidance document "Pesticides in Air: Considerations for Exposure Assessment" – Report of the FOCUS Working Group on Pesticides in Air ([FOCUS; 2008]).

According to that Guidance document the trigger values indicating the need to establish whether the substance has the potential to reach the air are:

- $V_p \geq 10^{-4}$ Pa at $T = 20^\circ\text{C}$ for volatilisation from soil, and
- $V_p \geq 10^{-5}$ Pa at $T = 20^\circ\text{C}$ for volatilisation from plants.

Using these criteria RMS identified the following compounds as those of potential concern:

- Flufenacet, being medium volatile according to the classification presented above and having a potential to reach air via volatilisation from plants;
- FOE Methylsulfone, being medium volatile according to the classification presented above and having a potential to reach air via volatilisation from soil and plants;
- FOE Methylsulfide, being medium volatile according to the classification presented above and having a potential to reach air via volatilisation from soil and plants; it shall be indicated however that for that compound the assessment is based on theoretically determined values;
- FOE Thiadone, being volatile according to the classification presented above and having a potential to reach air via volatilisation from soil and plants.

RMS also decided to take into consideration TFA. Although the experimental values presented in the table B.8.3.4._CA-1 does not indicate that it is a compound of concern, they were derived for trifluoroacetate. The examination of the available open-sources data showed that the non-dissociated acid displayed high volatility potential resulting from its high vapour pressure – 11 kPa at $T = 20^\circ\text{C}$ (source: Pubchem – open chemistry database, url: <https://pubchem.ncbi.nlm.nih.gov>). For that reason RMS decided to evaluate its fate and behaviour

in the atmosphere as well. **At the same time it shall be indicated that the $pK_a = 1.6$ value determined for TFA in aqueous solutions clearly indicate that when formed from Flufenacet either in soil or surface water compartments the compound, being entirely dissociated would display very limited volatility and hence risk to atmosphere, unless the environment becomes very acidic.**

The examination of the fate and behaviour of Flufenacet in air showed that that compound displayed some tendency for migration to the atmosphere, with the determined average level of volatilisation from soil surface equal to 16.5% of the applied dose (with range of 7.9 – 29.2%), but was not expected to be persistent in that compartment – the determined for the process of the photooxidative degradation initiated by the $\bullet OH$ radicals **$DT_{50} = 6.8$ hours**. That value, being significantly shorter than the $DT_{50} = 2$ days, indicates that Flufenacet, even in case of reaching the atmosphere in significant amounts, would not pose a serious threat to that compartment. It would also not be prone to medium- or long-range transport in that compartment and therefore it would not pose a threat of secondary pollution resulting from the wet and dry deposition from the atmosphere.

That statement may be confirmed by the results of the monitoring study carried out in the USA by the employees of USGS and aimed on the examination of the content of Flufenacet in the rainfall. The monitoring was performed in years 2003 – 2004 on four representative locations, in the areas of intensive agricultural activity, in California, Indiana, Nebraska and Maryland. Flufenacet was found only in two of 52 samples examined, and only at one location – in Nebraska, where the main crops were maize and soybean, on which Flufenacet was routinely used. The maximum concentration detected in rain samples was 0.05 $\mu g/L$ and it occurred on the 4th May 2004, presumably shortly after Flufenacet was applied. The median concentration reported in the study was $<0.02 \mu g/L$ and the wet deposition, estimated on the basis of the obtained results, was 3.09 $\mu g/m^2$ with maximum occurring on the 4th May 2004.

In none of the other examined locations Flufenacet was reported to be found in rainwater samples. It has to be indicated, that other herbicides being the target compounds in that study were detected more frequently and in much higher amounts, although their estimated use pattern was comparable to that of Flufenacet.

These results may indicate that Flufenacet, even in case of reaching the air compartment, will not be subjected to the medium- and long distance transport, but rather deposited locally, at the site of use. The aeric mean deposition determined in that study (for not precised application rates) was not significant, by comparison to e. g. that determined in the SW modelling exposure assessment at Step 3 for the use of that compound in Autumn on Winter cereals at application rate 240 g/ha – 0.05 – 0.46 g/m^2 .

Of seven major soil, aquatic or soil and aquatic major degradation products of Flufenacet, four were identified as posing potential threat to the atmosphere, being volatile or semivolatile – FOE Methylsulfone, FOE Methylsulfide, FOE Thiadone and Trifluoroacetic acid – TFA. For them the additional estimation of their persistence in air, by determining the DT_{50} values for the process of the photooxidative degradation initiated by the $\bullet OH$ radicals, was performed. The calculated for FOE Methylsulfide and FOE Methylsulfone DT_{50} values for that process were **0.517 days** and **0.563 days** respectively, what clearly indicates that even in case of reaching the atmosphere in significant amounts, these compounds would not pose a serious threat to that compartment. They would also not be prone to medium- or long-range transport in that compartment and therefore would not pose a threat of secondary pollution resulting from the wet and dry deposition from the atmosphere.

The model assessment of the persistence of FOE Thiadone in air showed that the compound would be very persistent in air. For the structural formula exactly matching that of FOE Thiadone the results indicated that no reaction with $\bullet OH$ radicals occurred. For the structure that was slightly altered by comparison to that of FOE Thiadone – the double bond was repositioned from $C=N$ to $N=N$, that reaction was demonstrated to be very slow with the half-life, calculated assuming 12-hours lasting day and the concentration of the $\bullet OH$ radicals of $1.5 E6 [radicals/cm^3]$, **$DT_{50} = 29.594$ days**. That value is significantly longer than the $DT_{50} = 2$ days. The results therefore indicate that FOE Thiadone in case of reaching the atmosphere in significant amounts, would pose a serious threat to that compartment. It would be prone to medium- or long-range transport in that compartment and therefore it may pose a threat of secondary pollution resulting from the wet and dry deposition from the atmosphere.

For that compound RMS was not able to identify any literature data dealing with its fate and behaviour in air. It shall however be indicated that FOE Thiadone was observed in soil in amounts not surpassing 10%. It was also demonstrated to be quickly degraded in that compartment. Additionally the results of the studies aimed on the examination of soil photolysis of FOE Thiadone showed that the compound would be mineralised to much greater extent than it would evaporate from soil surface (in irradiated samples within 14 days of the experiment only ~5% of the radioactivity applied was recovered as VOC fraction, in the dark control samples that amount was only ~2.5%). Also in the experiments with radiolabelled FOE Thiadone aimed on the determination of its persistence in aerobic soil under laboratory conditions the levels of radioactivity recovered as VOC fraction was

low: 2 – 4%AR at the study's end (10 – 14 days after the experiment was initiated) with no more than 5% of the initial amount of FOE Thiadone remaining in soil. That may indicate, assuming that the VOC fraction was entirely FOE Thiadone, that despite its high vapour pressure the compound would not migrate to atmosphere from soil in amounts that may pose any threat to that compartment. Also not relevant may be considered the volatilisation from plants as the route of exposure, because that compound would probably not be formed as a transformation product of Flufenacet on plant surfaces.

The only potential route of exposure of air is volatilisation from SW bodies, where FOE Thiadone was demonstrated to be formed as a major degradation product, but at present there is no clear methodology to assess that issue.

The model assessment of the persistence of TFA in air showed that the compound would be persistent in air, with the half-life, calculated assuming 12-hours lasting day and the concentration of the $\bullet\text{OH}$ radicals of $1.5 \text{ E6} [\text{radicals/cm}^3]$, **$\text{DT}_{50} = 20.569 \text{ days}$** . That value is significantly longer than the $\text{DT}_{50} = 2 \text{ days}$, what indicates that TFA in case of reaching the atmosphere in significant amounts, would pose a serious threat to that compartment. It may also be prone to medium- or long-range transport in that compartment and therefore it may pose a threat of secondary pollution resulting from the wet and dry deposition from the atmosphere.

The Applicant did not submit any relevant data enabling the elucidation of the fate and behaviour of TFA in air compartment. However in the documentation submitted for the evaluation it was stated several times that the TFA formed as a degradation product of Flufenacet will be present as Trifluoroacetate – the dissociated form displaying very low volatility potential and as such not posing any substantial risk to the atmosphere.

The literature search performed by the RMS resulted in identification of several scientific papers addressing the issue of behaviour of TFA in the atmosphere, four of which specifically with persistence, transformation mechanisms and mechanisms of elimination of TFA from air. On their basis it was possible to state that TFA clearly demonstrated high persistence in the atmosphere with the DT_{50} values for the process of photooxidative degradation initiated by the $\bullet\text{OH}$ radicals as high as 230 days. The only relevant mechanism of elimination of TFA from that compartment would therefore be, predominantly, wet deposition – with rain or fog with estimated $\text{DT}_{50} = \sim 9 \text{ days}$, and, to some extent also by dry deposition, with estimated $\text{DT}_{50} = 10\text{-}30 \text{ days}$. The identified products of photooxidative degradation of TFA in air initiated by the $\bullet\text{OH}$ radicals are COF_2 and FNO. It was also indicated that the dimerisation of TFA may be the factor limiting the rate of degradation of that compound in air in the process of photooxidative degradation initiated by the $\bullet\text{OH}$ radicals.

The determination of the Henry's law constant for TFA demonstrated that the compound displayed high affinity towards water, therefore atmospheric water, either in form of clouds or as for, may be an effective sink for that compound. At the same time however it was postulated that the evaporation of TFA from water phase to air cannot be totally excluded.

The examination of the available literature data showed that the presence of the TFA in the atmosphere was not expected to be related to the degradation in that environmental compartment of the active substances of the plant protection products containing in their molecules the CF_3 - functional groups, nor to the possible volatilisation from soil of TFA formed there as a result of degradation of such agrochemicals.

On the basis of the results obtained in the area of the examination of the fate and behaviour of Flufenacet and its major degradation products in air, as well as their transport via air it was stated that the further examination of the local and global effects related to their would be presence in air was not necessary.

The key results on the assessment of fate and behaviour of Flufenacet and its degradation products identified as possibly posing a risk to atmosphere are presented below in format recommended for the EU-agreed LoEP.

Fate and behaviour in air (Regulation (EU) N° 283/2013, Annex Part A, point 7.3.1)

Direct photolysis in air	<i>Not studied - no data requested</i>
Photochemical oxidative degradation in air	DT ₅₀ of <i>4.7</i> hours derived by the Atkinson model (version <i>1.55</i>). OH (<i>12 h</i>) concentration assumed = <i>1.5 E6</i>
Volatilisation	from plant surfaces (BBA guideline): <i>not examined</i> from soil surfaces (BBA guideline): <i>16.5% (7.9 – 29.2%) after 24 hours</i>
Metabolites	<p>Degradation products requiring assessment due to their medium/high volatilisation potential: FOE Methylsulfide, FOE Methylsulfone, FOE Thiadone, TFA</p> <p>Data for FOE Methylsulfide: Direct photolysis in air: <i>Not studied - no data requested</i> Photochemical oxidative degradation in air: DT₅₀ of <i>0.563 days</i> derived by the Atkinson model (version <i>1.92</i>). OH (<i>12 h</i>) concentration assumed = <i>1.5 E6</i> Volatilisation: - from soil surfaces (BBA guideline): <i>Not studied - no data requested, the compound is aquatic metabolite, not expected to be formed in soil;</i> - from plant surfaces (BBA guideline): <i>Not studied - no data requested, the compound is an aquatic metabolite, not expected to be formed on plant surfaces</i></p> <p>Data for FOE Methylsulfone: Direct photolysis in air: <i>Not studied - no data requested</i> Photochemical oxidative degradation in air: DT₅₀ of <i>0.517 days</i> derived by the Atkinson model (version <i>1.92</i>). OH (<i>12 h</i>) concentration assumed = <i>1.5 E6</i> Volatilisation: - from soil surfaces (BBA guideline): <i>not examined, not requested</i> - from plant surfaces (BBA guideline): <i>Not studied - no data requested, the compound is a soil metabolite, not expected to be formed on plant surfaces</i></p> <p>Data for FOE Thiadone: Direct photolysis in air: <i>Not studied - no data requested</i> Photochemical oxidative degradation in air: DT₅₀ derived by the Atkinson model (version <i>1.92</i>). OH (<i>12 h</i>) concentration assumed = <i>1.5 E6 not possible to be determined, therefore it may be assumed that the compound does not undergo the photochemical oxidative degradation in air</i> Volatilisation: - from soil surfaces (BBA guideline): <i>not examined, not requested – the compound being not persistent in soil is not expected to migrate from that compartment into the atmosphere in any significant amounts</i> - from plant surfaces (BBA guideline): <i>Not studied - no data requested, the compound is a soil and aquatic metabolite, not expected to be formed on plant surfaces</i></p> <p>Data for TFA: Direct photolysis in air: <i>Not studied - no data requested</i> Photochemical oxidative degradation in air: DT₅₀ <i>20.569 days</i> derived by the Atkinson model (version <i>1.92</i>). OH (<i>12 h</i>) concentration assumed = <i>1.5 E6</i>, Volatilisation: - from plant surfaces (BBA guideline): <i>not examined, not requested – in soil TFA will be present in dissociated form, what is a factor very strongly limiting its volatility and hence the would-be migration to the air compartment</i> - from plant surfaces (BBA guideline): <i>Not studied - no data requested, the compound is a soil metabolite, not expected to be formed on plant surfaces</i></p>

B.8.4 - Definition of the residue

For the purpose of the previous authorisation of Flufenacet in the EU the then-RMS – France presented in the Annex B.7 of the Assessment Report under the point B.7.9 – Definition of the residue, the following general residue definition for Flufenacet:

“In view of the findings in the different sections of this chapter, it can be concluded that FOE 5043 itself, as well as the metabolite FOE sulfonic acid (M2) have to be considered as relevant residue for quantification in soil and water. In soil only, FOE Oxalate (M1) has to be taken into consideration as additional relevant metabolite.

The relevant residue with regard to quantification in air is the active ingredient only. None of the environmental fate studies indicated volatile metabolites except CO₂.

That residue definition, in light of the findings of the current assessment, required updating. The updated residue definition for the risk assessment and monitoring purposes, proposed by the Applicant and then verified and corrected by the RMS, is presented below.

B.8.4.1 – Definition of the residue for risk assessment

In the document MCA-Section 7 for Flufenacet under the point 7.4.1. the Applicant proposed the following residue definition for the risk assessment:

Soil:

Flufenacet, FOE oxalate, FOE sulfonic acid, FOE methylsulfone, FOE-thiadone, FOE 5043-trifluoromethanesulfonic acid, trifluoroacetic acid;

Groundwater:

Flufenacet, FOE oxalate, FOE sulfonic acid, FOE methylsulfone, FOE-thiadone, FOE 5043-trifluoromethanesulfonic acid, trifluoroacetic acid (same as for soil compartment);

Surface water:

Flufenacet, FOE oxalate, FOE sulfonic acid, FOE methylsulfone, FOE methylsulfide, FOE-thiadone, FOE 5043-trifluoromethanesulfonic acid, trifluoroacetic acid;

Sediment:

Flufenacet;

Air:

Flufenacet;

Having verified the Applicant's proposal and on the basis of the information provided in this Report RMS proposes the following residue definition for the risk assessment:

Soil:

Flufenacet, FOE Oxalate, FOE Sulfonic acid, FOE Methylsulfone, FOE Thiadone, FOE Trifluoromethanesulfonic acid, Trifluoroacetic acid;

Justification: RMS with this confirms the Applicant's proposal. All listed degradation products are major soil degradation products.

Groundwater:

Flufenacet, FOE Oxalate, FOE Sulfonic acid, FOE Methylsulfone, FOE Thiadone, FOE Trifluoromethanesulfonic acid, Trifluoroacetic acid (same as for soil compartment); additional compounds that may require assessment (on the basis of the results of lysimeter studies) are FOE Alcohol and FOE TGS;

Justification: The proposed residue definition is the same as proposed by the Applicant and contains the degradation products classified as major soil metabolites and displaying high leaching potential (excluding FOE Thiadone). The reason for inclusion of FOE Alcohol and FOE TGS is that in the lysimeter studies despite being

minor soil degradates they were detected in leachates in quantifiable amounts. Therefore it cannot be excluded that under unfavourable conditions they would pose a risk to GW compartment.

Surface water:

Flufenacet, FOE Oxalate, FOE Sulfonic acid, FOE Methylsulfide, FOE Methylsulfone, FOE Thiadone, FOE Trifluoroethanesulfonic acid, Trifluoroacetic acid;

Justification: The proposed residue definition is the same as proposed by the Applicant and contains the degradation products classified as major soil, aquatic or soil and aquatic metabolites. At the same time it shall be indicated that in case of FOE Trifluoroethanesulfonic acid and TFA the assessment in the aquatic environment could not be finalised due to the fact that there was no water/sediment study with Flufenacet radiolabelled in position enabling adequately address the problem.

Sediment:

Flufenacet;

Justification: only Flufenacet was included into that residue definition because of the degradation products listed above in the definition for SW compartment none displayed any significant affinity to the sediment compartment – if detected there they were found in low amounts, not surpassing 5%.

Air:

Flufenacet, FOE Thiadone and Trifluoroacetic acid;

Justification: Flufenacet was included by default, although it shall be indicated that it does not pose a serious threat to the atmosphere; the reason for including FOE Thiadone and TFA is that they are volatile (although in case of TFA it was demonstrated that, being dissociated, that compound when formed from Flufenacet is not expected to migrate to air in any significant amounts) and persistent in air, so they may pose a serious threat to the atmosphere.

B.8.4.2. – Definition of the residue for monitoring

In the document MCA-Section 7 for Flufenacet under the point 7.4.2. the Applicant made the following statement with regard to the definition of the residue for monitoring:

“The proposed residue definition for monitoring is flufenacet only for all compartments since none of the major degradation products is of toxicological or ecotoxicological relevance.”

Having verified the Applicant’s proposal and on the basis of the information provided in this Report RMS proposes the following residue definition for the risk assessment:

Soil:

Flufenacet, FOE Sulfonic acid, FOE Methylsulfone, Trifluoroacetic acid;

Justification: all listed compounds, including Flufenacet, displayed some potential (in case of TFA significant) for accumulation in soil (conclusion based on the results of the calculations of PEC_{SOIL} values) ;

Groundwater:

Flufenacet, FOE Oxalate, FOE Sulfonic acid, FOE Methylsulfone, FOE Trifluoroethanesulfonic acid and Trifluoroacetic acid;

Justification: the parent compound was included by default. In case of the degradation products listed above the reason for their inclusion was that for the proposed EU-representative application pattern in the GW model exposure assessment they were demonstrated to leach to the groundwater recharge in amounts $> 0.1 \mu\text{g/L}$. In many cases the calculated $PEC_{GW} > 0.75 \mu\text{g/L}$ and in case of TFA the calculated $PEC_{GW} > 10 \mu\text{g/L}$. The high leaching potential of FOE Sulfonic acid was confirmed in regulatory lysimeter studies. Finally, it shall be indicated that FOE Oxalate and FOE Sulfonic acid were detected in Groundwater in some monitoring studies, the results of which were presented in the publications summarised under the point B.8.5.

Surface water:

Flufenacet, FOE Oxalate, FOE Sulfonic acid, FOE Methylsulfide, FOE Thiadone and Trifluoroacetic acid

Justification: the parent compound was included by default. In case two degradation products – FOE Methylsulfide and FOE Thiadone, they were included into the definition due the fact that they are major aquatic degradation products (additionally FOE Thiadone was identified as major soil degradation product) with not defined persistence in natural water. The reason for including FOE Oxalate and FOE Sulfonic acid was that they are major soil degradation products and potentially major aquatic degradation products (in the water/sediment

studies their formation potential was not fully assessed) with unknown persistence in water and highly mobile. Additionally in some monitoring studies, summarised below under the point B.8.5, they were detected in SW bodies in quite significant amounts, as was Flufenacet. The reason for including TFA is that it is very persistent and common pollutant. Additionally the problem of its formation from Flufenacet in SW compartment was not satisfactorily addressed.

Sediment:

Flufenacet;

Justification: the definition comprises the parent compound only, which was included by default, but also because the degradation in the SW bodies will comprise the migration from water phase to sediment (main dissipation process for Flufenacet in water), where it will undergo degradation. None of the degradation products listed for SW compartment were included due to the fact that they were either not detected in sediment or found in that compartment in very low amounts (<5% of the initial amount of Flufenacet).

Air:

Flufenacet, FOE Thiadone and Trifluoroacetic acid;

Justification: the parent compound was included by default. In case two degradation products – FOE Thiadone and TFA they were included because of their high volatility and persistence in air, what results in a high level of risk they pose to the atmosphere – the monitoring should exclude Flufenacet as a potential source of FOE Thiadone and, in particular TFA, in the air compartment.

Residue definition – a summary:

The Applicant presented the proposal for the residue definition in the document MCA-Section 7 for Flufenacet under the points 7.4.1. – definition of the residue for the risk assessment, and 7.4.2 – definition of the residue for monitoring. RMS, having verified that proposal, proposes the following residue definition, with its justification:

- **Definition of residue for the risk assessment:**

Soil:

Flufenacet, FOE Oxalate, FOE Sulfonic acid, FOE Methylsulfone, FOE Thiadone, FOE Trifluoroethanesulfonic acid, Trifluoroacetic acid;

Justification: RMS with this confirms the Applicant's proposal. All listed degradation products are major soil degradation products.

Groundwater:

Flufenacet, FOE Oxalate, FOE Sulfonic acid, FOE Methylsulfone, FOE Thiadone, FOE Trifluoroethanesulfonic acid, Trifluoroacetic acid (same as for soil compartment); additional compounds that may require assessment (on the basis of the results of lysimeter studies) are FOE Alcohol and FOE TGS;

Justification: The proposed residue definition is the same as proposed by the Applicant and contains the degradation products classified as major soil metabolites and displaying high leaching potential (excluding FOE Thiadone). The reason for inclusion of FOE Alcohol and FOE TGS is that in the lysimeter studies despite being minor soil degradates they were detected in leachates in quantifiable amounts. Therefore it cannot be excluded that under unfavourable conditions they would pose a risk to GW compartment.

Surface water:

Flufenacet, FOE Oxalate, FOE Sulfonic acid, FOE Methylsulfide, FOE Methylsulfone, FOE Thiadone, FOE Trifluoroethanesulfonic acid, Trifluoroacetic acid;

Justification: The proposed residue definition is the same as proposed by the Applicant and contains the degradation products classified as major soil, aquatic or soil and aquatic metabolites. At the same time it shall be indicated that in case of FOE Trifluoroethanesulfonic acid and TFA the assessment in the aquatic environment could not be finalised due to the fact that there was no water/sediment study with Flufenacet radiolabelled in position enabling adequately address the problem.

Sediment:

Flufenacet;

Justification: only Flufenacet was included into that residue definition because of the degradation products listed above in the definition for SW compartment none displayed any significant affinity to the sediment compartment – if detected there they were found in low amounts, not surpassing 5%.

Air:

Flufenacet, FOE Thiadone and Trifluoroacetic acid;

Justification: Flufenacet was included by default, although it shall be indicated that it does not pose a serious threat to the atmosphere; the reason for including FOE Thiadone and TFA is that they are volatile (although in case of TFA it was demonstrated that, being dissociated, that compound when formed from Flufenacet is not expected to migrate to air in any significant amounts) and persistent in air, so they may pose a serious threat to the atmosphere.

- **Definition of the residue for monitoring:**

Soil:

Flufenacet, FOE Sulfonic acid, FOE Methylsulfone, Trifluoroacetic acid;

Justification: all listed compounds, including Flufenacet, displayed some potential (in case of TFA significant) for accumulation in soil (conclusion based on the results of the calculations of PEC_{SOIL} values) ;

Groundwater:

Flufenacet, FOE Oxalate, FOE Sulfonic acid, FOE Methylsulfone, FOE Trifluorethanesulfonic acid and Trifluoroacetic acid;

Justification: the parent compound was included by default. In case of the degradation products listed above the reason for their inclusion was that for the proposed EU-representative application pattern in the GW model exposure assessment they were demonstrated to leach to the groundwater recharge in amounts $> 0.1 \mu\text{g/L}$. In many cases the calculated $PEC_{GW} > 0.75 \mu\text{g/L}$ and in case of TFA the calculated $PEC_{GW} > 10 \mu\text{g/L}$. The high leaching potential of FOE Sulfonic acid was confirmed in regulatory lysimeter studies. Finally, it shall be indicated that FOE Oxalate and FOE Sulfonic acid were detected in Groundwater in some monitoring studies, the results of which were presented in the publications summarised under the point B.8.5.

Surface water:

Flufenacet, FOE Oxalate, FOE Sulfonic acid, FOE Methylsulfide, FOE Thiadone and Trifluoroacetic acid

Justification: the parent compound was included by default. In case two degradation products – FOE Methylsulfide and FOE Thiadone, they were included into the definition due the fact that they are major aquatic degradation products (additionally FOE Thiadone was identified as major soil degradation product) with not defined persistence in natural water. The reason for including FOE Oxalate and FOE Sulfonic acid was that they are major soil degradation products and potentially major aquatic degradation products (in the water/sediment studies their formation potential was not fully assessed) with unknown persistence in water and highly mobile. Additionally in some monitoring studies, summarised below under the point B.8.5, they were detected in SW bodies in quite significant amounts, as was Flufenacet. The reason for including TFA is that it is very persistent and common pollutant. Additionally the problem of its formation from Flufenacet in SW compartment was not satisfactorily addressed.

Sediment:

Flufenacet;

Justification: the definition comprises the parent compound only, which was included by default, but also because the degradation in the SW bodies will comprise the migration from water phase to sediment (main dissipation process for Flufenacet in water), where it will undergo degradation. None of the degradation products listed for SW compartment were included due to the fact that they were either not detected in sediment or found in that compartment in very low amounts ($< 5\%$ of the initial amount of Flufenacet).

Air:

Flufenacet, FOE Thiadone and Trifluoroacetic acid;

Justification: the parent compound was included by default. In case two degradation products – FOE Thiadone and TFA they were included because of they high volatility and persistence in air, what results in a high level of risk they pose to the atmosphere– the monitoring should exclude Flufenacet as a potential source of FOE Thiadone and, in particular TFA, in the air compartment.

That residue definition is additionally presented below in format recommended for the EU-agreed LoEP.

Residues requiring further assessment (Regulation (EU) N° 283/2013, Annex Part A, point 7.4.1)

Environmental occurring residues requiring further assessment by other disciplines (toxicology and ecotoxicology) and or requiring consideration for groundwater exposure

Soil: Flufenacet, FOE Oxalate, FOE Sulfonic acid, FOE Methylsulfone, FOE Thiadone, FOE Trifluorethanesulfonic acid, Trifluoroacetic acid
 Surface water: Flufenacet, FOE Oxalate, FOE Sulfonic acid, FOE Methylsulfide, FOE Methylsulfone, FOE Thiadone, FOE Trifluorethanesulfonic acid, Trifluoroacetic acid
 Sediment: Flufenacet
 Ground water: Flufenacet, FOE Oxalate, FOE Sulfonic acid, FOE Methylsulfone, FOE Thiadone, FOE Trifluorethanesulfonic acid, Trifluoroacetic acid (same as for soil compartment)
 Air: Flufenacet, FOE Thiadone and Trifluoroacetic acid

Definition of the residue for monitoring (Regulation (EU) N° 283/2013, Annex Part A, point 7.4.2)

Definition proposed on the basis of the results of the evaluation of the environmental fate and behaviour
 Soil: Flufenacet, FOE Sulfonic acid, FOE Methylsulfone, Trifluoroacetic acid
 Surface water: Flufenacet, FOE Oxalate, FOE Sulfonic acid, FOE Methylsulfide, FOE Thiadone, Trifluoroacetic acid
 Sediment: Flufenacet
 Ground water: Flufenacet, FOE Oxalate, FOE Sulfonic acid, FOE Methylsulfone, FOE Trifluorethanesulfonic acid, Trifluoroacetic acid
 Air: Flufenacet, FOE Thiadone and Trifluoroacetic acid
 Additionally see section 5, Ecotoxicology

B.8.5 – Monitoring data concerning fate and behaviour of the active substance, metabolites, degradation and reaction products

The Applicant based the whole assessment in this area on the results of the three open-source publications, one for Flufenacet and two other for TFA. Justifying such approach the Applicant stated that although Flufenacet and its degradation products were often included into the monitoring programmes carried out by the competent authorities across Europe, the results were not made publicly available by means of presenting them in peer-reviewed literature. Therefore the Applicant decided to present only the results of the monitoring studies found during the performed literature search.

At the same time the Applicant stated that the detected concentrations of Flufenacet in surface water were always below the EU limit of 0.1 µg/L, set for drinking water and groundwater.

RMS evaluated the publications submitted by the Applicant for their relevance in the assessment of Flufenacet for the renewal of its authorisation in the EU. All three submitted publications were found relevant and will be summarised below, under the data point B.8.5.1.

The additional literature search resulted in identification of several other publications reporting the results of the monitoring studies aimed on the determination of the concentration of Flufenacet and its selected degradation products, mainly FOE Oxalate and FOE Sulfonic acid, in Groundwater and Surface water bodies. These studies were carried out in the USA and in Europe. Also the studies presenting the results of worldwide monitoring of TFA in various environmental compartments were identified as a result of that repeated literature search. All these results are presented below, under the data point B.8.5.1.

B.8.5.1 – Summary monitoring data

The literature search performed by the Applicant resulted in identification of one study presenting the results of the monitoring carried out for Flufenacet. RMS identified another twelve publications presenting the results of the monitoring projects or those containing the elements of monitoring, carried out in North America or Europe.

The monitoring data for the North America came predominantly from the United States and were presented in seven publications. In these publications were reported the results obtained by the researchers of the US Geological Survey monitoring the levels of various pesticides in groundwater, surface water and rain water samples collected in the decade of 1990s and in early 2000 years – until 2004 in the Midwestern states of the USA.

The methodology of the selection of the sampling areas was presented in the already cited in this report, under the point B.8.3.2., publication:

Capel P. D., McCarthy K. A., Barbash J. E., “*National, Holistic, Watershed-Scale Approach to Understand the Sources, Transport, and Fate of Agricultural Chemicals.*”; Journal of Environmental Quality, 2008, **37**, 983 – 993 (contains extended supplement available on-line on the journal editor’s web-site).

The research area covered by these studies were nine Midwestern states, the area of intensive agricultural production with maize, cereals and other arable crops being the main crops grown there.

The study period reported in these reports coincided with the highest estimated level of use of Flufenacet, presented in the following USGS report:

Baker N. T., Stone W. S., “*Estimated Annual Agricultural Pesticide Use for Counties of the Conterminous United States, 2008 – 12.*”; US Geological Survey Data Series 907, 2015.

According to the data presented in that report Flufenacet was used for the first time in 1998, in amounts close to 0.9 million US pounds (corresponding to ~408233 kg) to increase in the following years to the maximum level of ~1.5 million US pounds in 2004 (corresponding to 680389 kg. During the period 1999-2005, covered by the cited studies that level was in range 1.0 – 1.5 million US pounds (corresponding to the range 453592 – 680389 kg/year), with the aerial use rate in range 0.62 – >1.84 pound/mile², what corresponded to 0.108 – 0.322 kg/km² (assuming the conversion factors pound:kg 0.4535 and the ratio 1 mile²/1 km² 1:2.59). It shall be indicated that these values were related to the whole analysed area and not just treated fields, therefore they are different from

the label application rates. The main treated crop was maize, followed by soybean and cereals (all results are given for the E Pest-high estimates).

In two publications were presented the results of the determination of various pesticides and their degradation products in groundwater sampled in wells.

In 2001 Kolpin and co-workers examined the concentrations of 21 herbicides and their 24 degradation products in water of 86 municipal wells in Iowa. These wells were selected in 1992 within the Iowa Ground Water Monitoring programme (IGMW) and were representative for major types of aquifers of the area: alluvial (32), bedrock/karst (20), glacial drift (12) and bedrock/nonkarst (22) region. The research on the content of the residues of selected herbicides in water samples taken from them, carried out in 2001, was an extension of IGMW programme and followed the sample collection procedure developed within it. The samples were analysed for the content of the residues of herbicides using GC/MS and LC/MS techniques.

Flufenacet was among the substances selected for that study, as well as its two major degradation products: FOE Oxalate (in the study called flufenacet oxalinic acid) and FOE Sulfonic acid (in the study bearing the name Flufenacet ethanesulfonic acid). For all three compounds the reporting level (RL) was 0.05 µg/L. It was stated that neither Flufenacet nor its two metabolites of concern were detected in any examined samples in amounts > RL. The results of that examination were presented in the publication:

Kolpin D. W., Schnoebelen D. J., Thurman M. E., *“Degradates Provide Insight to Spatial and Temporal Trends of Herbicides in Ground Water.”*; Groundwater, 2004, **42** (4), 601 – 608.

In another publication:

Mills P. C., Kolpin D. W., Scribner E. A., Thurman E. M., *“Herbicides and degradates in shallow aquifers of Illinois: spatial and temporal trends.”*; JAWRA Journal of the American Water Resources Association, 2005, **41** (3), 537 – 547.

were presented the results of the similar research project performed in Illinois. The aim of that study was to determine the concentrations of selected herbicides and their degradates in 55 wells completed in unconsolidated aquifers (37 wells) and bedrock aquifers (18 wells), underlying grain producing regions in Illinois, in order to better understand the spatial and temporal occurrence of these compounds in Illinois groundwater. Samples were taken in October and November 2000 and analysed for the content of 16 herbicides and 13 their degradation products. Flufenacet, FOE Oxalate and FOE Sulfonic acid were among the analysed compounds. The reporting limit for them was 0.05 µg/L. It was stated that neither Flufenacet nor its degradation product of concern were detected in any water sample collected.

The results of the monitoring of Flufenacet and its selected degradation products in surface water were presented in four publications summarised below.

Rebich and co-workers examined the concentrations of selected herbicides in streams located in Mississippi River Basin. The research project, carried out from March 1999 to May 2001 was a part of the US Geological Survey (USGS) National Stream Quality Accounting Network (NASQAN). The results were presented in the following paper:

Rebich R. A., Coupe R. H., Thurman E. M., *“Herbicide concentrations in the Mississippi River Basin – the importance of chloroacetanilide herbicide degradates.”*; Science of the Total Environment, 2004, **321** (1-3), 189 – 199.

The analysed water samples were collected on four locations, which were four key junctures of the Mississippi River Basin:

- Mississippi River at Grafton, IL;
- Missouri River Herman, MO;
- Ohio River near Grand Chain, IL;
- Mississippi River at St. Francisville, LA.

The methods of sample collection and analysis were those developed and routinely used by the USGS. Flufenacet and its Oxalate- (OA) and Sulfonic acid- (ESA) degradates were among the chloroacetanilide herbicides and their degradates being analysed within the frame of that study. For them the method reporting level (MRL) was set to 0.05 µg/L. The levels of Flufenacet were determined in 39 samples, while those of OA and ESA in 38 samples collected during the study duration, all after September 2000. Flufenacet was detected in 3% of the analysed samples, in max. amount of 0.12 µg/L. Flufenacet OA and Flufenacet ESA were not detected in amounts > 0.05 µg/L (MRL) in any of the samples analysed for their content.

Another study aimed on the determination of the concentrations of acetamide herbicides – dimethenamid, Flufenacet and Metolachlor, as well as their OXA (Oxalate)- and SA (Sulfonic acid)- degradation products, in the SW water from the same catchment - Mississippi River Basin, was carried out by Zimmerman and co-workers in years 1999-2000. In this study samples were collected from one location – Mississippi river at Baton Rouge, LA, where the river bears 41% of water collected from the whole catchment. The drained area comprises major maize- and soybean-growing regions, where acetamide herbicides were commonly used. Water samples were collected in monthly intervals between March and December of each of the study years. In times considered to coincide with the spring flush of the herbicides they were collected more often.

The collected samples were subjected to SPE extraction and the analysed compounds, recovered after SPE, were analysed by GC-MS or HPLC-MS.

For Flufenacet and its degradates it was stated that during the experimental period they were not observed in any of the analysed samples in amounts $> 0.05 \mu\text{g/L}$ (method detection limit – MDL), with exception of two samples (6%) in which SA degradate of Flufenacet was observed in amounts above that level. That was postulated to be due to the fact that when the study was carried out Flufenacet was still a relatively new herbicide (n. b. same conclusions were drawn for dimethenamid, despite the fact that the frequency and levels of detection of that herbicide and its degradation products were higher).

The results of that study were presented in the following publication:

Zimmerman L. R., Schneider R. J., Thurman E. M., “*Analysis and Detection of the Herbicides Dimethenamid and Flufenacet and Their Sulfonic and Oxalinic Acid Degradates in Natural Degradates in Natural Water.*”; Journal of Agricultural and Food Chemistry, 2002, **50** (5), 1045 – 1052.

The concentrations of selected herbicides and their degradation products, as well as antibiotics, in 51 streams of nine Midwestern states of the USA – IOWA, Illinois, Indiana, Kansas, Minnesota, Missouri, Ohio and Wisconsin, were examined in 2002 Scribner and co-workers.

The results of that monitoring programme were presented in the following publication:

Scribner E. A., Battaglin W. A., Dieze J. E., Thurman E. M., “*Reconnaissance Data for Glyphosate, Other Selected Herbicides, Their Degradation Products, and Antibiotics in 51 Streams in Nine Mid-Western States 2002.*”; US Geological Survey Open-File Report 03-217, 2003. available online at the url: <http://ks.water.usgs.gov/pubs/reports/ofr.03-217.html>

Flufenacet was one of the acetamide herbicides listed among the analysed compounds, while the list of the degradates of the acetamide herbicides contained two of its degradation products – Oxalate (OXA) and Sulfonic acid (ESA). The reporting limit (LOQ) for all three of them was $0.05 \mu\text{g/L}$.

The sampling sites were selected on the basis of the ranking of 147 sampling sites used in 1989 to measure the concentrations of pesticides during the post-application period. The sites were divided into three categories, according to the total herbicide concentrations:

- having highest concentrations of herbicides; from that group 25 locations were randomly selected to be used in that study;
- having medium concentrations of herbicides; from that group 13 sites were randomly selected to be used in that study;
- with low concentration of pesticides; from that group 12 sites were selected.

From each site three samples were collected during the study period (in 2002): one in May-June, after the application of the pre-emergence herbicides (further called pre-emergence sample), another in June-July, when the post-emergence herbicides were applied (further called post-emergence samples) and the third in September – November, during or after harvest (further called harvest-season samples).

Samples were processed and analysed for the content of the test compounds using standardised USGS analytical methods.

The frequency of detection in case of Flufenacet and its degradation products was following:

- Flufenacet was detected in 11 of 51 pre-emergence samples, 9 of 52 post-emergence samples and 1 of 51 harvest season samples;
- FOE Oxalate was detected in 2 of 51 pre-emergence samples, 4 of 52 post-emergence samples and 3 of 51 harvest season samples;
- FOE Sulfonic acid was detected in 3 of 51 pre-emergence samples, 3 of 52 post emergence samples and 2 of 51 harvest season samples.

In pre-emergence samples the median concentration of Flufenacet was $<0.05 \mu\text{g/L}$, and the concentrations in those where it was detected (in samples from 11 of 51 monitored streams) were in range $0.06 - 0.93 \mu\text{g/L}$. It was measured in two streams in Iowa, one in Illinois, one in Kansas, one in Missouri, five streams in Nebraska,

where the concentrations were the highest and one in Ohio. It was not detected in any examined streams of Indiana, Minnesota and Wisconsin.

In post-emergence samples the median concentration of Flufenacet was $<0.05 \mu\text{g/L}$, and the concentrations in those where it was detected (in samples from 9 of 52 monitored streams) were in range $0.06 - 1.6 \mu\text{g/L}$. It was measured in four streams in Iowa, one in Illinois, one in Kansas and three in Nebraska, where the concentrations were the highest. It was not detected in any examined streams of Indiana, Minnesota, Missouri, Ohio and Wisconsin.

Finally, in harvest season samples the median concentration of Flufenacet was $<0.05 \mu\text{g/L}$, and the concentration in that, where it was detected - in sample from just one of the 51 monitored streams, was $0.13 \mu\text{g/L}$. It was measured in one stream in Illinois.

It is worth of indicating that the highest concentrations of Flufenacet in pre-emergence and post-emergence samples were recorded in Nebraska, the state in which that compound was detected in rain water by Vogel and co-workers (please refer to the point B.8.3.2.).

The frequency of detection and measured levels of FOE Oxalate and FOE Sulfonic acid were much lower. In pre-emergence samples the maximum measured concentration was $0.09 \mu\text{g/L}$ for both compounds, in post emergence ones it was $0.18 \mu\text{g/L}$ for FOE Oxalate and $0.13 \mu\text{g/L}$ for FOE Sulfonic acid, while for harvest season samples it was $0.13 \mu\text{g/L}$ for FOE Oxalate and $0.08 \mu\text{g/L}$ for FOE Sulfonic acid. The analysis of the results showed that when detected these two compound usually appeared in the same streams.

It shall be indicated that these results were also presented, in abridged form, in the following publication:

Battaglin W. A., Kolpin D. A., Scribner E. A., Kuivila K. M., Sandstrom M. W., "Glyphosate, other herbicides, and transformation products in Midwestern streams, 2002."; JAWRA Journal of the American Water Resources Association, 2005, **41** (2), 323 – 332.

Finally, the concentrations of Flufenacet in rainfall of the Midwestern states of the USA were examined by Vogel and co-workers. The results of that monitoring study were presented in the paper:

Vogel J. R., Majewski M. S., Capel P. D., "Pesticides in Rain in Four Agricultural Watersheds in the United States."; Journal of Environmental Quality, 2008, **37**, 1101 – 1115.

already summarised in this document under the data-point B.8.3.2. In that study Flufenacet was found only in two rain samples, both collected in Nebraska in early May 2004, in concentrations not surpassing $0.05 \mu\text{g/L}$.

The results of the monitoring of Flufenacet and its selected degradation products in Europe were presented in another seven publications, identified by either Applicant – 1 publication, or by RMS – six publications.

For the purpose of the present evaluation the Applicant submitted a paper presenting the results of the monitoring study examining the migration of the pesticides to surface water body in the agricultural catchment.

The publication submitted for the evaluation was:

Bishoff G., Pestmer W., Rodemann B.; "Entry of pesticides into surface waters – new results of Lamspringe run-off monitoring project 1999 – 2001."; Pesticide in Air, Plant, Soil and Water System, Proceedings of the Symposium Pesticide Chemistry, 12th, Piacenza, Italy, 2003, pp. 849 – 856.

The experiment was performed in Lamspringe catchment, located in Lower Saxony, Germany, the growing area for Winter cereals (winter wheat, winter barley), winter rape and sugar beet as the main crops. According to the characteristic provided in the paper the catchment had the area of approx. 110 ha, the fields on that area were managed with conservation tillage methods and the drainage system was set there transporting the surplus of precipitation water to the stream flowing across the catchment. The samples of the stream water were collected on the effluent side of the 100-ha area over almost three consecutive years – from October 1998 until May 2001 using automatic sampling device. The samples were collected as daily samples and then mixed to prepare weekly samples that were analysed. Additional samples were collected after each strong rain event. The weekly samples were filtered, processed by SPE extraction and the SPE extracts were subjected for GC/MS and LC/MS-MS analysis for the presence of 32 substances identified as used on the area. The monitored active substances of the plant protection products were: Azoxystrobin, Carbendazim, Carbetamid, Chloridazon, Cyprodinil, Diflufenican, Dimefuron, Epoxiconazole, Esfenvalerate, Ethofumesat, Fenpropidin, Fenpropimorph, Flufenacet, Isoproturon, Kresoxim-methyl, Lambda-cyhalothrin, Metazachlor, Metconazole, Phenmedipham, Propaquizafop, Propiconazole, Spiroxamine, Tebuconazole, Thiophanate-Methyl, Trinexapac-ethyl and Vinclozolin. During the experimental period – 1998 – 2001, Flufenacet was applied in two consecutive years – in 1999 and in 2000, twice during each of those years. It was not detected in any of the samples collected during the Period 1 – from

the 1st October 1998 to the 30th April 1999 and within the experimental Period 2 – from the 1st of May 1999 till the 31st December 2001, it was detected in three samples. The maximum level detected for that compound in any analysed sample was 0.07 µg/L. It shall be indicated that the LOQ value was set to 0.05 µg/L. The conclusions drawn from that study referred to the general concentrations of the pesticides detected in water samples, with no particular reference to Flufenacet.

Another publication presenting the results of the monitoring of Flufenacet in various water samples in Germany was, identified by the RMS, following paper:

Kowal S. Balsaa P., Werres F., Schmidt T. C., *“Fully automated standard addition method for the quantification of 29 polar pesticide metabolites in different water bodies using LC-MS/MS.”*; Analytical and Bioanalytical Chemistry, 2013, **405**, 6337 – 6351.

Although the main aim of the research presented in that paper was the development and validation of the novel, sensitive and high-precision analytical method enabling the routine quantitative analysis of the 29 polar degradation products of the active substances of the plant protection products, including FOE Oxalate and FOE Sulfonic acid, its performance was validated by analysing the concentrations of the test compounds in 200 natural water samples. The water samples used in validation were drinking water-, groundwater-, deep well water- surface water- and wastewater samples collected in Rhine and Ruhr region of North Rhine-Westphalia, Germany.

The developed method, standard addition method (SAM) for LC-MS/MS analysis, was demonstrated to be fully reliable, with recoveries of both Flufenacet degradation products in range 95 – 105%, LOD levels of 4 µg/L for FOE Oxalate and 8 µg/L for FOE Sulfonic acid and LOQ levels of 14 µg/L for FOE Oxalate and 29 µg/L for FOE Sulfonic acid.

As a part of the method's validation, 200 natural water samples were analysed – 6 of waste water, 14 of surface water, another 14 of deep well water, 156 of groundwater and 17 of drinking water. The results were presented in form of the bar graphs showing the range of the obtained concentrations. In case of all analysed samples of waste water, surface water, deep well water, and groundwater, the concentrations of both FOE Oxalate and FOE Sulfonic acid were well below 0.05 µg/L, usually in range of 0.00 – 0.25 µg/L. Only in case of drinking water samples the concentrations of FOE Sulfonic acid were above the level of 0.05 µg/L, but still below the threshold value of 0.1 µg/L.

It shall be indicated that in the paper little was said about the sampling procedure used to obtain those samples, including sampling period. For that reason the results may be considered only as indicative ones.

RMS identified four publications presenting the results of the determination of the concentrations of Flufenacet and its two degradation products – FOE Oxalate and FOE Sulfonic acid in SW water bodies in Switzerland.

Kern and co-workers carried out the research aimed on the comparison of the estimated using the numerical models concentrations of the selected active substances and their degradation products in the SW water bodies with the field data – the concentrations measured in surface water from existing catchment. Among the test substances were Flufenacet and its two degradation products – FOE Oxalate and FOE Sulfonic acid. The field data were collected from the river La Petite Glâne, located in western Switzerland (Canton Vaud), ~30 km long and having a catchment of 90 km², a tributary to the river La Broye, entering Lake Murten. The catchment of the river La Petite Glâne is an agriculture-dominated one with cereals (wheat, barley, maize), sugar beet, potatoes and rapeseed being the dominant crops. Water samples were taken from spring to autumn of 2008, mainly after intensive rainfall events – 20 samples. Additionally three samples were taken during the base flow to establish background concentrations. They were divided into three sets:

- application period samples, collected in May and June; nine such samples were analysed;
- post application periods samples, collected in July; eight such samples were analysed;
- harvesting period samples, collected between August and October; three such samples were analysed.

In case of the base-flow samples the concentrations of the test compounds were provided for two samples – that collected during the post-application period and that collected during the harvest period.

Additionally the concentrations of the test compounds in 22 groundwater samples from groundwater screening in the Swiss Plateau were determined.

Collected samples were processed by SPE extraction and analysed using LC-MS/MS method. The LOD and LOQ values for SW water samples were following:

- for Flufenacet LOD = 0.3 ng/L and LOQ = 1.0 ng/L;
- for FOE Oxalate LOD = 0.3 ng/L and LOQ = 1.0 ng/L;
- for FOE Sulfonic acid LOD = 0.3 ng/L and LOQ = 1.0 ng/L.

The results obtained in SW water samples for Flufenacet and its degradation products were following:

- **Flufenacet:** the median concentration in application period samples was 71 ng/L with range 26 – 350 ng/L, the median concentration in the post-application period samples was 8 ng/L with range 6 – 37 ng/L, the median concentration in harvesting period samples was 4 ng/L with range 3 – 4 ng/L;
- **FOE Oxalate:** the median concentration in application period samples was 3 ng/L with range 2 – 6 ng/L, the median concentration in the post-application period samples was 3 ng/L with range <1 – 6 ng/L, the median concentration in harvesting period samples was <1 ng/L with range <1 – 4 ng/L;
- **FOE Sulfonic acid:** the median concentration in application period samples was 4 ng/L with range 2 – 9 ng/L, the median concentration in the post-application period samples was 7 ng/L with range <1 – 25 ng/L, the median concentration in harvesting period samples was 8 ng/L with range 7 – 13 ng/L.

The concentrations of these compounds in the base-flow samples were following:

- in base-flow sample collected during the post-application period, the concentration of Flufenacet was 4 ng/L, that of FOE Oxalate <1 ng/L and that of FOE Sulfonic acid 8 ng/L;
- in base-flow sample collected during the harvesting period, the concentration of Flufenacet was 1 ng/L, that of FOE Oxalate <1 ng/L and that of FOE Sulfonic acid <1 ng/L.

In none of the analysed groundwater samples Flufenacet or its degradation products of interest were found.

The results of that study were presented in the following paper:

Kern S., Singer H., Hollender J., Schwarzenbach R. P., Fenner K., “*Assessing Exposure to Transformation Products of Soil-Applied Organic Contaminants in Surface Water: Comparison of Model Predictions and Field Data.*”; Environmental Science and Technology, 2011, **45** (7), 2833 – 2841 (with the supplement available on-line on the editor’s web-page).

Three other papers presented the results of the studies carried out by Moschet and co-workers.

That research team examined and then modelled the concentrations of selected organic micropollutants in a large river and lake catchment, using an international catchment of Lake Constance, located in the border area between Austria, Germany and Switzerland and collecting water from Alpine regions of these three countries, having a total catchment area of 11500 km². Its main tributary, also draining the lake, is Rhine river. Additionally the lake has 11 other tributary rivers.

Initially, to identify the organic micropollutants of concern samples of lake water were taken from four different spots and analysed by SPE-HPLC-Orbitrap method for the presence of 252 compounds – active substances of the plant protection products and their degradation products, pharmaceuticals and their transformation products, biocides and their transformation products, industrial chemicals cosmetics, food additives. These samples were collected in August 2008 and on the basis of the results obtained then the organic micropollutants for more detailed monitoring, performed from April till October of the year 2009 on twelve main tributaries of Lake Constance and on the lake itself.

The sampling points used in the preliminary monitoring in August 2008 were located in Bergenzer Bucht at the depth 0 and 50 metres, in the middle of the Upper Constance Lake at the depths 0, 10 and 230 metres, in Zellersee at the depths of 0 and 20 metres and in Rheinsee at the depths of 0 and 40 metres.

Flufenacet and its two degradates – FOE Oxalate (named Flufenacet OXA) and FOE Sulfonic acid (named Flufenacet-ESA) were listed among the compounds of concern during the preliminary monitoring study, with the LOD values 2 ng/L, 4 ng/L and 2 ng/L respectively.

The results of that preliminary monitoring, presented in the supplement SI 3 to the publication showed that neither Flufenacet nor its degradation products of concern were detected in the lake water sampled on these locations.

The results of that experiment were presented in the following publication:

Moschet C., Götz C., Longrée P., Hollender J., Singer H., “*Multi-Level Approach for the Integrated Assessment of Polar Organic Micropollutants in an International Lake Catchment: The Example of Lake Constance.*”; Environmental Science and Technology, 2013, **47** (13), 7028 – 7036 (with the supplement available on-line on the editor’s web-page).

It shall be indicated that RMS identified another publication dealing with the transboundary transport of Flufenacet in surface water. That publication presented the results of the investigation of the concentrations of various active substances in the border areas of the Netherlands. Flufenacet was indicated as one of the compounds present in the amounts above the acceptability limits in the border zone between the Netherlands and Belgium and that between the Netherlands and Germany. However its presence was limited only to that zone and

not beyond, possibly also due to the fact that Flufenacet at period of preparation and issuing the publication was not authorised in the Netherlands. The exceedence index for that compound was of order 0.6 - 0.7 for the border zone with Belgium and of 0.3 – 0.4 for that with Germany. On that basis it was stated that the presence of Flufenacet in the SW bodies of the borderland with Belgium and Germany was due to long-distance transport of that compound with water, possibly also from more distant areas where the compound was commonly used, e.g. France. These results were presented in the following paper:

Van't Zelfde M., Tamis W. L., Vijver M. G., De Snoo G. R., *"The contribution of neighbouring countries to pesticide levels in Dutch surface waters."*; Communications In Agricultural and Applied Biological Sciences (Univ. Ghent), 2011, **76** (4), 867 – 877.

RMS however decided, signalling it, not to include that publication into the list of the relevant open-source publications due to the fact that it did not contain any measured concentrations of Flufenacet, just a reference to their source – the Dutch Atlas of Pesticides. For that reason its utility is, in RMS's opinion, limited. It may however be more relevant for zonal or MS registration.

Another study by Moschet and co-workers was aimed on the monitoring of Flufenacet and its two degradation products – FOE Oxalate and FOE Sulfonic acid, in Swiss riverine water. Its results were presented in the following two papers:

Moschet C., Wittmer I., Simovic J., Junghans M., Piazzoli A., Singer H., Stamm C., Leu C. Hollender J., *"How a Complete Pesticide Screening Changes the Assessment of Surface Water Quality."*; Environmental Science and Technology, 2014, **48** (10), 5423 – 5432 (with the supplement available on-line on the editor's web-page).

Moschet C., Vermeirsser E. L. M, Singer H., Stamm C., Hollender J., *"Evaluation of in-situ calibration of Chemcatcher passive samplers for 322 micropollutants in agricultural and urban affected rivers."*; Water Research, 2015, **71**, 306 – 317 (with the supplement available on-line on the editor's web-page).

The monitoring was carried out during the period between 19th March and 23rd July 2012 on five river catchments distributed over Swiss plateau:

- Fürtbach river catchment located in northern Switzerland, having the area of 38 km²,
- Limpach river catchment in central Switzerland, having the area of 73 km²,
- Mentue river catchment in south-western Switzerland, having the area of 105 km²,
- Salmsacher Aach river catchment in north-eastern Switzerland, having the area of 47 km²,
- Surb river catchment located north-westerly to the Fürtbach river catchment, having the area of 66 km².

The two dominant crops in all these catchments were cereals and maize.

The samples at each sampling site were collected in weekly intervals and in the analysing laboratory were mixed to obtain the two-weeks representative samples, nine from each catchment, processed by SPE and then analysed using appropriate chromatographic technique – LC-HRMS/MS. They were analysed for the presence of 289 active substances of the plant protection products and their 136 degradates. Among the analysed herbicides and its degradates were Flufenacet, with the LOQ = 3 ng/L, FOE Oxalate, with the LOQ = 7 ng/L, and FOE Sulfonic acid with the LOQ = 3 ng/L.

Flufenacet was detected in samples from all five rivers, with average detection frequency of 53% and the maximum concentration of 290 ng/L. In individual rivers those parameters looked as follows:

- in Fürtbach river it was detected in 56% of the analysed samples with maximum concentration of 80 ng/L;
- in Limpach river it was detected in 78% of the analysed samples with maximum concentration of 160 ng/L;
- in Mentue river it was detected in 67% of the analysed samples with maximum concentration of 35 ng/L;
- in Salmsacher Aach river it was detected in 11% of the analysed samples with maximum concentration of 31 ng/L;
- in Surb river it was detected in 56% of the analysed samples with maximum concentration of 290 ng/L.

FOE Sulfonic acid was detected in samples from all five rivers, with average detection frequency of 62% and the maximum concentration of 38 ng/L. In individual rivers those parameters looked as follows:

- in Fürtbach river it was detected in 44% of the analysed samples with maximum concentration of 14 ng/L;
- in Limpach river it was detected in 100% of the analysed samples with maximum concentration of 30 ng/L;
- in Mentue river it was detected in 89% of the analysed samples with maximum concentration of 38 ng/L;

- in Salmsacher Aach river it was detected in 44% of the analysed samples with maximum concentration of 7.9 ng/L;
- in Surb river it was detected in 33% of the analysed samples with maximum concentration of 17 ng/L.

FOE Oxalate was not detected in any of the analysed water samples.

Analysing both papers RMS noticed that, providing the results of the same study, they had different aim. The paper published in 2014 in the “Environmental Science and Technology” had the aim to demonstrate the advantages of the full scale monitoring in the exposure and risk assessment, while that presented in 2015 in “Water research” compared the performance of two different analytical methods used to determine broad range of organic micropollutants in water samples.

Additionally, eight publications, considered relevant, were identified presenting the results of the quantitation of Trifluoroacetic acid (TFA) in various environmental compartments. Two of them were submitted by the Applicant as a result of the performed open-literature search. Six other publications were found by the RMS during the repeated literature search. All they are presented below.

Marine environment, in particular oceans, were indicated in numerous publications as a terminal sink for the TFA reaching the environment. Therefore the concentrations of that compound in marine water was examined by several research teams. The results of two such studies were presented in the publications submitted by the Applicant.

Hartmut and co-workers presented the results of the determination of the concentrations of TFA in water sampled in Mid-Atlantic Ocean in January 1998 and in Southern Ocean in December 1998 and January 1999. The water samples were taken by specialised oceanographic ships from various depths. The Mid-Atlantic water samples were taken from the depths of 0 – 4150 metres. Those from Southern Ocean were taken down to the depth of 2000 metres. Additionally for samples taken in 1998 approx. 400-years-old mineral water from the source in Germany was used.

The content of TFA in all samples was determined, after their pre-processing, comprising derivatisation of the analysed compound, by GC-MS.

The concentrations of TFA in Mid-Atlantic water samples were at relatively constant level of 190 – 210 ng/L, with the mean value of 200 ng/L. Similar results were obtained for Southern Ocean water samples for both sampling periods: 185 – 210 ng/L in case of samples collected in December 1998 and 165 – 220 ng/L for samples collected in January 1999 with the mean value of 200 ng/L. The authors stated that the concentrations of TFA in analysed samples were not dependent on the depth from which the samples were taken.

That implied that although in the perfluorinated haloalkanes, such as CFCs, emitted to the atmosphere were indicated as a substantial source of TFA in the environment, in ocean water that compound was demonstrated to originate from not identified natural sources, significantly surpassing contribution from any man-made sources.

These results were presented in the following publication:

Frank H., Christoph E. H., Holm-Hansen O., Bullister J. L., “Trifluoroacetate in Ocean Waters.”; Environmental Science and Technology, 2002, **36** (1), 12 – 15.

The second paper, written by Scott and co-workers, presented the results of much broader examination of the concentrations of TFA in oceans. The water profile samples were collected at 22 sites located in Arctic, North Atlantic, South Atlantic and Pacific oceans. The sampling depth was, depending on the location of the sampling site, down to 5300 m. below the sea surface (b. s. s.).

The exact locations of the sampling sites and their maximum monitored depths were following:

- Canada Basin in Western Arctic – two sampling sites with the sampling depths 1500 metres b. s. s. and 3000 metres b. s. s.;
- Nares Strait in Eastern Arctic – three sampling sites with the sampling 365 metres b. s. s., 489 metres b. s. s. and 579 metres b. s. s.;
- North Atlantic in the vicinity of the US shores – two sampling sites with the sampling depths of 974 metres b. s. s. and 1000 metres b. s. s.;
- North Atlantic near North-African shores – one sampling point with the sampling depth of 3800 metres b. s. s.;
- South Atlantic along the African shores and in the Antarctic zone – three sampling sites with sampling depths of 3875 metres b.s. s., 5300 metres b. s. s. and 5053 metres b. s. s.;
- South Pacific in the vicinity of South American shores – two sampling sites, one of them near the deep-sea volcanic vent, with sampling depths of 3830 metres b. s. s. and 2500 metres b. s. s.;
- Eastern North Pacific along Asian coast – six sampling sites the sampling depths 175 metres b. s. s., 200 metres b. s. s., and 300 metres b. s. s (for four sampling locations);

- Western North Pacific along the North American (Canadian) coast – two sampling sites, both near the deep-sea volcanic vents, with sampling depths 2200 metres b. s. s. and 3986 metres b. s. s.;
- Mediterranean Sea near the volcanic vent – one sampling site with the sampling depth of 200 metres b. s. s.;

The measured concentrations of TFA at these sites were following:

- for Canada Basin in Western Arctic: 34 – 181 ng/L and 61 – 172 ng/L;
- Nares Strait in Eastern Arctic: 120 – 170 ng/L (two sites) and 8 – 125 ng/L;
- North Atlantic in the vicinity of the US shores: 17 – 150 ng/L and 28 – 190 ng/L;
- North Atlantic near North-African shores: 120 – 150 ng/L;
- South Atlantic along the African shore and in the Antarctic zone: 64 – 155 ng/L, 100 – 145 ng/L and 130 – 200 ng/L;
- South Pacific in the vicinity of South American shores: 1 – 150 ng/L and 1 – 90 ng/L;
- Eastern North Pacific along Asian coast: 1 – 25 ng/L, 1 – 30 ng/L, 1 – 68 ng/L, 1 – 80 ng/L, 1 – 20 ng/L and 2 – 50 ng/L;
- Western North Pacific along the North American (Canadian) coast: 3 – 140 ng/L and 2 – 230 ng/L;
- Mediterranean Sea near the volcanic vent: 0.5 – 50 ng/L.

In general terms, the concentrations recorded in the Atlantic Ocean and estimated in Indian Ocean displayed higher degree of consistency with the average concentration of 175 ng/L down to the depth of 10000 metres. The same value was obtained for the Pacific Ocean when the layer 4000 – 10000 metres below the sea level was considered. However, in case of the upper layers the higher variability in concentrations was estimated with the average concentration of 9 ng/L in the layer 0 – 200 metres b. s. s., 31 ng/L for the layers 200 – 1000 metres b. s. s. and 1000 – 2000 metres b. s. s., 7.1 ng/L for the layer 2000 – 3000 metres b. s. s. and 40 ng/L for the layer 3000 – 4000 metres b. s. s.

These results were presented in the paper:

Durham L., Fisk A., Kannan K., Macdonald R. W., Muir D. C. G., Scott B. F., Spencer C., Witter A., Yamashita N., *“Trifluoroacetate profiles in the Arctic, Atlantic, and Pacific Oceans.”*; Environmental Science and Technology, 2005, **39** (17), 6555 – 6560.

There are numerous publications reporting the results of the monitoring of TFA in the other than sea environmental compartments – freshwater bodies, soil and precipitation. RMS identified six such publications, which may be considered exemplary publications with regard to monitoring of TFA in the environment.

The already summarised under the data point B.8.3.2. publication by Henne and co-workers:

Henne, S.; Shallcross, D. E.; Reimann, S.; Xiao, P.; Boulous, S.; Gerecke, A. C.; Brunner, D.; *“Environmental impacts of HFO-1234yf and other HFOs.”*; Moving Towards Sustainability, ASHRAE/NIST Refrigerants Conference, Gaithersburg, MD, United States, Oct. 29-30, 2012 (2012), 13/1-13/13.,

provides the results of the determination of the concentrations of TFA in rain samples collected in Europe and outside that continent during the last decade of the 20th century and the first decade of the 21st Century, reported in other publications. In case of Europe those values were following:

- in samples collected in 1995 in urban regions of Germany the mean concentration of TFA in precipitation was 100 ng/L with range of 25 – 280 ng/L;
- in samples collected in urban and rural Germany in years 1995 and 1996 the mean concentration of TFA in precipitation was 110 ng/L, with range 10 – 410 ng/L;
- in samples collected in rural areas of Germany in years 1998 and 1999 the mean concentration of TFA in precipitation was ~100 ng/L, ranging from ~20 ng/L to ~580 ng/L;
- the analysis of precipitation samples collected in urban and rural areas of Switzerland in 1995 showed that the concentration of TFA in precipitation was in range 40 – 80 ng/L;
- the mean concentration of TFA in samples of precipitation collected in 1996 in remote areas of Ireland was 39 ng/L with range 2 – 92 ng/L;
- the analysis of the precipitation samples collected in 1996 in urban areas of Poland showed that the mean concentration of TFA in them was 318 ng/L with range of 26 – 1100 ng/L.

These results were used as a reference for the values obtained in the precipitation samples collected and analysed specifically for purpose of the research activity described in the summarised publication in 2011 at following three locations in Switzerland:

- Dübendorf, a sub-urban site in northern Switzerland;
- Magadino, a rural site in southern Switzerland,
- Rigi-Seebodenalp – an elevated rural site in the foothills of the northern Alps.

From each sampling site 33 precipitation samples were analysed for the content of TFA. The determined mean concentrations were 126 ng/L for the Dübendorf site, 315 ng/L for Magadino site and 198 ng/L for Rigi-Seebodenalp site.

The result of another, broader monitoring study aimed on the determination of the concentrations of TFA in various water samples in Switzerland were presented in the following publication:

Berg M., Müller S. R., Mühlemann J., Wiedmer A., Schwarzenbach R. P., „*Concentrations and Mass Fluxes of Chloroacetic acids and Trifluoroacetic acid in Rain and Natural Waters in Switzerland.*”; Environmental Science and Technology, 2000, **34** (13), 2675 – 2683;

The paper presented the results of the determination of the concentrations of various haloacetic acids, including TFA in water samples collected at various locations in Switzerland during the period of 1996 – 1997. The analysed matrices were: rain and snow – 73 samples, riverine water – 80 samples, midland lakes water – 20 samples, mountain lakes water – 8 samples, moor water – 3 samples, very old groundwater – 3 samples, all representing natural waters, as well as drinking water – 6 samples, swimming pools water – 4 samples, communal wastewater – 17 samples and industrial wastewater – 5 samples.

The determined levels of TFA in those samples were as follows:

- in rain-and snow-water samples the mean concentration of TFA was 151 ng/L and its range was <3 – 1550 ng/L;
- in riverine water samples the mean concentration of TFA was 87 ng/L and its range was 12 – 328 ng/L;
- in water sampled from midland lakes the mean concentration of TFA was 119 ng/L and its range was 37 – 204 ng/L;
- in water samples from mountain lakes the mean concentration of TFA was 141 ng/L and its range was 46 – 360 ng/L;
- in moor water samples the mean concentration of TFA was 107 ng/L and its range was 59 – 175 ng/L;
- in very old groundwater samples (having the average age of 15000 ± 1800 years) the mean concentration of TFA was <5;
- in drinking water samples the mean concentration of TFA was 71 ng/L and its range was 16 – 123 ng/L;
- in water samples from the swimming pools the mean concentration of TFA was 4800 ng/L and its range was 4100 – 5700 ng/L;
- in communal wastewater samples the mean concentration of TFA was 230 ng/L and its range was 90 – 600 ng/L;
- in industrial wastewater samples the mean concentration of TFA was 47300 ng/L and its range was <100 – 206000 ng/L.

Estimating the annual mass fluxes of TFA the authors stated that of the yearly influx of $240 \text{ g}/(\text{km}^2 \cdot \text{year})$, 96%, corresponding to $230 \text{ g}/(\text{km}^2 \cdot \text{year})$, came from wet deposition, while another 4% ($10 \text{ g}/(\text{km}^2 \cdot \text{year})$) from communal wastewater. That load in 62% ($150 \text{ g}/(\text{km}^2 \cdot \text{year})$) went to soil and groundwater recharge with no degradation observed and in 38% ($90 \text{ g}/(\text{km}^2 \cdot \text{year})$) was exported with riverine water.

As the conclusion of that research it was stated that although TFA was demonstrated to be not harmful to the aquatic ecosystems in concentrations up to 100 µg/L, its concentrations in the environment should be monitored because of risk posed to terrestrial and groundwater compartments.

Römpf and co-workers in their study, summarised already in this RAR under the point B.8.3.2., examined the concentrations of TFA in rain and fog samples collected at ecological research site in northeast Bavaria from 17 July 1998 to 24 March 1999. The median concentration of TFA in fog water samples – 85 in total, collected during the experimental period was 230 ng/L with range of 20 – 1900 ng/L. The concentrations of that compound in rain samples were relatively lower, with maximum of ~600 ng/L, but generally being <200 ng/L.

These results were presented in the publication:

Römpf A., Klemm O., Fricke W., Hartmut F., „*Haloacetates in Fog and Rain.*”; Environmental Science and Technology, 2001, **35** (7), 1294 – 1298.

The results of the monitoring of TFA in air and natural waters in Germany were also presented in another publication:

Jordan A., Frank H., „*Trifluoroacetate in the Environment. Evidence for Sources Other Than HFC/HCFCs.*”; Environmental Science and Technology, 1999, **33** (4), 522 – 527.

That publication was also summarised earlier in this Renewal Assessment Report, under the data point B.8.3.2.

TFA in that study was measured in three types of environmental matrices collected in Bayreuth from March 1995 to September 1996: air samples, rain water samples (collected at the university of Bayreuth's Botanical Garden and in the nearby forest) and river water collected in Bayreuth from Roter Main river.

The concentrations of TFA in air were in range of 0.01 – 0.125 ng/m³, with an average of 0.044 ng/m³. They were similar to those obtained for Zürich, Switzerland, in September 1995 and at Waldstein, Northern Bavaria, Germany, in June 1995.

In precipitation the level of TFA were in range 10 – 410 ng/L, with an average of 110 ng/L and in riverine water it ranged from 60 to 280 ng/L with the average concentration of 140 ng/L.

For comparative purposes may serve two publications presenting the concentrations of TFA in precipitation and fresh surface water bodies in North America.

Wujcik and co-workers examined the levels of TFA in precipitation and surface water in Nevada and California. The samples were collected in years 1996 and 1997 from three locations for precipitation and three SW catchments.

The samples of precipitation – rainfall, were collected at two sites in California – Rohnert Park and Selma, and one in Nevada - Reno. Also at two Californian sites were collected samples of fog. That type of samples were not collected in Nevada because of the lack of that phenomenon. Precipitation samples were collected from December 1996 to September 1997

For the monitoring of the concentrations of TFA in surface water three water systems were selected:

- Truckee river from its sources in Sierra Nevada Mountains range – a tributary stream to Lake Tahoe to the terminal endpoint in Pyramid Lake;
- Carson River from its sources in the high Sierra Nevada Mountains to its ending at Stillwater National Wildlife Refuge;
- Mono Lake with its tributaries.

Fogwater was collected in duplicate using two portable high-volume fog sampling units. Six fog samples were collected on the site at Rohnert Park and twenty one on Selma sampling site.

The rain samples were collected in duplicate in 500-mL amber bottles. The total volume of the sample collected during one event was 100 – 800 mL. 31 samples were collected on Rohnert Park site, 23 on Selma site and 6 on Reno site.

The samples of surface water were collected in duplicate by submersing 1000-mL amber-glass bottles in the sampled water body near its shore. In case of Truckee River system 34 samples were collected, of which 19 samples upstream of Reno, 8 downstream of Reno and 7 from Pyramid Lake. From the Carson River system 20 samples were collected, of which 6 upstream of Carson City, 8 downstream of Carson City and 6 in Stillwater National Wildlife Refuge. 12 samples were collected in Mono Lake system, of which 2 from Rush Creek and 10 from Mono Lake.

Samples were filtered under vacuum through a GF/F filter, then their pH and conductivity was measured.

Samples having a conductivity <500 µS were subjected to direct anion exchange extraction. The extracts were derivatised and analysed by GC-ECD method for the content of TFA.

Samples having a conductivity > 500 µS were processed by liquid-liquid extraction and the extracts were subjected to GC-ECD analysis for the content of TFA.

The LOQ of the analytical method was set to 36 ng/L for 400-mL sample.

The results of the quantification of TFA in precipitation – fog and rain, were following:

- for samples collected in Rohnert Park, California, the mean concentration of TFA in rain water was 46.6 ng/L with range of 25.1 – 158 ng/L (in nine samples concentrations of that compound were the method's <LOQ) and in fog water the mean concentration of TFA was 723 ng/L with range 86.6 – 809 ng/L;
- for samples collected in Selma, California, the mean concentration of TFA in rain water was 63.9 ng/L with range of 20.7 – 463 ng/L (in five samples concentrations of that compound were the method's <LOQ) and in fog water the mean concentration of TFA was 689 ng/L with range 101 – 1390 ng/L;
- for samples collected in Reno, Nevada, the mean concentration of TFA in rain water was 136 ng/L with range of 108 – 763 ng/L.

The results of the determination of TFA in surface water are presented below, individually for each analysed water system.

The concentrations of TFA in Truckee River system were following:

- upstream of Reno the mean concentration of TFA was 28.9 ng/L with range of 12.8 – 47.7 ng/L (in 17 of 19 analysed samples the concentrations were < LOQ of 36 ng/L, so in the publication that value was indicated as bearing the high level of uncertainty);
- downstream of Reno the mean concentration of TFA was 50.8 ng/L with range of 31.0 – 66.5 and the concentration <LOQ recorded in one analysed sample;
- in Pyramid Lake the mean concentration of TFA was 79 ng/L with range 77.1 – 95.1 ng/L.

The concentrations of TFA in Carson River system were following:

- upstream of Carson City the mean concentration of TFA was 45.3 ng/L with range 36.6 – 60.5 ng/L;
- downstream of Carson City the mean concentration of TFA was 84.2 ng/L with range 76.9 – 154 ng/L;
- in water samples from Stillwater National Wildlife Refuge the mean concentration of TFA was 432.5 ng/L with range 314 – 472 ng/L.

Finally, in Mono Lake system the concentrations of TFA were following:

- in Rush Creek the mean concentration of TFA was 51.0 ng/L with range 50.1 – 52.0 ng/L;
- in Mono Lake the mean concentration of TFA was 192 ng/L with range 186 – 227 ng/L.

Additionally the yearly inputs of TFA into the terminal lakes in Truckee River system – Pyramid Lake, and Mono Lake system – Mono Lake, were estimated using the obtained results. The estimation was performed for two scenarios – **Scenario 1** in which dry deposition into the terminal lake was determined from the results of the experiment carried out by Zehavi and Seiber on the open reservoir flux, and **Scenario 2**, in which dry deposition was based on the estimates provided by Grosjean.

The results of that estimation for the Mono Lake were following:

- for **Scenario 1** the total content of TFA in lake was 677 kg, yearly inputs: from streams – 8.4 kg, from wet deposition onto lake – 6.9 kg, from dry deposition – 146.2 kg, what yielded in the total yearly input of 161.5 kg and the estimated time to accumulate TFA to the level of observed concentrations: 4.2 years;
- for **Scenario 2** the total content of TFA in lake was 677 kg, yearly inputs: from streams – 8.4 kg, from wet deposition onto lake – 6.9 kg, from dry deposition – 79.4 kg, what yielded in the total yearly input of 94.7 kg and the estimated time to accumulate TFA to the level of observed concentrations: 7.2 years.

The results of that estimation for the Pyramid Lake were following:

- for **Scenario 1** the total content of TFA in lake was 2478 kg, yearly inputs: from streams – 24.0 kg, from wet deposition onto lake – 13.3 kg, from dry deposition – 365.8 kg, what yielded in the total yearly input of 403.1 kg and the estimated time to accumulate TFA to the level of observed concentrations: 6.2 years;
- for **Scenario 2** the total content of TFA in lake was 2478 kg, yearly inputs: from streams – 24.0 kg, from wet deposition onto lake – 13.3 kg, from dry deposition – 153.0 kg, what yielded in the total yearly input of 190.3 kg and the estimated time to accumulate TFA to the level of observed concentrations: 13 years.;

In the analysis of the obtained results the man-made sources – mainly HFCs and HCFCs generated locally in the urban areas and transported from more distant locations, like San Francisco Bay area, were indicated as a possible source of TFA in the atmosphere and hence in precipitation. Also the processes occurring in the atmosphere were indicated as possible factor driving the distribution of TFA between phases.

The monitoring of TFA in the systems of Truckee River and Carson River showed a substantial increase downstream of the urbanized areas of Reno and Carson City respectively. That may indicate the significant contribution of these areas as anthropogenic sources of TFA.

The results of the study were presented in the following publication:

Wujcik C., Cahill T. M., Seiber J. N., “*Determination of Trifluoroacetic Acid in 1996 – 1997 Precipitation and Surface Waters in California and Nevada.*”; Environmental Science and Technology, 1999, **33** (10), 1747 – 1751.

In Canada Scott and co-workers carried out in 1997 the research project aimed on the determination of the levels of TFA in precipitation and lake water. The precipitation samples were taken at seven different locations across Canada (from west to east of the country): Saturna Island in British Columbia, Snare Rapids in Northwest Territories, Ester on the borderline between Alberta and Saskatchewan, Island Lake in Manitoba, Algoma in Ontario, on the Great Lakes, Chapais in Quebec and Kejimikujik in New Brunswick. Additionally two sampling points for precipitation were set at the Laurentian Great Lakes – Burnt Island and Point Petre.

The samples of lake water were taken from four lakes associated with the sampling points for precipitation – Loon Lake in British Columbia, Great Slave Lake in the Northwest Territories, Lake Winnipeg in Manitoba and Lake Kejimikujik in New Brunswick, as well as from ten locations on the Laurentian Great Lakes.

Additionally were analysed the drinking water samples from the city of Hamilton, Ontario, and the samples of cold tap water from Burlington city.

The precipitation samples were collected and analysed as 24-hours samples in polyethylene bags. The samples of lake water were taken in triplicate form 1 metre below the surface using Go-flo bottles. In the laboratory the samples were processed and, after derivatisation, analysed for the content of selected haloacetic acids – TFA, MCA, DCA, TCA and MBA, using GC-MS. For TFA the LOD was set to 0.5 ng/L.

The results of the determination of TFA in precipitation samples were following:

- for the **Saturna Island** sampling site: the number of precipitation events recorded on site was 9, the average concentration of TFA in collected samples was 29 ng/L with range of <0.1 – 170 ng/L;
- for the **Snare Rapids** sampling site: the number of precipitation events recorded on site was 4 with the average concentrations of TFA in collected samples of <0.1 ng/L;
- for **Ester** sampling site: the number of precipitation events recorded on site was 6, the average concentration of TFA in collected samples was 85 ng/L with range of 38 – 160 ng/L;
- for **Island Lake** sampling site: the number of precipitation events recorded on site was 9, the average concentration of TFA in collected samples was 40 ng/L with range of <0.1 – 59 ng/L;
- for **Algoma** sampling site: the number of precipitation events recorded on site was 11, the average concentration of TFA in collected samples was 48 ng/L with range of 4 – 120 ng/L;
- for **Chapais** sampling site: the number of precipitation events recorded on site was 11, the average concentration of TFA in collected samples was 24 ng/L with range of <0.1 – 69 ng/L;
- for **Kejimikujik** sampling site: the number of precipitation events recorded on site was 11, the average concentration of TFA in collected samples was 43 ng/L with range of <0.1 – 130 ng/L;

In case of precipitation samples collected on two sites at the Laurentian Great Lakes, the fluxes of TFA were reported together with the level of precipitation recorded for the period, for which the flux was determined. In case of the sampling site Burnt Island the results were following:

- for the period 20. 10. – 17. 11. 1997 the amount of precipitation was 32 mm and the flux of TFA 2330 ng/m²;
- for the period 17. 11. – 15. 12. 1997 the amount of precipitation was 32 mm and the flux of TFA 1260 ng/m²;
- for the period 15. 12. 1997 – 12. 01. 1998 the amount of precipitation was 32 mm and the flux of TFA <3.8 ng/m².

The results obtained for the sampling site Piont Petre were as follows:

- for the period 21. 10. – 18. 11. 1997 the amount of precipitation was 80 mm and the flux of TFA 3260 ng/m²;
- for the period 18. 11. – 16. 12. 1997 the amount of precipitation was 26 mm and the flux of TFA 1550 ng/m²;
- for the period 16. 12. 1997 – 13. 01. 1998 the amount of precipitation was 88 mm and the flux of TFA 1950 ng/m²;

The analysis of the concentration of TFA in lake water from four Canadian regional lakes gave the following results:

- in Loon Lake the concentration of TFA was <0.5 ng/L;
- in Great Slave Lake the concentration of TFA was in range <0.5 – 10 ng/L;
- in Lake Winnipeg the concentrations of TFA were in range 100 – 360 ng/L;
- in Lake Kejimikujik the concentrations of tFA were in range 12 – 28 ng/L.

High concentrations of TFA in water samples from Winnipeg Lake, in comparison to other lakes, were explained by its location downstream from the possible urban sources, while the three remaining lakes were situated in isolated locations and were not subjected to industrial or urban activity.

The results of the determination of TFA in Laurentian Great Lakes were following:

- in samples from Lake Superior the concentrations of TFA were 0.5 ng/L and 2 ng/L;
- in samples from Lake Huron the concentrations of TFA were 100 ng/L and 110 ng/L;
- in samples from Georgian Bay the concentration of TFA was 74 ng/L;
- in samples from Lake Erie the concentrations of TFA were 130 ng/L and 140 ng/L;

- in samples from Lake Ontario the concentrations of TFA were 130 ng/L and 150 ng/L;
- in samples of drinking water from Hamilton city the concentration of TFA was 183 ng/L;
- in samples of drinking water from the city of Burlington the concentration of TFA was 120 ng/L.

Additionally in Lake Superior the seasonal variation in concentrations of haloacetic acids was examined. For that purpose the water samples from three different locations were taken and analysed at spring and in summer. For TFA the results were following:

- for sampling site located in the western bassin (site 1) the concentration of TFA at spring was 16 ng/L and in summer 2 ng/L;
- for sampling site located in mid lake (site 2) the concentration of TFA at spring was 18 ng/L and in summer 3 ng/L;
- for sampling site located in eastern bassin (site 3) the concentration of TFA at spring was 17 ng/L and in summer <0.5 ng/L.

In conclusions it was stated that the levels of TFA, when that compound was detected in analysed samples, were comparable to the results obtained for Europe and North America (in general). It was also indicated that the atmospheric transport and deposition may play a significant role in distribution of TFA in the environment of Canada, including the aquatic compartment. Finally, it was postulated that the urban centers as well as such activities like pyrolysis of perfluorinated plastics may be a substantial sources of the emission of TFA to the environment.

Monitoring data: short summary:

The Applicant addressing the problem of the monitoring of Flufenacet in the environment stated that there were numerous monitoring programmes carried out by the competent authorities, into which that compound and its transformation products were included. These data however were not available, so the Applicant was not able to identify and present them. For that reason the presentation of the monitoring data was limited to the available literature data. The Applicant was able to identify three papers presenting the results of the monitoring studies for Flufenacet and its degradation products. One of them was aimed on the determination of the several active substances of the plant protection products in the watercourse of the small agricultural catchment located in Germany, other two presented the results of the determination of TFA (Trifluoroacetic acid) – the most persistent degradate of Flufenacet, in Oceans which are considered to be the terminal environmental sink of TFA.

RMS performing the repeated literature search was able to identify several publications presenting their results of the monitoring studies in which Flufenacet and two its major degradates – FOE Oxalate and FOE Sulfonic acid were the target compounds.

The results may be divided into two groups, according to the geographical location of the monitoring studies. To none of them belong the results obtained in the monitoring studies carried out from 1999 until 2004 in USA and more specifically in Mid-Western States, the so-called corn-belt states, by USGS (US Geological Service) employees.

The extensive monitoring of groundwater sampled from 55 wells in Indiana in 2000 showed that neither Flufenacet, nor its degradates FOE Oxalate and FOE Sulfonic acid were detected in analysed samples. The limit of detection in that study was set to 0.05 µg/L. Also neither Flufenacet nor its degradates – FOE Oxalate and FOE Sulfonic acid were found in groundwater analysed in a similar monitoring project carried out in Iowa in 2001, in which samples from 86 municipal wells were analysed for the content of several active substances of the plant protection products and their degradates.

The analysis of the concentrations of Flufenacet and its degradation products – FOE Oxalate and FOE Sulfonic acid in the Mississippi River basin showed that these compounds, if detected, were present sporadically and in low concentrations. In the study carried out in the year 2000 and aimed on the determination of the levels of selected chloroacetanilide plant protection products and their degradates in surface water bodies of the Mississippi River catchment, Flufenacet was detected in 3% of 39 analysed samples in maximum amount of 0.12 µg/L, while FOE Oxalate and FOE Sulfonic acid were not detected at all in 38 samples analysed for their presence. Samples were taken at for key junctures of the Mississippi River Basin. In another monitoring study on Mississippi River catchment with one sampling point set at Baton Rouge, LA, and carried out at the same period (1999 – 2000), neither Flufenacet nor FOE Oxalate were detected in any analysed samples, while FOE Sulfonic acid was detected in amounts > 0.05 µg/L in two of them (6% of analysed samples).

Finally, in 2002 within the big monitoring programme, the concentrations of Flufenacet, FOE Oxalate and FOE Sulfonic acid were monitored, alongside other herbicides, their degradates and pharmaceuticals, in 51

streams selected as representative for nine Mid-Western states of the USA. Samples were collected at spring during pre-emergence period (May – June), in summer during post-emergence period (June – July) and during the harvest period in autumn (September – November). Flufenacet was detected in 11 of 51 pre-emergence samples with the max amount 0.93 µg/L, 9 of 52 post-emergence samples with max amount 1.6 µg/L and only one of 51 harvest-period samples. It was found more frequently in samples taken from Nebraskan streams, while not detected at all during the whole experimental period in those from Indiana, Minnesota and Wisconsin.

The frequency of detection of FOE Oxalate and FOE Sulfonic acid was much lower – the compounds were found during each sampling period in max. 4 samples of analysed 51/52. Their maximum concentrations were up to 0.09 µg/L in pre-emergence samples, up to 0.18 µg/L in post-emergence samples and up to 0.13 µg/L in harvest samples.

Finally in the study in which the concentrations of Flufenacet were monitored in precipitation water in four agricultural catchments across the USA that compound was detected only in two samples taken in Nebraska in May.

For all those monitoring studies the method detection limit MDL, corresponding to LOQ, was 0.05 µg/L.

In case of Europe the quantitative results of the monitoring of the residues of Flufenacet in water samples were available for two countries – Germany and Switzerland. Additionally the qualitative results were available for the Netherlands.

The results of the monitoring study performed for the small rural catchment of Lamspringe in Lower Saxony, Germany, in years 1998 – 2000 showed that Flufenacet, applied to the fields in the research area in 1999 and 2000 was detected in stream water samples collected only in the year 2000. It was detected in three samples, in maximum amount 0.07 µg/L, slightly above the LOQ = 0.05 µg/L set for the analytical method used in the study.

In another study, in order to validate the developed novel analytical method for determination of polar degradates of organic micropollutants in water samples, including FOE Oxalate and FOE Sulfonic acid, 200 samples of natural water were analysed, of which six of waste water, fourteen of surface water, another fourteen of deep well water, 156 of groundwater and seventeen of drinking water. All samples were collected in Rhine and Rhur regions of the North Rhine-Westphalia, Germany. In case of all analysed samples of waste water, surface water, deep well water, and groundwater the concentrations of both FOE Oxalate and FOE Sulfonic acid were well below 0.05 µg/L, usually in range of 0.00 – 0.25 µg/L. Only in case of drinking water samples the concentrations of FOE Sulfonic acid were above the level of 0.05 µg/L, but still below the threshold value of 0.1 µg/L.

In case of Switzerland the results of monitoring were available for the catchment of the river La Petite Glâne, located in western Switzerland in the canton Vaud, for the Lake Constance – the example of the interboundary landlocked catchment collecting surface water from three countries, and five small- to medium in size river catchments located across Switzerland, displaying at least partly agricultural character. All results are quite recent, being collected in the first and second decades of the 21st century, between the years 2008 and 2012.

The monitoring of the surface water samples collected in the catchment of the river La Petite Glâne, carried out from May to October of the 2008 with aim of determination of selected active substances of the plant protection products and their degradates in the water collected after rainfall events from the stream passing through the catchment, showed that the highest concentrations of Flufenacet in analysed water were recorded at spring, during application period of that compound. The median concentration was 0.071 µg/L with range 0.026 – 350 µg/L. Much lower were concentrations recorded after the rainfall events in summer and at autumn – the median values were 0.008 µg/L and 0.004 µg/L respectively. In case of the two monitored degradation products – FOE Oxalate and FOE Sulfonic acid their levels in stream water samples collected after the rainfall events were generally much lower, in case of FOE Oxalate not surpassing 0.003 µg/L and for FOE Sulfonic acid 0.008 µg/L. It was noticed that while in case of FOE Oxalate the highest concentrations were recorded for the application period of Flufenacet – at spring, in case of FOE Sulfonic acid the highest levels were recorded in autumn, what may reflect the temporal formation patterns and persistence of these compounds in soil.

The levels of those three compounds in the base-flow samples – collected in periods between the occurrence of the rainfall events were very low, not surpassing 0.01 µg/L. Additionally the samples of groundwater collected in and around the catchment were analysed for the content of the compounds of concern. It was stated that in none of the analysed samples Flufenacet, FOE Oxalate or FOE Sulfonic acid were detected. The detection (LOD) and quantification (LOQ) limits for those compounds were set, for the purpose of that study, as follows:

- for Flufenacet LOD = 0.3 ng/L and LOQ = 1.0 ng/L;
- for FOE Oxalate LOD = 0.3 ng/L and LOQ = 1.0 ng/L;
- for FOE Sulfonic acid LOD = 0.3 ng/L and LOQ = 1.0 ng/L.

In another study, aimed on the determination of the levels of several organic micropollutants in the surface water collected from five river catchments located across Switzerland – Fürtbach river, Limpach river, Mentue river, Salmsacher river and Surb river, the results obtained for Flufenacet, FOE Sulfonic acid and FOE Oxalate were following:

Flufenacet was detected in samples from all five rivers, with average detection frequency of 53% and the maximum concentration of 290 ng/L. In individual rivers those parameters looked as follows:

- in Fürtbach river it was detected in 56% of the analysed samples with maximum concentration of 80 ng/L;
- in Limpach river it was detected in 78% of the analysed samples with maximum concentration of 160 ng/L;
- in Mentue river it was detected in 67% of the analysed samples with maximum concentration of 35 ng/L;
- in Salmsacher Aach river it was detected in 11% of the analysed samples with maximum concentration of 31 ng/L;
- in Surb river it was detected in 56% of the analysed samples with maximum concentration of 290 ng/L.

FOE Sulfonic acid was detected in samples from all five rivers, with average detection frequency of 62% and the maximum concentration of 38 ng/L. In individual rivers those parameters looked as follows:

- in Fürtbach river it was detected in 44% of the analysed samples with maximum concentration of 14 ng/L;
- in Limpach river it was detected in 100% of the analysed samples with maximum concentration of 30 ng/L;
- in Mentue river it was detected in 89% of the analysed samples with maximum concentration of 38 ng/L;
- in Salmsacher Aach river it was detected in 44% of the analysed samples with maximum concentration of 7.9 ng/L;
- in Surb river it was detected in 33% of the analysed samples with maximum concentration of 17 ng/L.

FOE Oxalate was not detected in any of the analysed water samples.

The quantitation limits for these compounds were following: for Flufenacet LOQ = 3 ng/L, for FOE Oxalate LOQ = 7 ng/L and for FOE Sulfonic acid LOQ = 3 ng/L.

The analysis of the concentrations of Flufenacet, FOE Oxalate and FOE Sulfonic acid in water samples from lake Constance was carried out as a preliminary part of the study aimed on the determination of the concentrations of selected micropollutants in that water body and in its tributaries. In none of the analysed samples, collected from four locations on the lake Constance the compounds of concern were detected.

In another study reporting results of the monitoring of Flufenacet in the borderline surface water bodies in the Netherlands it was stated that Flufenacet was detected in the borderland zones, but not hinterland. On that basis, as Flufenacet was not a compound authorised to be used in the Netherlands, but having such authorisation in the neighbouring countries – Belgium and Germany, it was stated that it may be prone to transboundary transport in surface water. However, the estimations provided in that study were rather qualitative than quantitative.

On the basis of the obtained monitoring results derived from the open-source literature data it may be stated that neither Flufenacet nor its two degradates – FOE Oxalate and FOE Sulfonic acid are expected to be present in natural water samples in amounts significantly surpassing the level of 0.1 µg/L – the drinking water limit.

Of the other degradation products of Flufenacet identified as major the monitoring data are available only for Trifluoroacetic acid – TFA, the compound considered to be common organic pollutant of the environment coming, originating from various sources.

As TFA is considered to be the organic pollutant found primarily in atmosphere as a result of the photooxidative transformation of several halogenated compounds, such as HCFs and HFCFs and is removed from there by means of wet and dry deposition, several studies were carried out with aim of the determination of the concentrations of trifluoroacetate in the atmospheric water – rain- and fog water. The concentrations of TFA determined in rain water are in general lower than those measured in fog water, usually not surpassing 500 ng/L on average. They strongly depend on the character of region, where they were collected, being higher in urbanised and industrial regions. The levels of TFA in fog samples were sometimes of the order of magnitude higher than those in water samples collected at the same sampling sites.

In the open-source literature oceans are indicated as the terminal environmental sink of the TFA with the surface water bodies, such as rivers, being the intermediate collectors. Also landlocked lakes were indicated as a possible sink for TFA.

In the global ocean the level of TFA was estimated to be, on the basis of the available results of the monitoring studies, ~200 ng/L and quite stable. The levels of TFA determined in fresh surface water bodies were similar, but it was indicated that in some landlocked lakes they may be higher. For example the results of the determination of the concentrations of TFA in Canadian lakes carried out in the year 1997 showed that the concentrations of TFA in those SW bodies were in range of <0.5 ng/L – 360 ng/L, being highest in lakes located in the highly urbanised and industrialised areas with high level of antropopression.

It shall be indicated that in all available publication presenting the results of the monitoring studies for TFA the man-made sources were indicated as a primary sources of that compound in inland environment. However, it was also indicated that in case of the oceans, and possibly also some inland ecosystems there may be some, still not identified natural sources contributing to the overall concentrations of TFA in the geosphere.

B.8.6 – Open literature review

Complying with the data requirement set in the Article 8 point 5 of the Regulation (EC) 1107/2009, the Applicant submitted the following report presenting the results of the search of the scientific peer-reviewed open literature, according to EFSA Guidance Document “Submission of scientific peer-reviewed open literature for approval of pesticide active substances under Regulation (EC) No 1107/2009 [EFSA Journal; **2011**; 9(2); 2092]:

Study 1:

Report: Derpmann J., Teubner. L.; **2014**: “Summary of the literature data for Flufenacet”; Bayer CropScience; Document MCA: Section 9 Literature Data Flufenacet (unpublished document No. M-482180-01-1); issuing date: 2014. 03. 18;

Guidelines: EFSA Guidance Document “Submission of scientific peer-reviewed open literature for approval of pesticide active substances under Regulation (EC) No 1107/2009 [EFSA Journal; **2011**; 9(2); 2092]

GLP: no, not required

RMS comments: The literature search was performed in line with the recommendations of the EFSA Guideline, therefore, from the formal point of view, it can be considered acceptable. However, the Thorough examination of the report showed that the correctness of the detailed assessment cannot be fully verified, as for the rejected papers only their citation data (authors, titles and data on periodicals in which they were published) were provided. As a results RMS performed additional literature search, the results of which are presented below the summary of the report provided by the Applicant.

Summary:

The aim was to carry out the literature search in a comprehensive and transparent way, in order to fulfil the data requirement set, as mandatory for the AIR 3 compounds (such as flufenacet), by, at the time of submission, Regulation (EU) No 844/2012, subsequently repealed by the Regulation (EC) 283/2013, but in which this requirement was maintained.

It was performed in line with the EFSA Guidance document on the “Submission of scientific peer-reviewed open literature for the approval of pesticide active substances under Regulation (EC) No 1107/2009” published in EFSA Journal; **2011**; 9(2); 2092 (further referred to as EFSA Guidance document on literature search).

Presenting the adopted search strategy the Applicant stated that the evaluation was based on the examination of the abstracts of all references identified as potentially relevant. Patents were not considered in the literature search, because they are not included into the definition of “scientific peer-reviewed open literature”.

The literature search covered the period of thirteen years predating the submission - from the 1st January 2000 to the 13th November 2013.

Several data bases were used by the Applicant to perform the search. Their list is provided below, on figure B.8.6_CA-1 (table reproduced from the report submitted by the Applicant).

Table 1: List of data bases for the literature search flufenacet and date of last database update

Database Name	Trifluoroacetic acid (C10)	Flufenacet and metabolites (except C10)
Agricola	2013-10-22	2013-11-05
Biosis	2013-10-30	2013-11-06
CABA	2013-10-30	2013-11-13
Chemical Abstracts	2013-11-01	2013-11-12
Derwent Drug File (DRUG)	2013-10-31	2013-11-07
EMBASE	2013-11-01	2013-11-12
Exlibase	2013-10-28	2013-11-11
IPA	2013-10-16	2013-11-04
Medline	2013-11-02	2013-11-12
Pascal	2013-10-28	2013-11-11
PQSciTech	2013-10-18	2013-11-12
Registry	2013-10-31	2013-11-11
Scisearch	2013-10-28	2013-11-11
Toxcenter	2013-10-29	2013-11-12
Ubidat	2013-08-14	2013-08-14
FSTA	2013-10-28	2013-11-11

Figure B.8.6_CA-1: List of data bases used by the Applicant in literature search for Flufenacet (reproduced from the Applicant’s report).

It was indicated that as a preferred provider was selected STN – a scientific information platform hosted by CAS, division of the American Chemical Society.

The search was performed using the following key pieces of information: IUPAC name, CAS name/number, common names, codes and abbreviations, molecular structure, molecular formula, molar mass and other available names and/or codes.

The example of search input parameters is given below (for flufenacet) on figure B.8.6_CA-2.

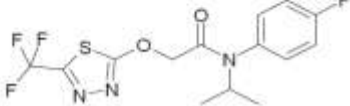
i) Flufenacet	
IUPAC name:	N-(4-fluorophenyl)-N-isopropyl-2-([5-(trifluoromethyl)-1,3,4-thiadiazol-2-yl]oxy)acetamide
CAS number:	142459-56-3
STN Query	(142459-56-3 OR FLUFENACET OR FLUTHIAMID OR FLUTHIAMIDE OR THIAFLUAMIDE OR FOE 504) OR (DRAGO OR DRADO OR CADOU OR TIARA OR FIREBRID OR FOEBURI OR HEROLD OR ANTILOPE(W)(RTM OR R OR TM)) AND PY>1999 NOT PDT
Molecular structure:	

Figure B.8.6_CA-2: The example of search input parameters used by the Applicant in the literature search for Flufenacet (reproduced from the Applicant's report).

The search was performed for Flufenacet and its following degradation products: **FOE oxalate (M1)** – code C01, **FOE sulfonic acid (M2)** – code C02, **FOE-Thiadone (M9)** – code C03, **FOE Methylsulfone (M7)** – code C04, **FOE Thioglycolate sulfoxide** – code C05, **3-((2-((4-fluorophenyl)(isopropyl)amino)-2-oxoethyl)sulfinyl)-2-hydroxypropanoic acid** – code C06, **FOE-conjugate with cysteine** – code C07, **FOE trifluoroethane sulfonic acid** – code C08, **FOE Methylsulfide (M5)** – code C09 and **Trifluoroacetic acid (TFA, M45)** – code C10.

In case of Flufenacet and its degradation products bearing the codes C01 – C09 no keyword filter was used. Such filter was however used in case of TFA, for which 53 chains of refining key words (L2 – L54), encompassing all areas of evaluation, were used. They were all listed by the Applicant in the Appendix II to the study report. In case of environmental fate and behaviour at least 11 chains of refining key words (L44 – L54 in the Appendix II) may be considered as directly or indirectly related to the search in that area.

The whole search and evaluation procedure followed the conceptual scheme presented below on the figure B.8.6_CA-3.

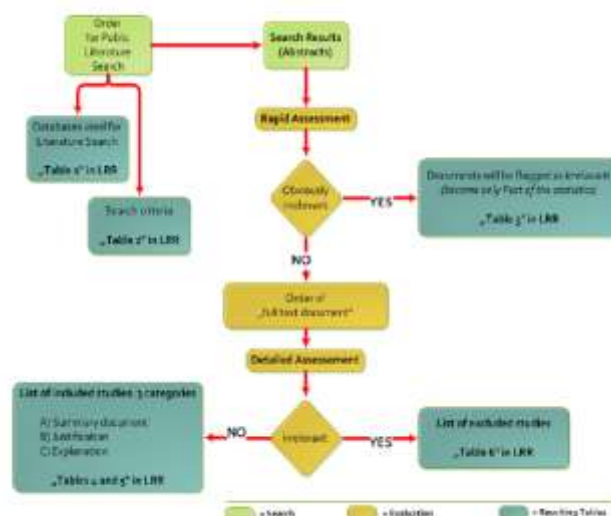


Figure B.8.6_CA-3: The conceptual scheme of search and evaluation procedure used in the literature search for Flufenacet (reproduced from the Applicant's report).

Initially 3489 publications were found, of which 369 were those for flufenacet and 3120 for its degradation products. Of that number 3089 were for TFA (including salts). No publications were found for either FOE Methylsulfide (M5) or FOE Trifluoroethane sulfonic acid. Of the remaining 31, 11 publications were found for FOE oxalate (M1) and the same number for FOE sulfonic acid (M2), 4 for FOE-Thiadone (M9) and 2 for FOE Methylsulfone (M7). In case of the remaining four degradation products, for each of them 1 potentially relevant publication was found.

Evaluation of the search results was performed according to the rules set by the *EFSA Guidance document on literature search*.

At the “Rapid assessment” stage the following topics were used in assessment of the relevance of publications (considered as the exclusion criteria):

- Efficacy;
- Analytical method development;
- New ways of synthesis;
- Studies on a molecular level, which cannot be related to risk assessment (RA);
- Non-EU monitoring studies;
- Publications in non-EU language without English abstract;
- Abstract refers to a conference contribution and does not contain data, full text not available;
- Not relevant due to missing information: Studies with target organisms.

Using these criteria the Applicant excluded from the further assessment as not relevant 278 of 369 publications found for Flufenacet, 3036 of 3089 of those found for TFA, 8 of 11 found for FOE Oxalate, 7 of 11 found for FOE sulfonic acid, 2 of 4 found for FOE-Thiadone and all found for four remaining degradation products. The remaining 153 publications – 91 for Flufenacet and 62 for its degradation products (including 53 for TFA) underwent the detailed assessment based on the examination of their full text versions.

The assessment criteria, considered as the non-relevance criteria, adopted at that stage were following:

- Target substance not a test item;
- Conversion into units useful for RA not possible;
- Study design/test system not sufficiently described;
- Study design/test system not adequate;
- Study design/test system not relevant to EU data requirements;
- Test system not relevant to representative uses/GAPs;
- Test method does not cover the right targets;
- Test material deviates from composition of BCS active ingredient/product;
- Findings not related to a certain test system;
- No endpoint can be derived;
- Observations are not attributable (i.e. ecotox) to a specific substance;
- Effects are caused by non-relevant route of exposure;
- Observations cannot be transferred into an endpoint;
- The information is already available in other peer-reviewed articles.

As a result of that detailed assessment of 91 of the publications for flufenacet qualified for the second stage, 89 were rejected and two considered as relevant or of unclear relevance. Of 153 publication for degradation products evaluated at the “Detailed assessment” step only seven were found relevant or of unclear relevance, all of them were the publications for TFA. In total 9 publications were found relevant or of unclear relevance and included into the dossier, as inform the results of the publication selection process presented in the Table 3 of the Applicant’s report.

The results of the detailed assessment were presented in three separate tables, in line with the recommendations given in the *EFSA Guidance document on literature search*. Tables 4 and 5 contain the relevant publications included into the dossier after the detailed assessment of full-text documents for relevance, ordered by data requirement (Table 4) and by authors (Table 5). These Tables contain 7 publications each.

In Table 6 were listed all remaining publications evaluated at the “Detailed assessment” step, but found not relevant. The table contains 137 positions arranged in alphabetical order with regard to their first authors. For each of the listed publication their full citation data were provided together with a short rationale for their non-relevance.

RMS noticed two discrepancies between the results presented in the Table 3 (general results of the assessment) and those given in Tables 4-6.

Of the 9 publications declared as relevant or potentially relevant, two were not included in the final list, one for the active substance and another for the degradation product TFA. The Applicant did not explain the reason for that difference in number of relevant publications.

It was also stated that the Table 6 lists only 137 publications, while their number should be higher – 144. This difference may however be explained by the fact that, as declared the Applicant, double entries, resulting from the separated search performed for the compounds, were removed from the Table 6.

Below are presented the results of the detailed assessment of the publications found during the literature search. They are given in tabularised form. First table – B.8.6_CA-1, provides the list of publications considered not relevant by the Applicant. RMS decided to maintain the format of the table proposed by the Applicant. At the same time the publications listed in that table were limited by the RMS to those, the title of which indicated that they were related to the assessment of the environmental fate and behaviour of flufenacet, according to the data requirements set by the Regulation (EC) 283/2013. It shall be noted that the provided list, consisting of 41 entries, may not be complete, or may contain the publications not fully relevant to this area of assessment, as Applicant compiling that list provided nor full neither texts nor even the summaries of rejected publications. That fact also significantly complicated the RMS's task of verification of the appropriateness of the justifications provided by the Applicant, what resulted in repeated literature search performed by the RMS, described below that summary.

Table B.8.6_CA-1: Results of the “Detailed assessment” stage of the literature search – publications not included into the dossier on the basis of their non-relevance (table reproduced from the Applicant's report, modified by the RMS).

Author(s)	Year	Title	Source	Reason(s) for not including publication in dossier
Barron, Leon; Paull, Brett [Reprint Author]	2004	Determination of haloacetic acids in drinking water using suppressed micro-bore ion chromatography with solid phase extraction.	Analytica Chimica Acta, (September 27 2004) Vol. 522, No. 2, pp. 153-161. print. ISSN: 0003-2670 (ISSN print).	Findings not related to a certain test system
Bazooobandi, M.; Yaduraju, N. T.; Kulshrestha, G.	2000	Analysis of flufenacet in soil, wheat grain and straw by gas chromatography	Journal of Chromatography, A (2000), 886(1+2), 319-322	The article does not contain information related to the substance of concern, as flufenacet was not detected in any of the investigated water samples and is therefore assessed as irrelevant.
Brimblecombe P (Reprint) Lifongo L L; Bowden D J	2004	Photodegradation of haloacetic acids in water	CHEMOSPHERE, (APR 2004) Vol. 55, No. 3, pp. 467-476. ISSN: 0045-6535.	The article does not contain information related to the substance of concern
Campagna, G.; Paci, F.; Fabbi, A.; Rapparini, G. Editor(S): Brunelli, A.; Canova, A.; Collina, M.	2006	Percolation of acetochlor, dimethenamid, flufenacet and s-metolachlor applied in columns. Studio in colonna della percolazione di alcuni diserbanti residuali del mais.	Giornate Fitopatologiche 2006, Riccione (RN), 27-29 marzo 2006. Atti, volume primo (2006) , pp. 591-598.	The test design used does not fulfill the requirements of current test guidelines. Furthermore, the test was performed with a formulation and hence, the results are not useable for RA of ai
Chen, Baiyang; Lee, Wontae; Westerhoff, Paul K.; Krasner, Stuart W.; Herckes, Pierre	2010	Solar photolysis kinetics of disinfection byproducts	Water Research (2010), 44(11), 3401-3409	The article does not contain information related to the substance of concern
Chiaia-Hernandez, Aurea C.; Krauss, Martin; Hollender, Juliane	2013	Screening of Lake Sediments for Emerging Contaminants by Liquid Chromatography Atmospheric Pressure Photoionization and Electrospray Ionization Coupled to High Resolution Mass Spectrometry	Environmental Science and Technology (2013), 47(2), 976-986;	The article does not contain information related to the substance of concern, as flufenacet was not detected in any of the investigated sediment samples.

Author(s)	Year	Title	Source	Reason(s) for not including publication in dossier
Conte, E.; Rossi, E.; Spera, G.; Pompei, V.; Carfi, F.; Spadoni, A. R.; Rosati, M.; Montereali, M. R.; Donnarumma, L.; Perconti, W.	2003	Presence of plant protection products in three agricultural areas of Regione Lazio	Communications in Agricultural and Applied Biological Sciences (2003), 68(4b), 865-874	The observations made are based upon unknown exposure. Flufenacet was only found in soil of agricultural fields and not in water or air. However, it is not known at all if FFA was used since the agricultural uses were not reported.
Deon, Jessica C.; Hurley, Michael D.; Wallington, Timothy J.; Mabury, Scott A.	2006	Atmospheric Chemistry of N-methyl Perfluorobutane Sulfonamidoethanol, C ₄ F ₉ SO ₂ N(CH ₃)CH ₂ CH ₂ OH: Kinetics and Mechanism of Reaction with OH	Environmental Science and Technology (2006), 40(6), 1862-1868	The article does not contain information related to the substance of concern
Finizio, A.; Villa, S.; Vighi, M.	2005	Predicting pesticide mixtures load in surface waters from a given crop.	Agric., Ecosyst. Environ., Volume 111, Issue 1-4, Page 111-118, Publication Year 2005	The article does not contain information related to the substance of concern
Godejohann, Markus; Berset, Jean-Daniel; Muff, Daniel.	2011	Non-targeted analysis of wastewater treatment plant effluents by high performance liquid chromatography-time slice-solid phase extraction-nuclear magnetic resonance/time-of-flight-mass spectrometry.	J. Chromatogr., A, Volume 1218, Issue 51, Page 9202-9209, Publication Year 2011	The investigation does not report results in values reflecting agreed determinants for the hazard or exposure characterization or risk assessment under Reg. EC No 1107/2009. Flufenacet not in the supplementary list of analysed compounds
Gupta, Suman; Gajbhiye, Vijay T.	2002	Effect of concentration, moisture and soil type on the dissipation of flufenacet from soil	Chemosphere (2002), 47(9), 901-906	The article descr. 4 tests in total. Only 1 was conducted in style of current guidelines. Its results are in line with known results, not influencing the RA. The other tests were performed at extreme conditions & are therefore not reliable & not usable for RA
Hamilton, M. C.; Woudneh, M.; Grace, R.	2007	Analysis of current use pesticides in environmental and wastewater samples by high resolution GC with high resolution mass spectrometric detection.	Organohalogen Compd., Volume 69, Page 600/1-600/4, Publication Year 2007	The article does not contain information related to the substance of concern, as flufenacet was not detected in any of the investigated water samples and is therefore assessed as irrelevant.
Henne, S.; Shallcross, D. E.; Reimann, S.; Xiao, P.; Boulos, S.; Gerecke, A. C.; Brunner, D.	2012	Environmental impacts of HFO-1234yf and other HFOs	Moving Towards Sustainability, ASHRAE/NIST Refrigerants Conference, Gaithersburg, MD, United States, Oct. 29-30, 2012 (2012), 13/1-13/13.	The observation made is based upon a route of exposure that cannot be considered representative for the intended use of the substance of concern
Henne, Stephan [Reprint Author]; Shallcross, Dudley E.; Reimann, Stefan; Xiao, Ping; Brunner, Dominik; Odoherly, Simon; Buchmann, Brigitte	2012	Future Emissions and Atmospheric Fate of HFC-1234yf from Mobile Air Conditioners in Europe.	Environmental Science and Technology, (FEB 7 2012) Vol. 46, No. 3, pp. 1650-1658.	The observation made is based upon a route of exposure that cannot be considered representative for the intended use of the substance of concern

Author(s)	Year	Title	Source	Reason(s) for not including publication in dossier
Hurley, M. D.; Sulbaek Andersen, M. P.; Wallington, T. J.; Ellis, D. A.; Martin, J. W.; Mabury, S. A.	2004	Atmospheric Chemistry of Perfluorinated Carboxylic Acids: Reaction with OH Radicals and Atmospheric Lifetimes	Journal of Physical Chemistry A (2004), 108(4), 615-620	The article addresses the kinetics of the atmospheric reaction of OH radicals with trifluoroacetic acid, not the substance of environmental relevance trifluoroacetate . In addition trifluoroacetate coming from herbicide use will not reach the atmosphere
Hurley, M. D.; Wallington, T. J.; Andersen, M. P. Sulbaek; Ellis, D. A.; Martin, J. W.; Mabury, S. A.	2004	Atmospheric Chemistry of Fluorinated Alcohols: Reaction with Cl Atoms and OH Radicals and Atmospheric Lifetimes	Journal of Physical Chemistry A (2004), 108(11), 1973-1979	The article does not contain information related to the substance of concern
Kern, Susanne; Singer, Heinz; Hollender, Juliane; Schwarzenbach, Rene P.; Fenner, Kathrin.	2011	Assessing Exposure to Transformation Products of Soil-Applied Organic Contaminants in Surface Water: Comparison of Model Predictions and Field Data.	Environ. Sci. Technol., Volume 45, Issue 7, Page 2833-2841, Publication Year 2011	This article assesses the quality of a new modeling approach, However, the modeled is not validated and the measured surface water concentrations of FFA, FOE sulfonic acid and FOE oxalate are in line with known results not influencing RA
Kutsuna, Shuzo [Reprint Author]; Hori, Hisao	2008	Experimental determination of Henry's law constants of trifluoroacetic acid at 278-298 K.	Atmospheric Environment, (MAR 2008) Vol. 42, No. 7, pp. 1399-1412. ISSN: 1352-2310.	The article addresses the Henry's law constant of trifluoroacetic acid. The substance of environmental relevance is the acetate for which measured data are available.
Lam, Christopher K.; McKinney, Mary K.; Clay, Val E.	2002	Evaluation of laboratory and field extraction methods: extraction of [phenyl-U-14C] flufenacet from aged soils	ACS Symposium Series (2002), 813(Pesticide Environmental Fate), 153-166	Only two sampling intervals (DAT-0 and DAT-32) were analyzed and no half-lives could be calculated. The reported max. occurrence of the DPs is in line with known results and thus, not influencing RA
Lifongo, Lydia L.; Bowden, Derek J.; Brimblecombe, Peter	2010	Thermal degradation of haloacetic acids in water	International Journal of Physical Sciences (2010), 5(6), 738-747	The article reports on chemical synthesis or development of methods for measurements of the chemical without its application to natural samples
Loos, Martin; Krauss, Martin; Fenner, Kathrin.	2012	Pesticide Nonextractable Residue Formation in Soil: Insights from Inverse Modeling of Degradation Time Series.	Environ. Sci. Technol., Volume 46, Issue 18, Page 9830-9837, Publication Year 2012	The article does not contain information related to the substance of concern
Mabury, Scott A.	2002	Redefining persistence .apprx. fluorinated pollutants in the environment	Proceedings of the Biennial International Conference on Monitoring and Measurement of the Environment, 4th, Toronto, ON, Canada, May 27-30, 2002 (2002), 35-40.	The observation made is based upon a route of exposure that cannot be considered representative for the intended use of the substance of concern. TFA as metabolite from thermolysis of perfluorinated polymers.

Author(s)	Year	Title	Source	Reason(s) for not including publication in dossier
Milan, Marco; Ferrero, Aldo; Letey, Marilisa; De Palo, Fernando; Vidotto, Francesco	2013	Effect of buffer strips and soil texture on runoff losses of flufenacet and isoxaflutole from maize fields	Journal of Environmental Science and Health, Part B: Pesticides, Food Contaminants, and Agricultural Wastes (2013), 48(12), 1021-1033	Experimental design not well reported (e.g. no application rates and used formulation reported - NO monitoring study)
Nilsson, E. J. K.; Nielsen, O. J.; Johnson, M. S.; Hurley, M. D.; Wallington, T. J.	2009	Atmospheric chemistry of cis-CF ₃ CH equals CHF: Kinetics of reactions with OH radicals and O ₃ and products of OH radical initiated oxidation	Chemical Physics Letters (2009), 473(4-6), 233-237	The article does not contain information related to the substance of concern
Oeberg, Tomas.	2005	A QSAR for the hydroxyl radical reaction rate constant: validation, domain of application, and prediction.	Atmos. Environ., Volume 39, Issue 12, Page 2189-2200, Publication Year 2005	This article is not relevant as trifluoroacetate derived from the use of a herbicide will not reach the atmosphere.
Perreau, Francois; Einhorn, Jacques	2006	Determination of frequently detected herbicides in water by solid-phase microextraction and gas chromatography coupled to ion-trap tandem mass spectrometry	Analytical and Bioanalytical Chemistry (2006), 386(5), 1449-1456	No endpoint can be derived; The article reports on chemical synthesis or development of methods for measurements of the chemical without its application to natural samples
Rani, Sunita; Kumari, Beena; Kathpal, T. S.	2006	Effect of pH on the dissipation behaviour of flufenacet (FOE-5043) in water	Pesticide Research Journal (2006), 18(2), 201-204	The test system is not clearly characterized, e.g. use of sterile aqueous buffer or natural, microbial active water, the obtained results can not be ranged in the overall environmental fate of FFA
Rayne, Sierra; Forest, Kaya	2009	Congener-specific organic carbon-normalized soil and sediment-water partitioning coefficients for the C1 through C8 perfluoroalkyl carboxylic and sulfonic acids	Journal of Environmental Science and Health, Part A: Toxic/Hazardous Substances and Environmental Engineering (2009), 44(13), 1374-1387	The investigation does not report results in values reflecting agreed determinants for the hazard characterization or risk assessment under Reg. EC No 1107/2009 and information is insufficient to transfer values into such determinants
Rouchaud, J.; Neus, O.; Eelen, H.; Bulcke, R.	2001	Persistence, mobility, and adsorption of the herbicide flufenacet in the soil of winter wheat crops	Bulletin of Environmental Contamination and Toxicology (2001), 67(4), 609-616	The test design used does not fulfill the requirements of current test guidelines
Sakkas, V. A.; Calza, P.; Vlachou, A. D.; Medana, C.; Minero, C.; Albanis, T.	2011	Photocatalytic transformation of flufenacet over TiO ₂ aqueous suspensions: Identification of intermediates and the mechanism involved	Applied Catalysis, B: Environmental (2011), 110, 238-250	The investigation does not report results in values reflecting agreed determinants for the hazard or exposure characterization or risk assessment under Reg. EC No 1107/2009. Phototransformation experiments all in combination with TiO ₂
Scott, B. F.; Spencer, C.; Martin, J. W.; Barra, R.; Bootsma, H. A.; Jones, K. C.; Johnston, A. E.; Muir, D. C. G.	2005	Comparison of Haloacetic Acids in the Environment of the Northern and Southern Hemispheres	Environmental Science and Technology (2005), 39(22), 8664-8670	Provides monitoring information in air (not relevant for TFA from PPPs); in soil (no trend was observed from 1865 - 1956. Therefore, no link to use of PPPs) and in conifer needles (source of exposure unknown). Sources (anthropogenic or not) not clarified

Author(s)	Year	Title	Source	Reason(s) for not including publication in dossier
Tsai, Wen-Tien	2009	Environmental hazards and health risk of common liquid perfluoro-n-alkanes, potent greenhouse gases	Environment International (2009), 35(2), 418-424	The observation made is based upon a route of exposure that cannot be considered representative for the intended use of the substance of concern
Tsai, Wen-Tien	2011	Environmental property modeling of perfluorodecalin and its implications for environmental fate and hazards	Aerosol and Air Quality Research (2011), 11(7), 903-907	The observation made is based upon a route of exposure that cannot be considered representative for the intended use of the substance of concern
Ulrich, U.; Dietrich, A.; Fohrer, N.	2013	Herbicide transport via surface runoff during intermittent artificial rainfall: A laboratory plot scale study	Catena (2013), 101, 38-49	Research paper employing an artificial study design at laboratory scale for basic research about runoff influencing factors. Results not transferable to real world situation, not suitable for regulatory risk assessments.
Ulrich, Uta (Reprint) Ulrich, Uta (Reprint); Fohrer, Nicola Zeiger, Marcus	2013	Soil structure and herbicide transport on soil surfaces during intermittent artificial rainfall	ZEITSCHRIFT FUR GEOMORPHOLOGIE, (MAR 2013) Vol. 57, Supp. [1], pp. 135-155. ISSN: 0372-8854.	Research paper employing an artificial study design at laboratory scale for basic research about runoff influencing factors. Results not transferable to real world situation, not suitable for regulatory risk assessments.
Vasilakoglou, I. B.; Eleftherohorinos, I. G.; Dhima, K. B.	2001	Activity, adsorption and mobility of three acetanilide and two new amide herbicides	Weed Research (2001), 41(6), 535-546	Test design used does not fulfill the requirements of current test guidelines. Test was performed with a formulation. Hence the results are not useable for RA of a.i.
Vecitis, Chad D.; Cheng, Jie; Hoffmann, Michael R. (Reprint) Park, Hyunwoong Choi, Wonyong Mader, Brian T.	2009	Reductive Defluorination of Aqueous Perfluorinated Alkyl Surfactants: Effects of Ionic Headgroup and Chain Length	JOURNAL OF PHYSICAL CHEMISTRY A, (29 JAN 2009) Vol. 113, No. 4, pp. 690-696. ISSN: 1089-5639.	The investigation does not report results in values reflecting agreed determinants for the hazard characterization or risk assessment under Reg. EC No 1107/2009 and information is insufficient to transfer values into such determinants
Wilson, S. R.; Solomon, K. R.; Tang, X.	2007	Changes in tropospheric composition and air quality due to stratospheric ozone depletion and climate change	Photochemical and Photobiological Sciences (2007), 6(3), 301-310	The article reports on chemical synthesis or development of methods for measurements of the chemical with application to natural samples outside Europe.
Włodarczyk, M.; Wybieralski, J.	2006	Adsorption kinetics of atrazine and flufenacet and their water/soil partition coefficients Kd and KOC	Ekologia i Technika (2006), 14(1), 16-22	The test design used does not fulfill the requirements of current test guidelines. Furthermore, the test was performed with a mixed formulation (atrazine + flufenacet)
Włodarczyk, Malgorzata	2009	Influence of adjuvant Adpros 850 SL on adsorption of flufenacet on soils with different organic carbon content	Progress in Plant Protection (2009), 49(3), 1456-1460	Test design used does not fulfill requirements of current test guidelines. Test was performed with a formulation. Hence, the results are not useable for RA of a.i.

Author(s)	Year	Title	Source	Reason(s) for not including publication in dossier
Xiang W (Reprint) Xiang J; Zhang J G; Wu F; Tang J H	2005	Geochemical transformation of trichloroacetic acid to chloroform in fresh waters - The results based upon laboratory experiments	WATER AIR AND SOIL POLLUTION, (NOV 2005) Vol. 168, No. 1-4, pp. 289-312. ISSN: 0049-6979.	The article does not contain information related to the substance of concern
Young, Cora J.; Hurley, Michael D.; Wallington, Timothy J.; Mabury, Scott A.	2009	Atmospheric chemistry of CF ₃ CF ₂ H and CF ₃ CF ₂ CF ₂ CF ₂ H: Kinetics and products of gas-phase reactions with Cl atoms and OH radicals, infrared spectra, and formation of perfluorocarboxylic acids	Chemical Physics Letters (2009), 473(4-6), 251-256	The article reports on chemical synthesis or development of methods for measurements of the chemical without its application to natural samples

In the second table – B.8.6_CA-2, are given the publications considered relevant by the Applicant after the detailed assessment and included into the documentation submitted for evaluation. As it was in case of the excluded publications, RMS presented only those publications that may be considered as addressing the issues related to the assessment of the environmental fate and behaviour according to the data requirements set by the Regulation (EC) 283/2013.

Table B.8.6_CA-2: Results of the “Detailed assessment” stage of the literature search – publications found relevant by the Applicant and included into the dossier (table reproduced from the Applicant’s report, modified by the RMS).

KCA - SANCO Data Point	KCP - SANCO Data Point	Author(s)	Year	Title	Source	Justification for classification of the publication
KCA 7.5. Monitoring data	KCP 9.2. Fate and behaviour in water and sediment	Bischoff, G.; Rodemann, B.; Pestemer, W.	2003	Entry of pesticides into surface waters - new results of the Lamspringe run-off monitoring project 1999-2001	Pesticide in Air, Plant, Soil and Water System, Proceedings of the Symposium Pesticide Chemistry, 12th, Piacenza, Italy, June 4-6, 2003 (2003), 849-856.	b) The literature describe findings of FFA in surface water from 1999-2001
KCA 7.5. Monitoring data		Frank, Hartmut; Christoph, Eugen H.; Holm-Hansen, Osmund; Bullister, John L.	2002	Trifluoroacetate in Ocean Waters	Environmental Science and Technology (2002), 36(1), 12-15.	b) Provides monitoring information in surface water (ocean), thus no change of endpoints.
KCA 7.5. Monitoring data		Scott B F; Macdonald R W; Kannan K; Fisk A; Witter A; Yamashita N; Durham L; Spencer C; Muir D C G	2005	Trifluoroacetate profiles in the Arctic, Atlantic, and Pacific Oceans.	Environmental Science and Technology, (2005 Sep 1) Vol. 39, No. 17, pp. 6555-6560.	b) Provides monitoring information in surface water (oceans); Contains information of anthropogenic and natural sources of TFA.

In light of the doubts related to the results of detailed assessment performed by the Applicant – Bayer CropSciences, RMS decided to repeat the literature search for Flufenacet, using the search criteria similar to those applied by the Applicant. The only difference was that the search was not limited to the last thirteen years predating the application (i. e. covering the period 2000 – 2013), but was broader, what enabled to find earlier or later publications, not found by the BCS. The repeated literature search for the degradation product TFA (trifluoroacetic acid) was not performed, because the information from the Applicant's report indicated that it may be considered thorough and exhaustive.

In case of the literature search for Flufenacet performed by RMS the following available literature data bases were used:

- Science Direct On Site – data base for Elsevier's publications (full texts) on ICM UW server;
- Science Direct On Line – data base for Elsevier's publications (full texts, including books and book chapters) on the editor's server;
- Springer – data base for Springer's publications (full texts) on ICM UW server;
- Springer link – data base for Springer's publication (full texts including books and book chapters) on the editor's server;
- Wiley – data base for Willey's publications (full texts) on the editor's server;
- ACS – data base for ACS publications (full texts) on the editor's server;
- EBSCOhost Web – search platform for grouping several more specialized scientific literature providers (e.g. Environment Complete, Academic Search Complete, Agricola, Medline), providing abstracts with the possible access to full texts;
- Environment Complete – search platform providing abstracts;
- SCOPUS – search platform providing abstracts with the possible access to full texts;
- Web of Science – data base for literature search, providing abstracts, on ICM UW server;
- Web of Science (Thomson Reuters) – search platform, providing abstracts, on the server of Thomson Reuters (service provider);
- Environmental Impact – data base for literature search, providing abstracts;

In case of EBSCOhost Web platform, the following data bases were selected for search:

- Environment Complete,
- Academic Search Complete,
- Agricola,
- Green File,
- Health source,
- Library, Information Science& Technology Abstracts,
- Masterfile Premium,
- Medline.

At the first step, the returned results – publications with its abstracts, were analysed for their potential relevance in the assessment of environmental fate and behaviour of Flufenacet and/or its degradation products. The results of the search at first step are summarised below.

The preliminary results of the search were following:

- **Science Direct On Site** returned 102 records, of which 16 were identified as potentially relevant and selected for further verification (further called **Science Direct on ICM UW**);
- **Science Direct On Line** returned 134 records, of which 17 were identified as potentially relevant and selected for further verification (further called **Science Direct – Elsevier**);
- **Springer data base on ICM UW server** returned same search results as Science Direct On Site, as Science Direct On Site is a common search engine for Elsevier and Springer; for that reason they are not presented here (further called **Springer on ICM UW**);
- **Springer link** returned 63 records, of which 13 were identified as potentially relevant and selected for further verification (further called **Springer link**);
- **Wiley data base** returned 90 records, of which 14 were identified as potentially relevant and selected for further verification (further called **Wiley**);
- **ACS data base** returned 49 records, of which 15 were identified as potentially relevant and selected for further verification (further called **ACS**);
- **EBSCOhost Web platform** returned initially 137 records, of which 78 were displayed after removal of the duplicates, and of which 15 were identified as potentially relevant and selected for further verification (further called **EBSCOhost**);
- **SCOPUS data base** returned 75 records, of which 15 were identified as potentially relevant and selected for further verification (further called **SCOPUS**);

- the data base **Web of Science – Thomson Reuters** returned 77 records, of which 19 were identified as potentially relevant and selected for further verification (further called **Web of Science**);
- the data base **Web of Science at ICM UW server** returned the same search results as cited above Web of Science – Thomson Reuters data base, so results obtained for this search engine were not further considered;
- **Environmental Impact** data base returned 67 records, of which 24 were identified as potentially relevant and selected for further verification (further called **Environmental Impact**);
- **Environment Complete** – data base consulted independently of EBSCOhost data base, it returned 41 records, of which 11 were identified as potentially relevant and selected for further verification (further called **Environment Complete**).

Additionally several smaller data bases were searched. These were:

- **Taylor and Francis Journals On-Line** – data base that returned 22 records, of which 1 was found relevant, but was also found elsewhere (further called **Taylor and Francis**);
- **Oxford Journals** webpage – the data base that returned 1 record, considered potentially relevant (further called **Oxford Journals**);
- **ASM (American Society for Microbiology)** webpage – the data base returned 2 records, considered potentially relevant (further called **ASM Journals**);
- **Journal of Environmental Quality** journal home page – returned 4 records, considered potentially relevant (further called **JEQ**);
- **Nature** journal webpage – no records meeting search criteria were returned;
- **Science** journal webpage – no records meeting search criteria were returned;
- **Freshwater Science** journal homepage – no records meeting search criteria were returned;
- **Lake and Reservoir Management** journal homepage – no records meeting search criteria were returned.

As a next step the results obtained from different data bases were compared and combined to identify the records that were repetitiously returned by them. The results are provided, in alphabetical order for the authors, in the table B.8.6_CA-3 below. The results were also compared to those identified by the Applicant as potentially relevant and selected for Step 2- detailed, assessment.

Table B.8.6_CA-3: The results of the literature search performed by the RMS – publications identified as potentially relevant in the area of environmental assessment and directed for the further assessment.

No	Publication data	Returned by the data base	Identified by the Applicant as potentially relevant?
1	Barriuso E., Benoit P., Dubus I. G., “ <i>Formation of Pesticide Nonextractable (Bound) Residues in Soil: Magnitude, Controlling Factors and Reversibility.</i> ”; Environmental Science and Technology, 2008, 42 (6), 1845 – 1854.	ACS;	No
2	Battaglin W. A., Kolpin D. A., Scribner E. A., Kuivila K. M., Sandstrom M. W., “ <i>Glyphosate, other herbicides, and transformation products in Midwestern streams, 2002.</i> ”; JAWRA Journal of the American Water Resources Association, 2005, 41 (2), 323 – 332.	Wiley;	No
3	Bazoobandi M., Yaduraju N. T., Kulshrestha G., “ <i>Analysis of flufenacet in soil, wheat grain and straw by gas chromatography.</i> ”; Journal of Chromatography A, 2000, 886 (1-2), 319 – 322.	Web of Science; Environmental Impact;	Yes
4	Bishop C. A., Ashpole S. L., Edwards M. A., van Aggelen G., Elliot J. E., “ <i>Hatching success and pesticide exposure in amphibians living in agricultural habitats of the South Okanagan Valley, British Columbia, Canada (2004 – 2006).</i> ”; Environmental Toxicology and Chemistry, 2010, 29 (7), 1593 – 1603.	Wiley;	No
5	Bloomberg A. M., Shadrack B. A., Arthur E. L., Clay V. E., “ <i>Outdoor soil metabolism of [Phenyl-U-¹⁴C] Flufenacet on California Soils.</i> ”; ACS Symposium Series, 2002, vol. 813 – “Pesticide Environmental Fate” (chapter 12), 167 – 182 (book chapter); published (print) 2009.	ACS; SCOPUS	No

No	Publication data	Returned by the data base	Identified by the Applicant as potentially relevant?
6	Boithias L., Sauvage S., Srinivasan R., Leccia O., Sánchez-Pérez J.-M., “Application date as a controlling factor of pesticide transfers to surface water during runoff events.”, Catena, 2014, 119 , 97 – 103.	Science Direct – Elsevier;	No
7	Campagna G., Paci F., Fabbi A., Rapparini G., “Percolation of acetochlor, dimethenamid, flufenacet and s-metolachlor applied in columns.” (“Studio in colonna della percolazione di alcuni diserbanti residuali del mais.”); Giornate Fitopatologiche 2006, Riccione (RN), 27-29 Marzo 2009 Atti, volume primo (University of Bologna) 2006, 591 - 598, (book chapter, conference paper)	Environmental Impact;	Yes
8	Cedergreen N., Streiberg J. C., “The toxicity of herbicides to non-target aquatic plants and algae: assessment of predicted factors and hazard.”; Pest Management Science, 2005, 61 (12), 1152 – 1160.	Wiley;	No
9	Chiaia-Hernandez A. C., Krauss M., Hollender J., “Screening of Lake Sediments for Emerging Contaminants by Liquid Chromatography Atmospheric Pressure Photoionization and Electrospray Ionization Coupled to High Resolution Mass Spectrometry.”; Environmental Science and Technology, 2013, 47 (2), 976 – 986.	ACS;	Yes
10	Chowdhury A., Pradhan S., Saha M., Sanyal N., “Impact of pesticides on soil microbiological parameters and possible bioremediation strategies.”; Indian Journal of Microbiology, 2008, 48 (1), 114 – 127.	Springer on ICM UW & Springer link;	No
11	Cross P., Edwards-Jones G., “Variation in pesticide hazard from arable crop production in Great Britain from 1992 to 2008: an extended time-series analysis.”; Crop Protection, 2011, 30 (12), 1579 – 1585.	Science Direct – Elsevier;	No
12	De Schamphelaere M., Sopanoghe P., Brusselman E., Sonck S., “Risk assessment of pesticide spray drift damage in Belgium.”; Crop Protection, 2007, 26 (4), 602 – 611.	Science Direct on ICM UW; Science Direct – Elsevier;	No
13	Dealtry S., Holmsgaard P. N., Dunon V., Jechalke S. Ding G.-C., Krögerrecklenfort E., Heuer H., Hansen L. H., Springael D., Zühlke S., Sørensen S. J., Smalla K., “Shifts in Abundance and Diversity of Mobile Genetic Elements after the Introduction of Diverse Pesticides into an On-Farm Biopurification System over a Course of a Year.”; Applied and Environmental Microbiology, 2014, 80 (13), 4012 – 4020.	ASM Journals	No
14	Delcour I., Spanoghe P., Uyttendaele M., “Literature review: Impact of climate change on pesticide use.”; Food Research International, 2015, 68 (complete), 7 – 15.	Science Direct on ICM UW;	No
15	Devos Y., Cougnon M., Vergucht S., Bulcke R., Haesaert G., Steurbaut W., Reheul D., “Environmental impact of herbicide regimes used with genetically modified herbicide-resistant maize.”; Transgenic Research, 2008, 17 (6), 1059 – 1077.	Springer on ICM UW & Springer link;	No
16	Dolan T., Parsons D. J., Howsam P., Whelan M. J., Varga L., “Identifying Adaptation Options and Constraints: The role of Agronomist Knowledge in Catchment Management Strategy.”, Water Resources Management, 2014, 28 (2), 511 – 526.	Springer on ICM UW & Springer link;	No
17	Fay E., Flynn J., Lundehehn J. R., Chapman P. J., Mason R. D., “The Joint Evaluation Procedure for Active Substances contained in Plant Protection Products within the European Community – 10 Years of the ECCO-Project.”; Journal für Verbraucherschutz und Lebensmittelsicherheit, 2007, 2 (1), 61 – 77.	Springer on ICM UW & Springer link;	No

No	Publication data	Returned by the data base	Identified by the Applicant as potentially relevant?
18	Finizio A., Villa S., Vighi M., “Predicting pesticide mixtures load in surface waters from a given crop.”; Agriculture, Ecosystems and Environment, 2005, 111 (1-4), 111 – 118.	Science Direct on ICM UW; Science Direct – Elsevier;	Yes
19	Fohrer N., Dietrich A., Kolychalov O., Ulrich U., “Assessment of the Environmental Fate of the Herbicides Flufenacet and Metazachlor with the SWAT Model.”; Journal of Environmental Quality, 2014, 43 (1), 75 – 85.	EBSCOhost; JEQ; Environment Complete; SCOPUS; Web of Science; Environmental Impact;	No
20	Fujiwara T., O’Hagan D., “Successful fluorine-containing herbicide agrochemicals.”, Journal of Fluorine Chemistry, 2014, 167 (complete), 16 – 29.	Science Direct on ICM UW; Science Direct – Elsevier;	No
21	Gajbhiye V. T., Gupta S., “Adsorption-desorption behaviour of flufenacet in five different soils of India.”; Pest Management Science, 2001, 57 (7), 633 – 639.	Wiley; EBSCOhost; Environment Complete; SCOPUS; Web of Science; environmental Impact;	No
22	Gajbhiye V. T., Gupta S., Agnihotri N. P., “Gas liquid chromatographic method of analysis for a herbicide flufenacet (FOE 5043).” ; Pesticide Research Journal, 2000, 12 (1), 41 – 47.	Environmental Impact	Yes
23	Gassman P. W., Sadeghi A. M., Srinivasan R., “Applications of the SWAT Model Special Section: Overview and Insights.”; Journal of Environmental Quality, 2014, 43 , 1 – 8.	JEQ	No
24	Greulich K. Alder L., “Fast multiresidue screening of 300 pesticides in water for human consumption by LC-MS/MS.”; Analytical and Bioanalytical Chemistry, 2008, 391 (1), 183 – 197.	Springer on ICM UW & Springer link;	No
25	Gupta S., Gajbhiye V. T., Agnihotri N. P., “Adsorption-Desorption, Persistence, and Leaching Behaviour of Flufenacet in Alluvial Soil of India.”; Bulletin of Environmental Contamination and Toxicology, 2001, 66 (1), 9 – 16.	Science Direct on ICM UW; Science Direct – Elsevier; Springer on ICM UW & Springer link; EBSCOhost; Environment Complete; SCOPUS; Web of Science; Environmental Impact;	No
26	Gupta S., Gajbhiye V. J., “Effect of concentration, moisture and soil type on the dissipation of flufenacet from soil.”; Chemosphere, 2002, 47 (9), 901 – 906.	Science Direct on ICM UW; EBSCOhost; Environment Complete; SCOPUS; Web of Science; Environmental Impact;	Yes
27	Guy M., Singh M., Mineau P., “Using field data to assess the effects of pesticides on crustacean in freshwater aquatic ecosystems and verifying the level of protection provided by water quality guidelines.”; Integrated Environmental Assessment and Management, 2011, 7 (3 – special issue: Challenges Posed by Radiation and Radionuclide releases to the Environment), 426 – 436.	Wiley;	No
28	Hillocks R. J., “Farming with fewer pesticides: EU pesticide review and resulting challenges for UK agriculture.”; Crop Protection, 2012, 31 (1), 85 – 93.	Science Direct – Elsevier;	No
29	Hollender J., Zimmermann S. G., Koepke S., Krauss M., McArdell C. S., Ort C., Singer H., von Gunten U., Siegrist H., “Elimination of Organic Micropollutants in a Municipal Wastewater Treatment Plant Upgraded with Full-Scale –Ozonation Followed by Sand Filtration.”; Environmental Science and Technology, 2009, 43 (20), 7862 – 7869;	ACS;	No
30	Jähnig S. C., Kuemmerlen M., Kiesel J., Domisch S. Cai Q., Schmalz B., Fohrer N., “Modelling of riverine ecosystems by integrating models: conceptual approach, a case study and research agenda.”; Journal of Biogeography, 2012, 39 (12), 2253 – 2263.	Wiley;	No

No	Publication data	Returned by the data base	Identified by the Applicant as potentially relevant?
31	Kannan K., Ridal J., Sturges J., <i>"Pesticides in the Great Lakes."</i> ; The Handbook of Environmental Chemistry, Volume 5N – Persistent Organic Pollutants in the Great Lakes, 2006, 151 – 199 (book chapter).	Springer on ICM UW & Springer link;	No
32	Katagi T., <i>"Behaviour of Pesticides in Water-Sediment systems."</i> ; Reviews in Environmental Contamination and Toxicology, 2006, 187 , 133 – 251 (book chapter)	Springer on ICM UW & Springer link;	No
33	Kern S., Singer H., Hollender J., Schwarzenbach R. P., Fenner K., <i>"Assessing Exposure to Transformation Products of Soil-Applied Organic Contaminants in Surface Water: Comparison of Model Predictions and Field Data."</i> ; Environmental Science and Technology, 2011, 45 (7), 2833 – 2841.	ACS;	Yes
34	Klaus J., Zehe E., Elsner M., Palm J. Schneider D., Schröder B., Steinbeiss S., van Schaik L., West S., <i>"Controls of event-based pesticide leaching in natural soil: a systematic study based on replicated field scale irrigation experiments."</i> ; Journal of Hydrology, 2014, 512 (complete), 528 – 539.	Science Direct on ICM UW; Science Direct – Elsevier;	No
35	Kolpin D., Battaglin W. A., Conn K. E., Furlong E. T., Glassmeyer S. T., Kalkhoff S. J., Meyer M. T., Schnoebelen D. J., <i>"Occurrence of Transformation Products in the Environment."</i> ; Handbook of Environmental Chemistry Volume 2P – Transformation Products of Synthetic Chemicals in the Environment, 2009, 83 – 100 (book chapter).	Springer on ICM UW & Springer link;	No
36	Kolpin D. W., Schnoebelen D. J., Thurman M. E., <i>"Degradates Provide Insight to Spatial and Temporal Trends of Herbicides in Ground Water."</i> ; Groundwater, 2004, 42 (4), 601 – 608.	Wiley; ACS;	No
37	Kuster M., López de Alda M., Barceló D., <i>"Liquid chromatography-tandem mass spectrometric analysis and regulatory issues of polar pesticides in natural and treated waters."</i> ; Journal of Chromatography A, 2009, 1216 (3), 520 – 529.	Science Direct – Elsevier;	No
38	Lam C. K., McKinney M. K., Clay V. E., <i>"Evaluation of Laboratory and Field Extraction Methods: Extraction of [Phenyl-¹⁴C] Flufenacet from Aged Soils."</i> ; ACS Symposium Series, 2002, vol. 813 – "Pesticide Environmental Fate" (chapter 11), 153 – 166 (book chapter); published (print) 2009.	ACS; SCOPUS	Yes
39	Machefer G., <i>"Alternatives to isoproturon-based products for the control of grasses and broad-leaved weeds in cereals."</i> ("Alternative Lösungen zu Isoproturon-haltigen Produkten bei der Ungras- und Unkrautbekämpfung in Getreide."); Zeitschrift für Pflanzenkrankheiten und Pflanzenschutz, 2000, Sonderh. 17 , 501 – 508.	Environmental Impact	Yes
40	Meffe R., de Bustamante I., <i>"Emerging organic contaminants in surface water and groundwater: A first overview of the situation in Italy."</i> ; Science of the Total Environment, 2014, 481 (complete), 280 – 295.	Science Direct on ICM UW;	No
41	Milan M., Ferrero A., Letey M., DePalo F., Vidotto F., <i>"Effect of buffer strips and soil texture on runoff losses of flufenacet and isoxaflutole from maize fields."</i> ; Journal of Environmental Science and Health, Part B – Pesticides, Food Contaminants & Agricultural Wastes, 2013, 48 (12), 1021 – 1033.	EBSCOhost; Environment Complete; SCOPUS; Web of Science; Environmental Impact	Yes
42	Mills P. C., Kolpin D. W., Scribner E. A., Thurman E. M., <i>"Herbicides and degradates in shallow aquifers of Illinois: spatial and temporal trends."</i> ; JAWRA Journal of the American Water Resources Association, 2005, 41 (3), 537 – 547.	Wiley;	No

No	Publication data	Returned by the data base	Identified by the Applicant as potentially relevant?
43	Moschet C., Götz C., Longrée P., Hollender J., Singer H., “Multi-Level Approach for the Integrated Assessment of Polar Organic Micropollutants in an International Lake Catchment: The Example of Lake Constance.”; Environmental Science and Technology, 2013, 47 (13), 7028 – 7036.	ACS;	No
44	Moschet C., Wittmer I., Simovic J., Junghans M., Piazzoli A., Singer H., Stamm C., Leu C. Hollender J., “How a Complete Pesticide Screening Changes the Assessment of Surface Water Quality.”; Environmental Science and Technology, 2014, 48 (10), 5423 – 5432.	ACS;	No
45	Moschet C., Vermeirsser E. L. M., Singer H., Stamm C., Hollender J., “Evaluation of in-situ calibration of Chemcatcher passive samplers for 322 micropollutants in agricultural and urban affected rivers.”; Water Research, 2015, 71 , 306 – 317.	Science Direct – Elsevier;	No
46	Müller M., Mentel M., van Hellemond J. J., Henze K., Woehle A. G. M., Martin W. F., “Biochemistry and Evolution of Anaerobic energy Metabolism in Eukaryotes.”; Microbiology and Molecular Biology Reviews, 2012, 76 (2), 444 – 495.	ASM Journals	No
47	Osteen C. D., Fernandez-Cornejo J., “Economic and Policy issues of U.S. agricultural pesticide use trends.”; Pest Management Science, 2013, 69 (9), 1001 – 1025.	Wiley;	No
48	Paci F., Bartolini D., Rapparini G., “Residual effects of various herbicides on wheat after vegetables.” (“Effetti residuali di diversi erbicidi su frumento dopo orticole.”); Informatore agrario, 2002, 58 (32), 71 – 74.	Environmental Impact	No
49	Parker D. C., Simmons F. W., Wax. L. M., “Fall and Early Preplant Application Timing Effects on Persistence and Efficacy of Acetamide Herbicides.”; Weed Technology, 2005, 19 (1), 6 – 13.	EBSCOhost; SCOPUS; Web of Science; Environmental Impact;	No
50	Perreau F., Einhorn J., “Determination of frequently detected herbicides in water by solid-phase microextraction and gas chromatography coupled to ion-trap tandem mass spectrometry.”; Analytical and Bioanalytical Chemistry, 2006, 386 (5), 1449 – 1456.	Springer on ICM UW & Springer link;	Yes (the publication not listed in the table B.8.6-CA-1 because the Applicant’s justification indicated that it was not relevant for that section).
51	Pfannerstill M., Guse B., Fohrer N., “A multi-storage groundwater concept for the SWAT model to emphasize nonlinear groundwater dynamics in lowland catchments.”; Hydrological Processes, 2014, 28 (12), 5599 – 5612.	Wiley;	No
52	Postigo C., Barceló D., “Synthetic organic compounds and their transformation products in groundwater: Occurrence, fate and migration.”; Science of the Total Environment, 2015, 503 – 504 (complete), 32 – 47.	Science Direct on ICM UW; Science Direct – Elsevier;	No
53	Rani Sunita, Kumari Beena., Kathpal T. S., “Effect of pH on the dissipation behaviour of flufenacet (FOE-5043) in water.”; Pesticide Research Journal, 2006, 18 (2), 201 – 204.	Environmental Impact;	Yes
54	Rebich R. A., Coupe R. H., Thurman E. M., “Herbicide concentrations in the Mississippi River Basin – the importance of chloroacetanilide herbicide degradates.”; Science of the Total Environment, 2004, 321 (1-3), 189 – 199.	Science Direct on ICM UW	No
55	Roberti R., Badiali F., Pisi A., Veronesi A., Pancaldi D., Cesari A., “Sensitivity of Clonostachys rosea and Trichoderma spp. As potential biocontrol agents to pesticides.”; Journal of Phytopathology, 2006, 154 (2), 100 – 109.	Environmental Impact;	Yes

No	Publication data	Returned by the data base	Identified by the Applicant as potentially relevant?
56	Robles-Molina J., Lara-Ortega F. J., Gilbert-López B., García-Reyes J. F., Molina-Díaz A., “Multi-residue method for the determination of over 400 priority and emerging pollutants in water and wastewater by solid-phase extraction and liquid chromatography-time-of-flight mass spectrometry.”; Journal of Chromatography A, 2014, 1350 , 30 – 43.	Science Direct – Elsevier;	No
57	Rouchaud J., Neus O., Eelen H., Bulcke R., “Persistence, Mobility, and Adsorption of the Herbicide Flufenacet in the Soil of Winter Wheat Crops.”; Bulletin of Environmental Contamination and Toxicology, 2001, 67 (4), 609 – 616.	Science Direct on ICM UW; Springer on ICM UW & Springer link; EBSCOhost; Environment Complete; SCOPUS; Web of Science; Environmental Impact;	Yes
58	Rouchaud J., Neus O., Cools K., Bulcke R., “Dissipation and mobility of the oxyacetamide flufenacet herbicide in corn and wheat crops.”; Mededelingen – Faculteit Landbouwkundige en Toegepaste Biologische Wetenschappen, Universiteit Gent, 1999, 64 (3b), 673 – 677.	Environmental Impact;	No
59	Rouchaud J., Neus O., Cools K., Bulcke R., “Flufenacet Soil Persistence and Mobility in Corn and Wheat Crops.”; Bulletin of Environmental Contamination and Toxicology, 1999, 63 (4), 406 – 466.	Springer on ICM UW & Springer link; EBSCOhost; Environment Complete; SCOPUS; Web of Science; Environmental Impact	No
60	Sakkas V. A., Calza P., Vlachou A. D., Medana C., Minero C., Albanis T., “Photocatalytic transformation of flufenacet over TiO ₂ aqueous suspensions: Identification of intermediates and the mechanisms involved.”, Applied Catalysis, B: Environmental, 2011, 110 (complete), 238 – 250;	Science Direct on ICM UW; Science Direct – Elsevier; EBSCOhost; Environment Complete; Web of Science;	Yes
61	Schulte-Oehlmann U., Oehlmann J., Keil F., “Before the Curtain Falls: Endocrine-active Pesticides – a German Contamination Legacy.”; Reviews of Environmental Contamination and Toxicology, 2011, 213 , 137 – 159 (book chapter).	Springer on ICM UW & Springer link;	No
62	Simončič A., Sušin J., Baša-Česnik H., Bolta Š. V., Gregorčič A., Vrščaj B., “The investigation of agricultural soil pollution in groundwater protection areas of Ljubljana Municipality by plant protection products from 2005 to 2010.” („Spremljanje onesnaženosti kmetijskih zemljišč no vodovarstvenih območjih v Mestni občini Ljubljana med leti 2005 in 2010.”); Zbornik Predavanj Referatov, 10, Slovenskega Posvetovanja o Varstvu Rastlin, Podčetrtek, Slovenia, 1.-2. Marec 2011, 2011, 157 – 163.	Environmental Impact;	No
63	Sinclair C. J., Boxall A. B. A., Parsons S. A., Thomas M. R., “Prioritization of Pesticide Environmental Transformation Products in Drinking Water Supplies.”; Environmental Science and Technology, 2006, 40 (23), 7283 – 7289.	ACS;	No
64	Singh K. P., Gupta S., Basat N., Mohan N., “QSTR Modelling for Qualitative and Quantitative Toxicity Predictions of Diverse Chemical Pesticides in Honey Bee for Regulatory Purposes.”; Chemical Research in Toxicology, 2014, 27 (9), 1504 – 1515.	ACS;	No
65	Steckel L. E., Simmons W. F., Sprague C. L., “Soil Factor Effects on Tolerance of Two Corn (Zea mays) Hybrids to Isoxaflutole Plus Flufenacet.”; Weed Technology, 2003, 17 (3), 599 – 604,	EBSCOhost; Environment Complete;	No
66	Stuart M., Lapworth D., Crane E., Hart A., “Review of risk from potential emerging contaminants in UK groundwater.”; Science of the Total Environment, 2012, 416 (complete), 1 – 21.	Science Direct on ICM UW; Science Direct – Elsevier;	No

No	Publication data	Returned by the data base	Identified by the Applicant as potentially relevant?
67	Tallevi G., Rapparini G., “ <i>New ideas emerging from COLUMA '98</i> ” (“ <i>Le novità emerse al COLUMA '98.</i> ”); <i>Informatore Fitopatologico</i> , 1999, 49 (7/8), 32 – 39.	Environmental Impact;	No
68	Truong L., Reif D. M., St Mary L., Geier M. C., Truong H. D., Tanguay R. L., “ <i>Multidimensional In Vivo Hazard Assessment using Zebra Fish.</i> ”; <i>Toxicological Sciences</i> , 2014, 137 (1), 212 – 233.	Oxford Journals	No
69	Tucci S., Vacula R., Krajcovic J., Proksch P., Martin W., “ <i>Variability of Wax Ester Fermentation in Natural and Bleached Euglena gracilis Strains in Response to Oxygen and the Elongase Inhibitor Flufenacet.</i> ”; <i>Journal of Eukaryotic Microbiology</i> , 2010, 57 (1), 63 – 69.	Web of Science;	No
70	Ulrich U., Dietrich A., Fohrer N., “ <i>Herbicide transport via surface runoff during intermittent artificial rainfall: A laboratory plot scale study.</i> ”; <i>Catena</i> , 2013, 101 (complete), 38 – 49.	Science Direct on ICM UW; Science Direct – Elsevier; EBSCOhost; Environment Complete; SCOPUS, Web of Science; Environmental Impact;	Yes
71	Ulrich U., Schulz F., Hugenschmidt C., Fohrer N., “ <i>Comparing measurements of herbicides lossess on three different scales.</i> ” (“ <i>Vergleichende Messungen zu Herbizidausträgen auf drei unterschiedlichen Größenskalen.</i> ”); <i>Hydrologie und Wasserbewirtschaftung</i> , 2012, 56 (4), 215 – 228.	SCOPUS; Web of Science;	No
72	Ulrich U., Zeiger M., Fohrer N., “ <i>Soil structure and herbicide transport on soil surfaces during intermittent artificial rainfall.</i> ”; <i>Zeitschrift für Geomorphologie</i> , 2013, 57 Supplement 1, 135 – 155.	Web of Science;	Yes
73	Unterreiner G. A., Kehew A. E., “ <i>Spatial and temporal distribution of herbicides and herbicide degradates in a shallow glacial drift aquifer/surface water system, south-central Michigan.</i> ”; <i>Groundwater Monitoring & Remediation</i> , 2005, 25 (2), 87 – 95.	Wiley; ACS;	No
74	Van’T Zelfde M., Tamis W. L., Vijver M. G., De Snoo G. R., “ <i>The contribution of neighbouring countries to pesticide levels in Dutch surface waters.</i> ”; <i>Communications In Agricultural and Applied Biological Sciences (Univ. Ghent)</i> , 2011, 76 (4), 867 – 877.	EBSCOhost; SCOPUS; web of Science;	No
75	Vargo J. D., Lee E. A., Fuhrman J. D., “ <i>Interlaboratory Comparison and Validation of Methods for Chloroacetanilide and Chloroacetamide Soil Degradates in Environmental Waters.</i> ”; <i>ACS Symposium Series</i> , 2003, vol. 850 – “ <i>Liquid Chromatography/Mass Spectrometry MS/MS and Time of Flight MS</i> ” (chapter 16), 273 – 290 (book chapter); published (print) 2009.	ACS;	Yes
76	Vasilakoglou I. B., Eleftherohorinos I. G., Dhima K. B., “ <i>Activity, adsorption and mobility of three acetanilide and two new amide herbicides.</i> ”; <i>Weed Research</i> , 2001, 41 (6), 535 – 546.	Wiley; EBSCOhost; Environment Complete; SCOPUS; Web of Science;	Yes
77	Vasilakoglou I. B., Eleftherohorinos I. G., “ <i>Persistence, efficacy and selectivity of amide herbicides in corn.</i> ”; <i>Weed Technology</i> , 2003, 17 (2), 381 – 388.	SCOPUS; Web of Science; Environmental Impact;	No
78	Verro R., Finizio A., Otto S., Vighi S., “ <i>Predicting Pesticide Environmental Risk in Intensive Agricultural Areas. I: Screening Level Risk Assessment of Individual Chemicals in Surface Waters.</i> ”; <i>Environmental Science and Technology</i> , 2009, 43 (2), 522 – 529.	ACS;	No
79	Verro R., Finizio A., Otto S., Vighi S., “ <i>Predicting Pesticide Environmental Risk in Intensive Agricultural Areas. II: Screening Level Risk Assessment of Complex Mixtures in Surface Waters.</i> ”; <i>Environmental Science and Technology</i> , 2009, 43 (2), 530 – 537.	ACS;	No

No	Publication data	Returned by the data base	Identified by the Applicant as potentially relevant?
80	Verstraeten I. M., Thurman E. M., Lindsey M. E., Lee E. C., "Changes in concentrations of triazine and acetamide herbicides by bank filtration, ozonation, and chlorination in a public water supply.", <i>Journal of Hydrology</i> , 2002, 266 (3-4), 190 – 208.	Science Direct on ICM UW; Science Direct – Elsevier;	No
81	Vogel J. R., Majewski M. S., Capel P. D., "Pesticides in Rain in Four Agricultural Watersheds in the United States.", <i>Journal of Environmental Quality</i> , 2008, 37 , 1101 – 1115.	JEQ	No
82	von der Ohe P. C., Dulio V., Slobodnik J., De Deckere E., Kühne R., Ebert R.-U., Ginebreda A., De Cooman W., Schüürmann G., Brack W., "A new risk assessment approach for the prioritization of 500 classical and emerging organic microcontaminants as potential river basin specific pollutants under the European Water Framework Directive.", <i>Science of the Total Environment</i> , 2011, 409 (11), 2064 – 2077.	Science Direct on ICM UW; Science Direct – Elsevier;	No
83	Wheeler J. R., Maynard S. K., Crane M., "An evaluation of fish early life stage tests for predicting reproductive and longer-term toxicity from plant protection product active substances.", <i>Environmental Toxicology and Chemistry</i> , 2014, 33 (8), 1874 – 1878.	Wiley;	No
84	Whiteside M., Mineau P., Morrison C., Knopper L. D., "Comparison of a score-based approach with risk-based ranking in-use agricultural pesticides in Canada to aquatic receptors.", <i>Integrated Environmental Assessment and Management</i> , 2008, 4 (2), 215 – 236.	Wiley;	No
85	Włodarczyk M., Wybieralski J., Praczyk T., "Influence of dose of flufenacet on its degradation on light soil." ("Wpływ wielkości dawki flufenacetu na jego trwałość w glebie lekkiej."); <i>Progress in Plant Protection</i> , 2007, 47 (3), 306 – 309.	Environmental Impact	No
86	Włodarczyk M., Wybieralski J., Praczyk T., "Influence of adjuvants on flufenacet degradation in light soil in field condition." ("Wpływ adiuwantów na trwałość flufenacetu w glebie lekkiej w warunkach polowych."); <i>Progress in Plant Protection</i> , 2008, 48 (4), 1271 – 1275.	Environmental Impact;	No
87	Włodarczyk M., "Influence of adjuvant Adpros 850 SL on adsorption of flufenacet on soils with different organic carbon content." ("Wpływ adiuwantu Adpros 850 SL na adsorpcję flufenacetu na glebach o różnej zawartości węgla organicznego."); <i>Progress in Plant Protection</i> , 2009, 49 (3), 1456 – 1460.	Environmental Impact;	Yes
88	Woudnech M. B., Ou Z., Sekela M., Tuominen T., Gledhik M., "Pesticide Multiresidues in Waters of the Lower Fraser Valley, British Columbia, Canada. Part I. Surface Water.", <i>Journal of Environmental Quality</i> , 2009, 38 , 940 – 947.	JEQ	No
89	Zimmerman L. R., Schneider R. J., Thurman E. M., "Analysis and Detection of the Herbicides Dimethenamid and Flufenacet and Their Sulfonic and Oxalonic Acid Degradates in Natural Degradates in Natural Water.", <i>Journal of Agricultural and Food Chemistry</i> , 2002, 50 (5), 1045 – 1052.	ACS; EBSCOhost; Web of Science; Environmental Impact;	No

At that stage all publications potentially relevant in the area of the assessment of the impact on environment were considered without differentiation between those related to the assessment of fate and behaviour in the environment and those dealing with ecotoxicity of Flufenacet.

As a next stage RMS checked the availability of the full texts of the publications identified as potentially relevant in the area of the influence of Flufenacet on the Environment, including those found by the Applicant and listed in the table B.8.6_CA-2. In case of difficulties with gaining the access to the full texts the Applicant was asked for providing them (mainly if these were at his disposal) and/or the requests for the copies were sent to the corresponding authors.

Next the available full texts were checked for their relevance. At that stage the publications dealing mainly with ecotoxicological aspects of the influence of Flufenacet on environment were identified and checked for their relevance in the area of the assessment of environmental fate and behaviour, mainly with regard to the information on the determined concentrations in examined habitats (monitoring issues) or transformation patterns.

RMS decided, unlike the Applicant, not to reject the monitoring data coming from the USA and Canada. The justification for that is that although such results are not fully relevant to the situation in the EU, because of the well developed monitoring strategies they may be considered as supplementary and providing a sound insight of behaviour of Flufenacet in the environment and the risk it may pose to the various environmental compartments.

It shall be noted that the detailed assessment enabled the identification of several publications not previously found as potentially relevant, which were subsequently verified for their relevance for the assessment of flufenacet. These publications are listed below in the table B.8.6_CA-4.

Table B.8.6_CA-4: The list of publications found as a cross-reference resulting from the detailed examination of the potentially relevant publications.

No	Publication data	With cross-reference to the publication:
1	anon., "Final Report of Project WT1246- Understanding changes in pesticide usage to inform water company risk assessment.", DEFRA 2013, available: http://dwi.defra.gov.uk/research/completed-research/2000today.htm	No direct cross-reference – publication found as an additional when DEFRA site was scanned for additional potentially relevant publications
2	Baker N. T., Stone W. S., "Estimated Annual Agricultural Pesticide Use for Counties of the Conterminous United States, 2008 – 12.", US Geological Survey Data Series 907, 2015. available:	No direct cross-reference – publication found as an additional when USGS site was scanned for additional potentially relevant publications.
3	Bowden D. J., Clegg S. L., Brimblecombe P. "The Henry's law constant of Trifluoroacetic acid and its partitioning into liquid water in the atmosphere."; Chemosphere, 1996, 32 (2), 405 – 420;	Kutsuna S., Hori H., "Experimental determination of Henry's law constants of trifluoroacetic acid at 278-298 K."; Atmospheric Environment, 2008, 42 (7), 1399 – 1412.
4	Berg M., Müller S. R., Mühlemann J., Wiedmer a., Schwarzenbach R. P., „Concentrations and Mass Fluxes of Chloroacetic acids and Trifluoroacetic acid in Rain and Natural Waters in Switzerland."; Environmental Science and Technology, 2000, 34 (13), 2675 – 2683;	Henne, S.; Shallcross, D. E.; Reimann, S.; Xiao, P.; Boulos, S.; Gerecke, A. C.; Brunner, D.; "Environmental impacts of HFO-1234yf and other HFOs."; Moving Towards Sustainability, ASHRAE/NIST Refrigerants Conference, Gaithersburg, MD, United States, Oct. 29-30, 2012 (2012), 13/1-13/13.
5	Capel P. D., McCarthy K. A., Barbash J. E., "National, Holistic, Watershed-Scale Approach to Understand the Sources, Transport, and Fate of Agricultural Chemicals."; Journal of Environmental Quality, 2008, 37 , 983 – 993.	Vogel J. R., Majewski M. S., Capel P. D., "Pesticides in Rain in Four Agricultural Watersheds in the United States."; Journal of Environmental Quality, 2008, 37 , 1101 – 1115.
6	Ellis D. A., Hanson M. L., Sibley P. K., Shahid T., Fineberg N. a., Solomon K. R., Muir D. C. G., Mabury S. A., "The fate and persistence of trifluoroacetic and chloroacetic acids in pound water."; Chemosphere, 2001, 42 , 309 – 318.	Hanson M., Sibley P. K., Ellis D. A., Fineberg N. A., Mabury S. A., Salomon K. R., Muir D. C. "Trichloroacetic acid fate and toxicity to the macrophytes <i>Myriophyllum spicatum</i> and <i>Myriophyllum sibiricum</i> under field conditions."; Aquatic Toxicology, 2002, 56 , 241 – 255;
7	Gilliom R. J., Barbash J. E., Crawford C. G., Hamilton P. A., Martin J. D., Nakagi N., Nowell L. H., Scott J. C., Stackelberg P. E. Thelin G. P., Wolock D. M., "Quality of Our Nation's Waters. Pesticides in the Nation's Streams and Ground Water, 1992 – 2001."; USGS Circular 1291, 2006, US Geological Survey 2007 (revised version 15 February 2007). available: http://water.usgs.gov/nawqa/pnsp	No direct cross-reference – publication found as an additional when USGS site was scanned for additional potentially relevant publications.
8	Hanson M. L., Sibley P. K., Mabury S. A., Muir D. C., Solomon K. R., "Chlorodifluoroacetic acid fate and toxicity to the macrophytes <i>Lemna gibba</i> , <i>Myriophyllum spicatum</i> and <i>Myriophyllum sibiricum</i> in aquatic microcosm."; Environmental Toxicology and Chemistry, 2001, 20 , 2758 – 2767.	Hanson M., Sibley P. K., Ellis D. A., Fineberg N. A., Mabury S. A., Salomon K. R., Muir D. C. "Trichloroacetic acid fate and toxicity to the macrophytes <i>Myriophyllum spicatum</i> and <i>Myriophyllum sibiricum</i> under field conditions."; Aquatic Toxicology, 2002, 56 , 241 – 255;

No	Publication data	With cross-reference to the publication:
9	Jordan A., Frank H., “Trifluoroacetate in the Environment. Evidence for Sources Other Than HFC/HCFCs.”; Environmental Science and Technology, 1999, 33 (4), 522 – 527;	Henne, S.; Shallcross, D. E.; Reimann, S.; Xiao, P.; Boulos, S.; Gerecke, A. C.; Brunner, D.; “Environmental impacts of HFO-1234yf and other HFOs.”; Moving Towards Sustainability, ASHRAE/NIST Refrigerants Conference, Gaithersburg, MD, United States, Oct. 29-30, 2012 (2012), 13/1-13/13.
10	Kowal S., Balsaa P., Werres F., Schmidt T. C., “Fully automated standard addition method for the quantification of 29 polar pesticide metabolites in different water bodies using LC-MS/MS.”; Analytical and Bioanalytical Chemistry, 2013, 405 , 6337 – 6351.	Postigo C., Barceló D., “Synthetic organic compounds and their transformation products in groundwater: Occurrence, fate and migration.”; Science of the Total Environment, 2015, 503 – 504 (complete), 32 – 47.
11	Manoj A. Lazar, Shaji Varghese, Santhosh S. Nair, “Photocatalytic Water Treatment by Titanium Dioxide: Recent Updates.”; Catalysis, 2012, 2 , 572 – 601.	No direct cross-reference – publication found during further expolaroion of the issue of drinking water processing in AOP process; related to the relevant paper by Sakkas et al. (2011).
12	Martin J. W., Franklin J., Hanson M. L., Solomon K. R., Mabury S. A., Ellis D. A., Scott B. F., Muir D. G. C., “Detection of Chlorodifluoroacetic Acid in Precipitation: A Possible Product of Fluorocarbon Degradation.”; Environmenral Science and Technology, 2000, 34 , 274 – 281.	Hanson M., Sibley P. K., Ellis D. A., Fineberg N. A., Mabury S. A., Salomon K. R., Muir D. C. “Trichloroacetic acid fate and toxicity to the macrophytes Myriophyllum spicatum and Myriophyllum sibiricum under field conditions.”; Aquatic Toxicology, 2002, 56 , 241 – 255;
13	Paris P., Citro L., Di Carlo E., Maschio G., Pace E., Ursino S., “Rapporto nazionale pesticidi nelle acque, dati 2009 – 2010.”; ISPRA Rapporti 175/2013, ISPRA Roma, Italy, 2013. available: http://www.ispraambiente.gov.it/it/publicazioni/rapporti	Meffe R., de Bustamante I., “Emerging organic contaminants in surface water and groundwater: A first overview of the situation in Italy.”; Science of the Total Environment, 2014, 481 (complete), 280 – 295.
14	Paris P., Biscceglie S., Maschio G., Pacer E., Parisi Pressice D., Ursino S., “Rapporto nazionale p esticidi nelle acque, dati 2011 – 2012.”; ISPRA Rapporti 208/2014, ISPRA Roma, Italy, 2014. available: http://www.ispraambiente.gov.it/it/publicazioni/rapporti	Paris P., Citro L., Di Carlo E., Maschio G., Pace E., Ursino S., “Rapporto nazionale pesticidi nelle acque, dati 2009 – 2010.”; ISPRA Rapporti 175/2013, ISPRA Roma, Italy, 2013.
15	Römpf A., Klemm O., Fricke W., Hartmut F., “Haloacetates in Fog and Rain.”; Environmental Science and Technology, 2001, 35 (7), 1294 – 1298.	Henne, S.; Shallcross, D. E.; Reimann, S.; Xiao, P.; Boulos, S.; Gerecke, A. C.; Brunner, D.; “Environmental impacts of HFO-1234yf and other HFOs.”; Moving Towards Sustainability, ASHRAE/NIST Refrigerants Conference, Gaithersburg, MD, United States, Oct. 29-30, 2012 (2012), 13/1-13/13.
16	Ryberg K. R., Vecchia A. V., Martin J. D., Gilliom R. J., “Trends in Pesticide Concentrations in Urban Streams in the United States, 1992 – 2008.”; US Geological Survey Scientific Investigations Report 2010-5139, 2010. available: http://water.usgs.gov/nawqa/pnsp	No direct cross-reference – publication found as an additional when USGS site was scanned for additional potentially relevant publications.
17	Ryberg K. R., Vecchia A. V., Gilliom R. J., Martin J. D., “Pesticide Trends in Major Rivers of the United States, 1992 – 2010.”; US Geological Survey Scientific Investigations Report 2014-5135, 2014. available: http://water.usgs.gov/nawqa/pnsp	No direct cross-reference – publication found as an additional when USGS site was scanned for additional potentially relevant publications.
18	Scott C., Pandey G., Hartley C. J., Jackson C. J., Cheesman M. J., Taylor M. C., Pandey R., Khurena J. L., Teese M., Coppin Weir K. M., Jain R. K. Lal R., Russel R. J., Oakeshott J. G., “The enzymatic basis for pesticide bioremediation.”; Indian Journal of Microbiology, 2008, 48 , 65 – 79.	Chowdhury A., Pradhan S., Saha M., Sanyal N., “Impact of pesticides on soil microbiological parameters and possible bioremediation strategies.”; Indian Journal of Microbiology, 2008, 48 (1), 114 – 127.
19	Scott B. F., MacTavish D., Spencer C., Strachan W. M. J., Muir D. C., “Haloacetic Acids in Canadian Lake Waters and Precipitation.”; Environmental Science and Technology, 2000, 34 (20), 1266 – 4272.	Henne, S.; Shallcross, D. E.; Reimann, S.; Xiao, P.; Boulos, S.; Gerecke, A. C.; Brunner, D.; “Environmental impacts of HFO-1234yf and other HFOs.”; Moving Towards Sustainability, ASHRAE/NIST Refrigerants Conference, Gaithersburg, MD, United States, Oct. 29-30, 2012 (2012), 13/1-13/13.

No	Publication data	With cross-reference to the publication:
20	Scribner E. A., Battaglin W. A., Dieze J. E., Thurman E. M., “ <i>Reconnaissance Data for Glyphosate, Other Selected Herbicides, Their Degradation Products, and Antibiotics in 51 Streams in Nine Mid-Western States 2002.</i> ”; US Geological Survey Open-File Report 03-217, 2003. available: http://ks.water.usgs.gov/pubs/reports/ofr.03-217.html	Kolpin D., Battaglin W. A., Conn K. E., Furlong E. T., Glassmeyer S. T., Kalkhoff S. J., Meyer M. T., Schnoebelen D. J., “ <i>Occurrence of Transformation Products in the Environment.</i> ”; Handbook of Environmental Chemistry Volume 2P – Transformation Products of Synthetic Chemicals in the Environment, 2009, 83 – 100 (book chapter).
21	Sinclair C. J., van Beinum W., Adams C., Bevan R., Levy L., Parsons S., et al., “ <i>A desk study on pesticide metabolites, degradation and reaction products to inform the Inspectorate’s position on monitoring requirements.</i> ”; Final Report for Drinking Water Inspectorate, York: Food and Environment Research Agency (FERA), 2010. available: http://dwi.defra.gov.uk/research/completed-research/2000todate.htm	Stuart M., Lapworth D., Crane E., Hart A., “ <i>Review of risk from potential emerging contaminants in UK groundwater.</i> ”; Science of the Total Environment, 2012, 416 (complete), 1 – 21.
22	Stone W. W., Gilliom R. J., Martin J. Q., “ <i>An Overview Comparing Results from Two Decades of Monitoring for Pesticides in the Nation’s Streams and Rivers, 1992 – 2001 and 2002 – 2011.</i> ”; US Geological Survey Scientific Investigation Report 2014-5154, 2014. available: http://water.usgs.gov/nawqa/pnsp	No direct cross-reference – publication found as an additional when USGS site was scanned for additional potentially relevant publications.
23	Toccalino P. L., Gilliom R. J., Lindsey B. D., Rupert M. D., “ <i>Pesticides in Groundwater of the United States: Decadal –Scale Changes, 1993 – 2011.</i> ”; Groundwater, 2014, 52 (Focus Issue), 112 – 125; available: http://water.usgs.gov/nawqa/pnsp	No direct cross-reference – publication found as an additional paper when USGS site was scanned for additional potentially relevant publications.
24	Wujcik C., Cahill T. M., Seiber J. N., “ <i>Determination of Trifluoroacetic Acid in 1996 – 1997 Precipitation and Surface Waters in California and Nevada.</i> ”; Environmental Science and Technology, 1999, 33 (10), 1747 – 1751.	Henne, S.; Shallcross, D. E.; Reimann, S.; Xiao, P.; Boulos, S.; Gerecke, A. C.; Brunner, D.; “ <i>Environmental impacts of HFO-1234yf and other HFOs.</i> ”; Moving Towards Sustainability, ASHRAE/NIST Refrigerants Conference, Gaithersburg, MD, United States, Oct. 29-30, 2012 (2012), 13/1-13/13.

The results of the detailed examination of the relevance of the publications found is provided below in two tables. The first of them – table B.8.6_CA-5, lists the publications that were found not relevant by the RMS in course of the repeated literature search. For each publication non-included the rationale for its rejection is given, together with information, where reliable, whether RMS’s conclusions were similar to those drawn by the Applicant. The publications in that table, except those identified as potentially relevant and subsequently verified with regard to that, are presented in alphabetical order for their first author.

In the second table – B.8.6_CA-6 are listed the publications that RMS found relevant and included into the assessment. In that table the order of publications follows the SANCO data point in the assessment, for which they are considered relevant.

Table B.8.6_CA-5: Results of the “Detailed assessment” stage of the literature search performed by the RMS – publications not included into the RAR on the basis of their non-relevance.

No	Publication data	Reason(s) for considering the publication not relevant for the assessment	RMS' and Applicant's conclusions similar Yes/No
1	Barriuso E., Benoit P., Dubus I. G., “ <i>Formation of Pesticide Nonextractable (Bound) Residues in Soil: Magnitude, Controlling Factors and Reversibility.</i> ”; Environmental Science and Technology, 2008, 42 (6), 1845 – 1854.	Paper initially considered relevant as a supplementary study, helpful in concluding on the nature of NER fraction formed during transformation of Flufenacet in aerobic soil. However, careful examination of the publication showed that it contained very general conclusions, based rather on the results obtained for other active substances. Although the numerical results for Flufenacet with regard to the amount of bound residues formed from it were provided, these were taken from the EU registration report, therefore it was stated that the paper contained no new/adverse data for Flufenacet in this area. As a result, RMS changed the initial decision with regard to the relevance of the publication for the assessment of Flufenacet. The paper, as well as the supporting information, is available on request.	Not applicable – the paper not identified by the Applicant as potentially relevant.
2	Barron L., Brett P., “ <i>Determination of haloacetic acids in drinking water using suppressed micro-bore ion chromatography with soil phase extraction</i> ”; Analytica Chimica Acta 2004, 522, 153 – 161	Paper focuses mainly on the development and validation of the analytical method. Although it provides levels of TFA in drinking water as a final product of water abstraction plants, the source of that compound is different that considered in the assessment of flufenacet – TFA is a by product of the process of fluorination of treated water.	No , Applicant stated that findings were not related to a certain test system.
3	Bazoobandi M., Yaduraju N. T., Kulshrestha G., “ <i>Analysis of flufenacet in soil, wheat grain and straw by gas chromatography.</i> ”; Journal of Chromatography A, 2000, 886 (1-2), 319 – 322.	Paper focuses mainly on the development and validation of the analytical method that was not used by the Applicant. Also the paper provides no information on the results obtained with that method for natural not spiked samples	Yes , Applicant also indicated that the paper did not contain the information related to the substance of concern in the natural samples.
4	Bishop C. A., Ashpole S. L., Edwards M. A., van Aggelen G., Elliot J. E., “ <i>Hatching success and pesticide exposure in amphibians living in agricultural habitats of the South Okanagan Valley, British Columbia, Canada (2004 – 2006).</i> ”; Environmental Toxicology and Chemistry, 2010, 29 (7), 1593 – 1603.	Flufenacet was listed among the compounds of concern, with given LOD of 1.1 ng/L, but the concentrations measured in environment were not reported. Additionally, the SW exposure was determined in the ponds located in orchards, so not relevant for the proposed EU use pattern, and the application regime for flufenacet was not reported, so the paper is of little relevance for monitoring purposes. The relevance for the assessment in the area of ecotoxicology to be confirmed by the expert performing the evaluation.	Not applicable – the paper not identified by the Applicant as potentially relevant.
5	Boithias L., Sauvage S., Srinivasan R., Leccia O., Sánchez-Pérez J.-M., “ <i>Application date as a controlling factor of pesticide transfers to surface water during runoff events.</i> ”; Catena, 2014, 119 , 97 – 103.	Study did not contain any referenced to the compounds of interest – flufenacet or any of its degradation products.	Not applicable – the paper not identified by the Applicant as potentially relevant.

No	Publication data	Reason(s) for considering the publication not relevant for the assessment	RMS' and Applicant's conclusions similar Yes/No
6	Cedergreen N., Streiberg J. C., "The toxicity of herbicides to non-target aquatic plants and algae: assessment of predicted factors and hazard."; Pest Management Science, 2005, 61 (12), 1152 – 1160.	Paper contains no data related to the environmental fate and behaviour of Flufenacet. Its relevance, or lack of it, to the assessment in the area of ecotoxicology to be conformed by the expert performing evaluation in that area.	No , The justification for non-inclusion into the Dossier concerns the evaluation in the area of ecotoxicology with no reference to the assessment in the area of e-fate.
7	Chen B., Lee W., Westerhoff P. K., Krasner S. W., Herckes, P., "Solar photolysis kinetics of disinfection byproducts."; Water Research, 2010, 44 (11), 3401 – 3409.	Paper bears no reference to any compound of concern in the evaluation, in particular to TFA.	Yes , Applicant also indicated that the paper did not contain the information related to the substance of concern.
8	Chiaia-Hernandez A. C., Krauss M., Hollender J., "Screening of Lake Sediments for Emerging Contaminants by Liquid Chromatography Atmospheric Pressure Photoionization and Electrospray Ionization Coupled to High Resolution Mass Spectrometry."; Environmental Science and Technology, 2013, 47 (2), 976 – 986.	Paper mainly focused on the developed analytical method. Flufenacet listed among the compounds of potential interest, but subsequently not listed among those screened for in the natural samples taken from the lake Greifensee.	Yes , Applicant also indicated that the paper did not contain the information related to the substance of concern in the natural (sediment) samples.
9	Chowdhury A., Pradhan S., Saha M., Sanyal N., "Impact of pesticides on soil microbiological parameters and possible bioremediation strategies."; Indian Journal of Microbiology, 2008, 48 (1), 114 – 127.	Paper provides a reference to Flufenacet, but focuses on the general evaluation of the impact of pesticides on soil microflora, with emphasis on other pesticides, for instance 2,4-D.	Not applicable – the paper not identified by the Applicant as potentially relevant.
10	Conte, E., Rossi, E., Spera, G., Pompei, V., Carfi, F., Spadoni, A. R., Rosati, M., Montereali, M. R., Donnarumma, L., Perconti, W., "Presence of plant protection products in three agricultural areas of Regione Lazio."; Communications in Agricultural and Applied Biological Sciences, 2003, 68 (4b), 865-874	Study refers to the concentrations of Flufenacet in soils and water on examined areas, but does it in a general and rather qualitative than quantitative way. Additionally no history of the use of Flufenacet on the examined areas is provided.	Yes , Applicant gave the same rationale.
11	Cross P., Edwards-Jones G., "Variation in pesticide hazard from arable crop production in Great Britain from 1992 to 2008: an extended time-series analysis."; Crop Protection, 2011, 30 (12), 1579 – 1585.	Study did not contain any reference to the compounds of interest – flufenacet or any of its degradation products.	Not applicable – the paper not identified by the Applicant as potentially relevant.
12	D'Eon (Appl. Deon) J. C., Hurley M. D., Wallington, T. J., Mabury S. A., "Atmospheric Chemistry of N-methyl Perfluorobutane Sulfonamidoethanol, C ₄ F ₉ SO ₂ N(CH ₃)CH ₂ CH ₂ OH: Kinetics and Mechanism of Reaction with OH."; Environmental Science and Technology, 2006, 40 (6), 1862 – 1868.	TFA was identified as a terminal product within a transformation scheme, with no further assessment of its fate and behaviour in the environment	Yes , Applicant also indicated that the paper did not contain the information related to the substance of concern.

No	Publication data	Reason(s) for considering the publication not relevant for the assessment	RMS' and Applicant's conclusions similar Yes/No
13	De Schamphelleire M., Sopanoghe P., Brusselman E., Sonck S., <i>"Risk assessment of pesticide spray drift damage in Belgium."</i> ; Crop Protection, 2007, 26 (4), 602 – 611.	Flufenacet was not an active substance examined in detail. The spray drift-related risk for use of flufenacet was examined for its application on potatoes – crop not listed in the EU-representative use pattern.	Not applicable – the paper not identified by the Applicant as potentially relevant.
14	Delcour I., Spanoghe P., Uyttendaele M., <i>"Literature review: Impact of climate change on pesticide use."</i> ; Food Research International, 2015, 68 (complete), 7 – 15.	Paper presents in general the factors influencing the use pattern of plant protection products and changes in it, but with no reference to any specific PPP.	Not applicable – the paper not identified by the Applicant as potentially relevant.
15	Devos Y., Cougnon M., Vergucht S., Bulcke R., Haesaert G., Steurbaut W., Reheul D., <i>"Environmental impact of herbicide regimes used with genetically modified herbicide-resistant maize."</i> ; Transgenic Research, 2008, 17 (6), 1059 – 1077.	The publication does not contain any information on the environmental fate and behaviour of Flufenacet. The relevance for the assessment in the area of ecotoxicology to be conformed by the expert performing the evaluation.	Not applicable – the paper not identified by the Applicant as potentially relevant.
16	Dolan T., Parsons D. J., Howsam P., Whelan M. J., Varga L., <i>"Identifying Adaptation Options and Constraints: The role of Agronomist Knowledge in Catchment Management Strategy."</i> , Water Resources Management, 2014, 28 (2), 511 – 526.	Study did not contain any referenced to the compounds of interest – flufenacet or any of its degradation products.	Not applicable – the paper not identified by the Applicant as potentially relevant.
17	Fay E., Flynn J., Lundehehn J. R., Chapman P. J., Mason R. D., <i>"The Joint Evaluation Procedure for Active Substances contained in Plant Protection Products within the European Community – 10 Years of the ECCO-Project."</i> ; Journal für Verbraucherschutz und Lebensmittelsicherheit, 2007, 2 (1), 61 – 77.	Paper characterizes the activities of ECCO Project during the period of its functioning. It provides a reference to Flufenacet, but very general and not in the area of its environmental fate and behaviour.	Not applicable – the paper not identified by the Applicant as potentially relevant.
18	Finizio A., Villa S., Vighi M., <i>"Predicting pesticide mixtures load in surface waters from a given crop."</i> ; Agriculture, Ecosystems and Environment, 2005, 111 (1-4), 111 – 118	Paper presents the results of the assessment of risk to the freshwater organisms resulting from the use of the mixtures various pesticides in maize. The assessment was based on the determination of the PEC values and their use in the determination of the risk factors for algae, aquatic invertebrates represented by Daphnia spp. and fish. Flufenacet was one of the compounds of concern and the PEC values for it were determined, however their utility, and hence the paper as such, for the current assessment was low, because the modelling approach was different from that currently used in the EU for regulatory purposes.	No – the Applicant stated that the paper did not contain any reference to the substance of concern – Flufenacet.

No	Publication data	Reason(s) for considering the publication not relevant for the assessment	RMS' and Applicant's conclusions similar Yes/No
19	Fohrer N., Dietrich A., Kolychalov O., Ulrich U., "Assessment of the Environmental Fate of the Herbicides Flufenacet and Metazachlor with the SWAT Model."; Journal of Environmental Quality, 2014, 43 (1), 75 – 85.	The publication presents the results of the model estimation of the concentrations of Flufenacet in water of a small river. The calculations were performed for an existing, well characterised catchment located within the EU – Kielstau watershed, and it was validated against the experimental data obtained for that catchment, however these data were not presented. Instead were briefly characterised the results of the modelling exposure assessment obtained using the modelling tool alternative to that used in the regulatory process in the EU – SWAT model. For that reason, after careful examination of the publication, RMS decided to classify it as not relevant.	Not applicable – the paper not identified by the Applicant as potentially relevant.
20	Forest K., Rayne S., "Congener-specific organic carbon-normalized soil and sediment-water partitioning coefficients for the C1 through C8 perfluoroalkyl carboxylic and sulfonic acids."; Journal of Environmental Science and Health, Part A: Toxic/Hazardous Substances and Environmental Engineering, 2009, 44 (13), 1374 – 1387.	Paper provides the values for TFA, but these are determined using QSAR, so of limited utility for regulatory purposes, unless no corresponding measurable values are provided.	Yes, Applicant also indicated the problem of the similar nature.
21	Fujiwara T., O'Hagan D., "Successful fluorine-containing herbicide agrochemicals."; Journal of Fluorine Chemistry, 2014, 167 (complete), 16 – 29.	Publication presents the mechanism of synthesis of various fluorinated active substances of the Plant Protection Products. Authors indicated that the described mechanisms may not be those used by the industry. Publication bears no reference to the environmental fate and behaviour of Flufenacet.	Not applicable – the paper not identified by the Applicant as potentially relevant.
22	Gajbhiye V. T., Gupta S., Agnihotri N. P., "Gas liquid chromatographic method of analysis for a herbicide flufenacet (FOE 5043)."; Pesticide Research Journal, 2000, 12 (1), 41 – 47.	Paper focuses mainly on the development and validation of the analytical method that was not used by the Applicant. Also the paper provides no information on the results obtained with that method for natural not spiked samples	Yes, Applicant also indicated that the paper did not contain the information related to the substance of concern in the natural samples.
23	Gassman P. W., Sadeghi A. M., Srinivasan R., "Applications of the SWAT Model Special Section: Overview and Insights."; Journal of Environmental Quality, 2014, 43 , 1 – 8.	The paper presents the concept and applicability of the novel modelling tool – SWAT. It was initially selected as a supplementary study, supporting selected the assessment presented in the literature study by [Fohrer et al., 2014], also finally not included in the assessment.	Not applicable – the paper not identified by the Applicant as potentially relevant.
24	Gilliom R. J., Barbash J. E., Crawford C. G., Hamilton P. A., Martin J. D., Nakagi N., Nowell L. H., Scott J. C., Stackelberg P. E., Thelin G. P., Wolock D. M., "Quality of Our Nation's Waters. Pesticides in the Nation's Streams and Ground Water, 1992 – 2001."; USGS Circular 1291, 2006, US Geological Survey 2007 (revised version 15 February 2007).	Paper does not contain any reference to Flufenacet or any of its degradation products.	Not applicable – the paper not identified by the Applicant as potentially relevant.

No	Publication data	Reason(s) for considering the publication not relevant for the assessment	RMS' and Applicant's conclusions similar Yes/No
25	Godejohann M., Berset. J.-D., Muff D., "Non-targeted analysis of wastewater treatment plant effluents by high performance liquid chromatography-time slice-solid phase extraction-nuclear magnetic resonance/time-of-flight-mass spectrometry."; Journal of Chromatography, A, 2011, 1218 (51), 9202 – 9209.	Paper focuses on the development and validation of the analytical procedure for determining the micropollutants in WWTP effluents. Although Flufenacet was one of the target compounds, as indicate the data presented in the supplement, and it was found in the effluents, the data, because of their qualitative rather than quantitative nature are difficult in interpretation.	Yes , Applicant also indicated the problem of the similar nature.
26	Greulich K. Alder L., "Fast multiresidue screening of 300 pesticides in water for human consumption by LC-MS/MS."; Analytical and Bioanalytical Chemistry, 2008, 391 (1), 183 – 197.	The publication focused totally on the development and validation of the analytical method for determination of the active substances of plant protection products in water samples. Although flufenacet was one of the test compounds, the publication was considered not valid, as it provided no results of the examination of natural, not spiked, samples.	Not applicable – the paper not identified by the Applicant as potentially relevant.
27	Guy M., Singh M., Mineau P., "Using field data to assess the effects of pesticides on crustacean in freshwater aquatic ecosystems and verifying the level of protection provided by water quality guidelines."; Integrated Environmental Assessment and Management, 2011, 7 (3 – special issue: Challenges Posed by Radiation and Radionuclide releases to the Environment), 426 – 436.	The publication does not contain any information on the environmental fate and behaviour of Flufenacet. The relevance for the assessment in the area of ecotoxicology to be conformed by the expert performing the evaluation.	Not applicable – the paper not identified by the Applicant as potentially relevant.
28	Hanson M. L., Sibley P. K., Mabury S. A., Muir D. C., Solomon K. R., "Chlorodifluoroacetic acid fate and toxicity to the macrophytes Lemna gibba, Myriophyllum spicatum and Myriophyllum sibiricum in aquatic microcosm."; Environmental Toxicology and Chemistry, 2001, 20 , 2758 – 2767.	The publication does not contain any information on the environmental fate and behaviour of Flufenacet. The relevance for the assessment in the area of ecotoxicology to be conformed by the expert performing the evaluation.	Not applicable – the paper not identified by the Applicant as potentially relevant.
29	Hanson M. L., Solomon K. R., "New technique for estimating thresholds of toxicity in ecological risk assessment."; Environmental Science and Technology, 2002, 36 (15), 3257 – 3264.	Publication focuses on the determination of the risk for aquatic plants with no reference to the concentrations measured in the environment. Additionally, the test substance was MCA and not TFA – the compound of concern. The relevance for the assessment in the area of ecotoxicology to be conformed by the expert performing the evaluation.	Yes , Applicant also indicated that the paper did not contain the information related to the substance of concern.
30	Hanson M., Sibley P. K., Ellis D. A., Fineberg N. A., Mabury S. A., Salomon K. R., Muir D. C., "Trichloroacetic acid fate and toxicity to the macrophytes Myriophyllum spicatum and Myriophyllum sibiricum under field conditions."; Aquatic Toxicology, 2002, 56 , 241 – 255;	The publication not relevant because it deals with TCA, not TFA – compound of concern being the metabolite of Flufenacet. However it provided a cross-reference to two other papers dealing with fate and behaviour of TFA in water, which were in turn checked for their relevance in the assessment. The relevance for the assessment in the area of ecotoxicology to be conformed by the expert performing the evaluation.	Yes , Applicant also indicated that the paper did not contain the information related to the substance of concern.

No	Publication data	Reason(s) for considering the publication not relevant for the assessment	RMS' and Applicant's conclusions similar Yes/No
31	Hanson M., Sibley P. K., Ellis D. A., Mabury S. A., Muir D. G. C., Salomon K. R., "Evaluation of monochloroacetic acid (MCA) degradation and toxicity to Lemna gibba, Myriophyllum spicatum and Myriophyllum sibiricum in aquatic microcosm."; Aquatic Toxicology, 2002, 56 , 241 – 255;	The publication not relevant because it deals with MCA, not TFA – compound of concern being the metabolite of Flufenacet. However it provided a cross-reference to other papers dealing with fate and behaviour of TFA in water, which were in turn checked for their relevance in the assessment. The relevance for the assessment in the area of ecotoxicology to be conformed by the expert performing the evaluation.	Yes , Applicant also indicated that the paper did not contain the information related to the substance of concern.
32	Hanson M. L., Sibley P. K., Mabury S. A., Muir D. C. G., Solomon K. R., "Field level evaluation and risk assessment of the toxicity of dichloroacetic acid to the aquatic macrophytes Lemna gibba, Myriophyllum spicatum, and Myriophyllum sibiricum."; Ecotoxicology and Environmental Safety, 2003, 55 (1), 46 – 63.	The publication not relevant because it deals with DCA, not TFA – compound of concern being the metabolite of Flufenacet. However it provided a cross-reference to other papers dealing with behaviour of TFA in water nad its ecotoxicity. The relevance for the assessment in the area of ecotoxicology to be conformed by the expert performing the evaluation.	Yes , Applicant also indicated that the paper did not contain the information related to the substance of concern.
33	Harris K. A. Dangerfield N., Woudneh M., Brown T., Verrin S., Ross P. S., "Partitioning of current-use and legacy pesticides in salmon habitat in British Columbia, Canada."; Environmental Toxicology and Chemistry, 2008, 27 (11), 2253 – 2262.	The impact of 80 active substances was examined. Flufenacet was among 19 active substances considered under the general name "others", not included into the top 10 active substances for which the detailed assessment was performed. The reason for that was not clear, as the LOD was not reported. Its relevance, or lack of it, to the assessment in the area of ecotoxicology to be conformed by the expert performing evaluation in that area.	No , Applicant also indicated that the paper did not contain the information related to the substance of concern.
34	Henne S., Shallcross D. E., Reimann S., Xiao P., Brunner D., O' Doherty S., Buchmann B., "Future Emissions and Atmospheric Fate of HFC-1234yf from Mobile Air Conditioners in Europe."; Environmental Science and Technology, 2012, 46 (3), 1650 – 1658.	The publication presents the estimated levels of concentration of TFA in air over Europe and its deposition with precipitation. The estimations were performed for the estimated levels of emission of various HFCs and HCFCs to the atmosphere, therefore its utility is limited. Additionally, these results, together with the measured amounts of TFA in different environmental compartments, were presented in another publication by the same research team.	Yes , Applicant also indicated the problem of the similar nature.
35	Hillocks R. J., "Farming with fewer pesticides: EU pesticide review and resulting challenges for UK agriculture."; Crop Protection, 2012, 31 (1), 85 – 93.	The publication contains a reference to flufenacet only with regard to its current and future use, but does not deal with any environmental issue related to it.	Not applicable – the paper not identified by the Applicant as potentially relevant.
36	Hurley M. D., Wallington T. J., Sulbaek Andersen M. P., Ellis D. A., Martin J. W., Mabury S. A., "Atmospheric Chemistry of Fluorinated Alcohols: Reaction with Cl Atoms and OH Radicals and Atmospheric Lifetimes."; Journal of Physical Chemistry, A, 2004, 108 (11), 1973 – 1979.	Paper deals with perfluorinated alcohols and no reference in it was made to TFA – the compound of concern in the assessment for Flufenacet.	Yes , Applicant also indicated that the paper did not contain the information related to the substance of concern.

No	Publication data	Reason(s) for considering the publication not relevant for the assessment	RMS' and Applicant's conclusions similar Yes/No
37	Jähniq S. C., Kuemmerlen M., Kiesel J., Domisch S. Cai Q., Schmalz B., Fohrer N., <i>"Modelling of riverine ecosystems by integrating models: conceptual approach, a case study and research agenda."</i> ; Journal of Biogeography, 2012, 39 (12), 2253 – 2263.	The publication presents the results of the model estimation of the concentrations of Flufenacet in water of a small river. The calculations were performed for an existing, well characterised catchment located within the EU – Kielstau watershed. It presents the results of the modelling obtained using the modelling tool alternative to that used in the regulatory process in the EU – SWAT model. It was selected as a supplementary data supporting the assessment presented in the literature study by [Fohrer et al., 2014], also finally not included in the assessment.	Not applicable – the paper not identified by the Applicant as potentially relevant.
38	Kannan K., Ridal J., Sturges J., <i>"Pesticides in the Great Lakes."</i> ; The Handbook of Environmental Chemistry, Volume 5N – Persistent Organic Pollutants in the Great Lakes, 2006, 151 – 199 (book chapter).	Publication contains the reference to Flufenacet and its major degradates, but none of the compounds of concern was a subject of more extensive examination.	Not applicable – the paper not identified by the Applicant as potentially relevant.
39	Katagi T., <i>"Behaviour of Pesticides in Water-Sediment systems."</i> ; Reviews in Environmental Contamination and Toxicology, 2006, 187 , 133 – 251 (book chapter)	Publication provides the detailed information on the transformation of Flufenacet in water/sediment system, but these data are taken from the Assessment Report prepared for the first authorisation of that compound in the EU.	Not applicable – the paper not identified by the Applicant as potentially relevant.
40	Klaus J., Zehe E., Elsner M., Palm J. Schneider D., Schröder B., Steinbeiss S., van Schaik L., West S., <i>"Controls of event-based pesticide leaching in natural soil: a systematic study based on replicated field scale irrigation experiments."</i> ; Journal of Hydrology, 2014, 512 (complete), 528 – 539.	The usefulness of the publication for the regulatory purposes was limited, even though Flufenacet was one of the test compounds, as it mainly focused on the factors influencing the movement of the test compounds through the soil profile to the drainage system on the test field. It could only be used as conformatory for the SW modelling, conforming the relevance of drainage as migration route of Flufenacet to Sw bodies.	Not applicable – the paper not identified by the Applicant as potentially relevant
41	Kolpin D., Battaglin W. A., Conn K. E., Furlong E. T., Glassmeyer S. T., Kalkhoff S. J., Meyer M. T., Schnoebelen D. J., <i>"Occurrence of Transformation Products in the Environment."</i> ; Handbook of Environmental Chemistry Volume 2P – Transformation Products of Synthetic Chemicals in the Environment, 2009, 83 – 100 (book chapter).	Publication as such is of the limited relevance, but it provides several cross-references to other relevant publications.	Not applicable – the paper not identified by the Applicant as potentially relevant.
42	Kuster M., López de Alda M., Barceló D., <i>"Liquid chromatography-tandem mass spectrometric analysis and regulatory issues of polar pesticides in natural and treated waters."</i> ; Journal of Chromatography A, 2009, 1216 (3), 520 – 529.	The publication focused totally on the development and validation of the analytical method for determination of the active substances of plant protection products in water samples. The substances of concern were those registered in the EU up to 2008, so flufenacet was included. However, it provided no results of the examination of natural, not spiked, samples.	Not applicable – the paper not identified by the Applicant as potentially relevant.

No	Publication data	Reason(s) for considering the publication not relevant for the assessment	RMS' and Applicant's conclusions similar Yes/No
43	Lechelt-Kunze C., Meissner R. C., Drewes M., Tietjen, K., <i>"Flufenacet herbicide treatment phenocopies the fiddlehead mutant in Arabidopsis thaliana."</i> ; Pest Management Science, 2003, 59 (8), 847 – 856.	Paper contains no data related to the environmental fate and behaviour of Flufenacet. Its relevance, or lack of it, to the assessment in the area of ecotoxicology to be conformed by the expert performing evaluation in that area.	No , The justification for non-inclusion into the Dossier concerns the evaluation in the area of ecotoxicology with no reference to the assessment in the area of e-fate.
44	Lifongo L. L.; Bowden D. J., Brimblecombe. P., <i>"Photodegradation of haloacetic acids in water."</i> ; Chemosphere, 2004, 55 (3), 467 – 476.	Paper bears no reference to any compound if concern in the evaluation, in particular to TFA.	Yes , Applicant also indicated that the paper did not contain the information related to the substance of concern.
45	Loos M., Krauss M., Fenner K., <i>"Pesticide Nonextractable Residue Formation in Soil: Insights from Inverse Modeling of Degradation Time Series."</i> ; Environmental Science and Technology, 2012, 46 (18), 9830 – 9837.	Paper provides information with regard to the mechanisms of formation of NER in soil for several compound, but flufenacet was not among them.	Yes , Applicant also indicated that the paper did not contain the information related to the substance of concern.
46	Mabury, Scott A.; <i>"Redefining persistence - Fluorinated pollutants in the environment"</i> ; Proceedings of the Biennial International Conference on Monitoring and Measurement of the Environment, 4th, Toronto, ON, Canada, May 27-30, 2002 (2002), 35-40.	Paper informs in a very general way about the mechanisms of the formation of TFA that reaches the environment, but with no reference to the active substances of the Plant Protection Products as its potential source.	Yes , Applicant also indicated that the paper did not contain the information related to the evaluated route of exposure.
47	Machefer G., <i>"Alternatives to isoproturon-based products for the control of grasses and broad-leaved weeds in cereals."</i> (<i>"Alternative Lösungen zu Isoproturon-haltigen Produkten bei der Ungras- und Unkrautbekämpfung in Getreide."</i>); Zeitschrift für Pflanzenkrankheiten und Pflanzenschutz, 2000, Sonderh. 17 , 501 – 508.	Paper deals with the determination of the efficacy of the Plant Protection Products that could be considered the replacements for isoproturon-based herbicides. Flufenacet was one of the examined active substances, used in combination with diflufenican. Paper provides no reference to the environmental fate and behaviour of Flufenacet.	Yes, partly ; Applicant stated that the article reported "effects on organisms considered as such target organisms".
48	Martin J. W., Franklin J., Hanson M. L., Solomon K. R., Mabury S. A., Ellis D. A., Scott B. F., Muir D. G. C., <i>"Detection of Chlorodifluoroacetic Acid in Precipitation: A Possible Product of Fluorocarbon Degradation."</i> ; Environmental Science and Technology, 2000, 34 , 274 – 281.	Paper provided information on the behaviour of TFA in natural water and its sources in the atmosphere, but these were rather references to other publications. Instead it focused mainly on other haloacetic acid – chlorodifluoroacetic acid. As a result, RMS, after thorough examination of the publication decided that it was not relevant for the present assessment.	Not applicable – the paper not identified by the Applicant as potentially relevant. By RMS it was identified as potentially relevant by means of cross-reference.
49	Meffe R., de Bustamante I., <i>"Emerging organic contaminants in surface water and groundwater: A first overview of the situation in Italy."</i> ; Science of the Total Environment, 2014, 481 (complete), 280 – 295.	Paper informs that monitoring concerned 137 active substances, of which 79 were herbicides, but Flufenacet was not listed among them.	Not applicable – the paper not identified by the Applicant as potentially relevant.

No	Publication data	Reason(s) for considering the publication not relevant for the assessment	RMS' and Applicant's conclusions similar Yes/No
50	Milan M., Ferrero A., Letey M., DePalo F., Vidotto F., "Effect of buffer strips and soil texture on runoff losses of flufenacet and isoxaflutole from maize fields."; Journal of Environmental Science and Health, Part B – Pesticides, Food Contaminants & Agricultural Wastes, 2013, 48 (12), 1021 – 1033.	The paper was aimed on the examination of the efficiency of vegetated buffer stripes of variable size and the way of preparation of the seedbed on in reducing runoff from maize fields. Some key parameters, enabling the appropriate interpretation of the results, such as exact application rates and timing, were missing.	Yes , the justification for rejection provided by the Applicant was similar.
51	Müller M., Mentel M., van Hellemond J. J., Henze K., Woehle A. G. M., Martin W. F., "Biochemistry and Evolution of Anaerobic energy Metabolism in Eukaryotes."; Microbiology and Molecular Biology Reviews, 2012, 76 (2), 444 – 495.	Publication contains no reference to either Flufenacet or any of its transformation products. Its relevance, or lack of it, to the assessment in the area of ecotoxicology to be conformed by the expert performing evaluation in that area.	Not applicable – the paper not identified by the Applicant as potentially relevant.
52	Nilsson, E. J. K.; Nielsen, O. J.; Johnson, M. S.; Hurley, M. D.; Wallington, T. J., "Atmospheric chemistry of cis-CF ₃ CH=CHF: Kinetics of reactions with OH radicals and O ₃ and products of OH radical initiated oxidation."; Chemical Physics Letters, 2009, 473 (4-6), 233 – 237.	Paper bears no reference to any compound of concern in the evaluation, in particular to TFA.	Yes , Applicant also indicated that the paper did not contain the information related to the substance of concern.
53	Osteen C. D., Fernandez-Cornejo J., "Economic and Policy issues of U.S. agricultural pesticide use trends."; Pest Management Science, 2013, 69 (9), 1001 – 1025.	Although publication contains few references to Flufenacet, they are not in the area of its environmental fate and behaviour, because that was not the aim of the paper.	Not applicable – the paper not identified by the Applicant as potentially relevant.
54	Paci F., Bartolini D., Rapparini G., "Residual effects of various herbicides on wheat after vegetables." ("Effetti residui di diversi erbicidi su frumento dopo orticole."); Informatore agrario, 2002, 58 (32), 71 – 74.	Paper focuses on the determination of the phytotoxicity of the residues of Plant Protection Products in soil on the succeeding crops. Flufenacet was one of the tested active substances, but it was used as a part of the mix formulation, consisting of Flufenacet and Metribuzin or Flufenacet, Metribuzin and Pendimethalin – the combination not being the subject of the current evaluation. Additionally, no data were provided for the tested mix formulations	Not applicable – the paper not identified by the Applicant as potentially relevant.
55	Paris P., Citro L., Di Carlo E., Maschio G., Pace E., Ursino S., "Rapporto nazionale pesticidi nelle acque, dati 2009 – 2010."; ISPRA Rapporti 175/2013, ISPRA Roma, Italy, 2013.	Paper does not contain any reference to Flufenacet or any of its degradation products.	Not applicable – the paper not identified by the Applicant as potentially relevant.
56	Paris P., Biscceglie S., Maschio G., Pacer E., Parisi Pressice D., Ursino S., "Rapporto nazionale pesticidi nelle acque, dati 2011 – 2012."; ISPRA Rapporti 208/2014, ISPRA Roma, Italy, 2014.	Paper does not contain any reference to Flufenacet or any of its degradation products.	Not applicable – the paper not identified by the Applicant as potentially relevant.

No	Publication data	Reason(s) for considering the publication not relevant for the assessment	RMS' and Applicant's conclusions similar Yes/No
57	Park H., Vecitis C. D., Cheng J., Choi W., Mader B. T., Hoffmann M. R., "Reductive Defluorination of Aqueous Perfluorinated Alkyl Surfactants: Effects of Ionic Headgroup and Chain Length."; Journal of Physical Chemistry, A, 2009, 113 (4), 690 – 696.	Contains no reference to the compound of concern – TFA.	No , the provided rationale stressed on the lack of the values relevant in light of the Regulation EC 1107/2009.
58	Parker D. C., Simmons F. W., Wax L. M., "Fall and Early Preplant Application Timing Effects on Persistence and Efficacy of Acetamide Herbicides."; Weed Technology, 2005, 19 (1), 6 – 13.	The paper presented the results of the efficacy testing for several active substances applied in autumn, including Flufenacet. The compound was applied as a combined formulation containing also metribuzin. Although the persistence of the test compounds in soil was examined, by measuring their concentrations at different time points after application, that was not done for Flufenacet. As a result, it was stated that the publication did not contain any information related to the environmental fate and behaviour of Flufenacet.	Not applicable – the paper not identified by the Applicant as potentially relevant.
59	Perreau F., Einhorn J., "Determination of frequently detected herbicides in water by solid-phase microextraction and gas chromatography coupled to ion-trap tandem mass spectrometry."; Analytical and Bioanalytical Chemistry, 2006, 386 (5), 1449 – 1456.	The publication focused totally on the development and validation of the analytical method for determination of the active substances of plant protection products in water samples. Although flufenacet was one of the test compounds, the publication was considered not valid, as it provided no results of the examination of natural, not spiked, samples.	Yes , Applicant also indicated that the publication also focused on the characterisation of the newly developed analytical method.
60	Pfannerstill M., Guse B., Fohrer N., "A multi-storage groundwater concept for the SWAT model to emphasize nonlinear groundwater dynamics in lowland catchments."; Hydrological Processes, 2014, 28 (12), 5599 – 5612.	Paper was focused on the performance of SWAT model with no reference to any specific compound.	Not applicable – the paper not identified by the Applicant as potentially relevant.
61	Postigo C., Barceló D., "Synthetic organic compounds and their transformation products in groundwater: Occurrence, fate and migration."; Science of the Total Environment, 2015, 503 – 504 (complete), 32 – 47.	Publication provides the concentrations of the two degradation products of Flufenacet – M2 and FOE OXA, in GW compartment, but with no additional information. There is however a reference to the source study, which was consulted for its relevance.	Not applicable – the paper not identified by the Applicant as potentially relevant.
62	Renner R., "A tale of two fish."; Environmental Science and Technology, 2008, 42 (18), 6784 – 6785.	Paper not relevant as it bears no reference to Flufenacet or any of its degradation products. Its relevance, or lack of it, to the assessment in the area of ecotoxicology to be conformed by the expert performing evaluation in that area.	Yes , Applicant also indicated that the paper did not contain the information related to the substance of concern
63	Roberti R., Badiali F., Pisi A., Veronesi A., Pancaldi D., Cesari A., "Sensitivity of <i>Clonostachys rosea</i> and <i>Trichoderma</i> spp. As potential biocontrol agents to pesticides."; Journal of Phytopathology, 2006, 154 (2), 100 – 109.	Paper contains no data related to the environmental fate and behaviour of Flufenacet. Its relevance, or lack of it, to the assessment in the area of ecotoxicology to be conformed by the expert performing evaluation in that area.	No , The justification for non-inclusion into the Dossier concerns the evaluation in the area of ecotoxicology with no reference to the assessment in the area of e-fate.

No	Publication data	Reason(s) for considering the publication not relevant for the assessment	RMS' and Applicant's conclusions similar Yes/No
64	Robles-Molina J., Lara-Ortega F. J., Gilbert-López B., García-Reyes J. F., Molina-Díaz A., "Multi-residue method for the determination of over 400 npriority and emerging pollutants in water and wastewater by solid-phase extraction and liquid chromatography-time-of-flight mass spectrometry."; Journal of Chromatography A, 2014, 1350 , 30 – 43.	The publication focused totally on the development and validation of the analytical method for determination of the active substances of plant protection products in water samples. Although flufenacet was one of the test compounds, the publication was considered not valid, as it provided no results of the examination of natural, not spiked, samples.	Not applicable – the paper not identified by the Applicant as potentially relevant.
65	Ryberg K. R., Vecchia A. V., Martin J. D., Gilliom R. J., "Trends in Pesticide Concentrations in Urban Streams in the United States, 1992 – 2008."; US Geological Survey Scientific Investigations Report 2010-5139, 2010.	Paper does not contain any reference to Flufenacet or any of its degradation products.	Not applicable – the paper not identified by the Applicant as potentially relevant.
66	Ryberg K. R., Vecchia A. V., Gilliom R. J., Martin J. D., "Pesticide Trends in Major Rivers of the United States, 1992 – 2010."; US Geological Survey Scientific Investigations Report 2014-5135, 2014.	Paper does not contain any reference to Flufenacet or any of its degradation products.	Not applicable – the paper not identified by the Applicant as potentially relevant.
67	Schulte-Oehlmann U., Oehlmann J., Keil F., "Before the Curtain Falls: Endocrine-active Pesticides – a German Contamination Legacy."; Reviews of Environmental Contamination and Toxicology, 2011, 213 , 137 – 159 (book chapter).	Paper provides very limited relevant information for Flufenacet in the area of its environmental fate and behaviour – it was only stated that, being one of the compounds of concern of Germany with regard to its relevance for water pollution control, it was detected in Surface Water, but displayed no endocrine disruption activity.	Not applicable – the paper not identified by the Applicant as potentially relevant.
68	Scott B. F., Spencer C., Martin J. W., Barra R., Bootsma H. A., Jones K. C., Johnston A. E., Muir D. C. G., "Comparison of Haloacetic Acids in the Environment of the Northern and Southern Hemispheres."; Environmental Science and Technology, 2005, 39 (22), 8664 – 8670.	The publication provided the data on the distribution of various haloacetic acids, including TFA in selected environmental matrices of selected countries. One of them was the UK. However, the potential sources of TFA in examined environmental matrices were not identified. For the paper it is also not fully clear what soils (agriculturally used or others) were examined, what limits the publication's utility	Yes , Applicant gave the similar rationale.
69	Scott C., Pandey G., Hartley C. J., Jackson C. J., Cheesman M. J., Taylor M. C., Pandey R., Khurena J. L., Teese M., Coppin Weir K. M., Jain R. K. Lal R., Russel R. J., Oakeshott J. G., "The enzymatic basis for pesticide bioremediation."; Indian Journal of Microbiology, 2008, 48 , 65 – 79.	Publication provides the information on the mode of action of several enzymes and classes of enzymes catalysing the transformation of the active substances of Plant Protection Products, but it contains no specific reference to Flufenacet or any of its degradation products.	Not applicable – the paper not identified by the Applicant as potentially relevant.

No	Publication data	Reason(s) for considering the publication not relevant for the assessment	RMS' and Applicant's conclusions similar Yes/No
70	Simončič A., Sušin J., Baša-Česnik H., Bolta Š. V., Gregorčič A., Vrščaj B., "The investigation of agricultural soil pollution in groundwater protection areas of Ljubljana Municipality by plant protection products from 2005 to 2010." („Spremljanje onesnaženosti kmetijskih zemljišč no vodovarstvenih območjih v Mestni občini Ljubljana med leti 2005 in 2010."); Zbornik Predavanj Referatov, 10, Slovenskega Posvetovanja o Varstvu Rastlin, Podčetrtek, Slovenia, 1.-2. Marec 2011, 2011, 157 – 163.	Flufenacet was one of the examined compounds, but no results were presented for it or any other individual compound under examination	Not applicable – the paper not identified by the Applicant as potentially relevant.
71	Singh K. P., Gupta S., Basat N., Mohan N., "QSTR Modelling for Qualitative and Quantitative Toxicity Predictions of Diverse Chemical Pesticides in Honey Bee for Regulatory Purposes."; Chemical Research in Toxicology, 2014, 27 (9), 1504 – 1515.	Study not relevant as it bears no reference to the assessment in the area of environmental fate and behaviour. Its relevance, or lack of it, to the assessment in the area of ecotoxicology to be conformed by the expert performing evaluation in that area.	Not applicable – the paper not identified by the Applicant as potentially relevant.
72	Steckel L. E., Simmons W. F., Sprague C. L., "Soil Factor Effects on Tolerance of Two Corn (<i>Zea mays</i>) Hybrids to Isoxaflutole Plus Flufenacet."; Weed Technology, 2003, 17 (3), 599 – 604,	Paper presented the results of the examination of the phytotoxicity of Flufenacet to maize, also in relation to some soil properties. However the experiment was performed not for Flufenacet alone, but for its combined formulation – with isoxaflutole. Publication contained no reference to the environmental fate and behaviour of Flufenacet.	Not applicable – the paper not identified by the Applicant as potentially relevant.
73	Stone W. W., Gilliom R. J., Martin J. Q., "An Overview Comparing Results from Two Decades of Monitoring for Pesticides in the Nation's Streams and Rivers, 1992 – 2001 and 2002 – 2011."; US Geological Survey Scientific Investigation Report 2014-5154, 2014.	Paper does not contain any reference to Flufenacet or any of its degradation products.	Not applicable – the paper not identified by the Applicant as potentially relevant.
74	Stuart M., Lapworth D., Crane E., Hart A., "Review of risk from potential emerging contaminants in UK groundwater."; Science of the Total Environment, 2012, 416 (complete), 1 – 21.	Paper contains no data related to the environmental fate and behaviour of Flufenacet. It provides however the cross-reference to other publications that were checked for their relevance.	Not applicable – the paper not identified by the Applicant as potentially relevant.
75	Tallevi G., Rapparini G., "New ideas emerging from COLUMA '98" ("Le novità emerse al COLUMA '98."); Informatore Fitopatologico, 1999, 49 (7/8), 32 – 39;	Paper contains reference to Flufenacet as newly developed herbicide to be used in cereals, maize, soya and some other crops, but no data related to the environmental fate and behaviour of Flufenacet.	Not applicable – the paper not identified by the Applicant as potentially relevant.
76	Toccalino P. L., Gilliom R. J., Lindsey B. D., Rupert M. D., "Pesticides in Groundwater of the United States: Decadal –Scale Changes, 1993 – 2011."; Groundwater, 2014, 52 (Focus Issue), 112 – 125.	Paper does not contain any reference to Flufenacet or any of its degradation products.	Not applicable – the paper not identified by the Applicant as potentially relevant.

No	Publication data	Reason(s) for considering the publication not relevant for the assessment	RMS' and Applicant's conclusions similar Yes/No
77	Truong L., Reif D. M., St Mary L., Geier M. C., Truong H. D., Tanguay R. L., "Multidimensional In Vivo Hazard Assessment using Zebra Fish."; Toxicological Sciences, 2014, 137 (1), 212 – 233.	Paper contains no data related to the environmental fate and behaviour of Flufenacet. Its relevance, or lack of it, to the assessment in the area of ecotoxicology to be conformed by the expert performing evaluation in that area.	Not applicable – the paper not identified by the Applicant as potentially relevant.
78	Tsai W.-T., "Environmental hazards and health risk of common liquid perfluoro-n-alkanes, potent greenhouse gases."; Environment International, 2009, 35 (2), 418 – 424	Study is not relevant as it deals mainly with perfluoro-n-alkanes and not their carboxylic acids. Although they are considered as potential precursors of TFA and other perfluorinated carboxylic acids in the atmosphere little is said about the impact of the latter on the environment. Additionally no numerical data are given on the global emissions of perfluoroalkanes into atmosphere and their turnover rates to carboxylic acids.	Yes , Applicant indicated that observations were made for exposure route not representative for the intended use of the compound of concern.
79	Tsai W.-T., "Environmental property modeling of perfluorodecalin and its implications for environmental fate and hazards"; Aerosol and Air Quality Research, 2011, 11 (7), 903 - 907;	Compound of concern is perfluorodecalin – fluoroinated alkane with C ₁₀ chain. The compound is considered to be a potential precursor of TFA – compound of concern in the atmosphere, but its contribution to formation of TFA is estimated to be minimal , as expected concentrations in air are <0.1 ppt.	Yes , Applicant indicated that observations were made for exposure route not representative for the intended use of the compound of concern.
80	Tucci S., Vacula R., Krajcovic J., Proksch P., Martin W., "Variability of Wax Ester Fermentation in Natural and Bleached Euglena gracilis Strains in Response to Oxygen and the Elongase Inhibitor Flufenacet."; Journal of Eukaryotic Microbiology, 2010, 57 (1), 63 – 69.	The paper contains no information related to the fate and behaviour of Flufenacet in the environment. Its relevance, or lack of it, to the assessment in the area of ecotoxicology to be conformed by the expert performing evaluation in that area.	Not applicable – the paper not identified by the Applicant as potentially relevant.
81	Ulrich U., Schulz F., Hugenschmidt C., Fohrer N., "Comparing measurements of herbicides lossess on three different scales." ("Vergleichende Messungen zu Herbizidaustragen auf drei unterschiedlichen Größenskalen."); Hydrologie und Wasserbewirtschaftung, 2012, 56 (4), 215 – 228.	The paper should be considered as relevant, in the area of monitoring, for the purpose of the current assessment. It shall however be indicated that only its abstract and the headings of tables and figures are in english, while the body text is in German. That was the limiting factor with regard to the possibility of verifying its relevance for the assessment. For that reason, although it provides relevant results, RMS decided not to include it into the list of the relevant publications.	Not applicable – the paper not identified by the Applicant as potentially relevant.
82	Ulrich U., Zeiger M., Fohrer N., "Soil structure and herbicide transport on soil surfaces during intermittent artificial rainfall."; Zeitschrift fur Geomorphologie, 2013, 57 Supplement 1, 135 – 155.	The paper examines the run-off of Flufenacet on a laboratory scale – the design of the study is not realistic, therefore of limited utility for the regulatory purpose.	Yes , the reasons for the non-relevance of the paper given by the Applicant were the same.
83	Ulrich U., Dietrich A., Fohrer N., "Herbicide transport via surface runoff during intermittent artificial rainfall: A laboratory plot scale study."; Catena, 2013, 101 (complete), 38 – 49.	The paper examines the run-off of Flufenacet on a laboratory scale – the design of the study is not realistic, therefore of limited utility for the regulatory purpose.	Yes , the reasons for the non-relevance of the paper given by the Applicant were the same.

No	Publication data	Reason(s) for considering the publication not relevant for the assessment	RMS' and Applicant's conclusions similar Yes/No
84	Unterreiner G. A., Kehew A. E., <i>"Spatial and temporal distribution of herbicides and herbicide degradates in a shallow glacial drift aquifer/surface water system, south-central Michigan."</i> ; Groundwater Monitoring & Remediation, 2005, 25 (2), 87 – 95.	Paper contains the reference to Flufenacet and its degradation products, but without providing any measurable values for them, because they were not target compounds in that particular study.	Not applicable – the paper not identified by the Applicant as potentially relevant.
85	Van't Zelfde M., Tamis W. L., Vijver M. G., De Snoo G. R., <i>"The contribution of neighbouring countries to pesticide levels in Dutch surface waters."</i> ; Communications In Agricultural and Applied Biological Sciences (Univ. Ghent), 2011, 76 (4), 867 – 877.;	Paper reported the results of the extensive monitoring study performed in the Netherlands and focused on the transboundary pollution of SW bodies in that country with pesticides. Flufenacet is one of the compounds indicated as causing problems. However the whole assessment is rather qualitative than quantitative, with no concentrations reported. For that reason it is of the limited utility for the assessment and RMS decided not to include it into the list of relevant publications.	Not applicable – the paper not identified by the Applicant as potentially relevant.
86	Vasilakoglou I. B., Eleftherohorinos I. G., <i>"Persistence, efficacy and selectivity of amide herbicides in corn."</i> ; Weed Technology, 2003, 17 (2), 381 – 388.	Paper focused mainly on examining phytotoxicity of Flufenacet to maize. There are references to the persistence of that compound in soil under field conditions, but they are presented in rather qualitative than quantitative way.	Not applicable – the paper not identified by the Applicant as potentially relevant.
87	Vasilakoglou I. B., Eleftherohorinos I. G., Dhima K. B., <i>"Activity, adsorption and mobility of three acetanilide and two new amide herbicides."</i> ; Weed Research, 2001, 41 (6), 535 – 546.	Paper provides the data on the soil sorption of Flufenacet, however due to the several identified deficiencies, mainly related to the analytical protocol, cannot be considered as providing reliable estimates of the adsorption parameters for Flufenacet. For that reason, after thorough examination, it was not included into the list of reliable scientific papers to be used in the assessment.	Yes , the Applicant also indicated that the deficiencies of the experimental protocol excluded the paper from the list of publications that may be used in the assessment.
88	Verro R., Finizio A., Otto S., Vighi S., <i>"Predicting Pesticide Environmental Risk in Intensive Agricultural Areas. I: Screening Level Risk Assessment of Individual Chemicals in Surface Waters."</i> ; Environmental Science and Technology, 2009, 43 (2), 522 – 529.	The paper provides a very general evaluation, although for a specific catchment. Flufenacet was one of the compounds of concern, but the paper contains no specific data related to it. The paper provides the numerical values, but obtained by means of modelling using the approach alternative to that currently used in the EU for regulatory purposes.	Not applicable – the paper not identified by the Applicant as potentially relevant.
89	Verro R., Finizio A., Otto S., Vighi S., <i>"Predicting Pesticide Environmental Risk in Intensive Agricultural Areas. II: Screening Level Risk Assessment of Complex Mixtures in Surface Waters."</i> ; Environmental Science and Technology, 2009, 43 (2), 530 – 537.	Paper deals with toxicity and the risk posed to aquatic environment by the mixtures of the active substances. From that point of view its relevance for the assessment in the area of environmental fate and behaviour, although Flufenacet is listed among the examined compounds, is very limited. Its relevance, or lack of it, to the assessment in the area of ecotoxicology to be confirmed by the expert performing evaluation in that area.	Not applicable – the paper not identified by the Applicant as potentially relevant.

No	Publication data	Reason(s) for considering the publication not relevant for the assessment	RMS' and Applicant's conclusions similar Yes/No
90	von der Ohe P. C., Dulio V., Slobodnik J., De Deckere E., Kühne R., Ebert R.-U., Ginebreda A., De Cooman W., Schüürmann G., Brack W., "A new risk assessment approach for the prioritization of 500 classical and emerging organic microcontaminants as potential river basin specific pollutants under the European Water Framework Directive."; Science of the Total Environment, 2011, 409 (11), 2064 – 2077.	The paper contains the reference to Flufenacet, but of a very limited utility for the regulatory process.	Not applicable – the paper not identified by the Applicant as potentially relevant.
91	Wheeler J. R., Maynard S. K., Crane M., "An evaluation of fish early life stage tests for predicting reproductive and longer-term toxicity from plant protection product active substances."; Environmental Toxicology and Chemistry, 2014, 33 (8), 1874 – 1878.	Paper does not contain any reference to the environmental fate and behaviour of flufenacet or its degradation products. Its relevance, or lack of it, to the assessment in the area of ecotoxicology to be conformed by the expert performing evaluation in that area.	Not applicable – the paper not identified by the Applicant as potentially relevant.
92	Whiteside M., Mineau P., Morrison C., Knopper L. D., "Comparison of a score-based approach with risk-based ranking in-use agricultural pesticides in Canada to aquatic receptors."; Integrated Environmental Assessment and Management, 2008, 4 (2), 215 – 236.	Paper provides the data on categorisation of active substances on the basis of their exposure-to effect factor. Flufenacet is among the substances of concern, but with no clear reference to its environmental fate and behaviour. The paper focuses more on the ecotoxicological aspects of the problem. Its relevance, or lack of it, to the assessment in the area of ecotoxicology to be conformed by the expert performing evaluation in that area.	Not applicable – the paper not identified by the Applicant as potentially relevant.
93	Włodarczyk M., Wybieralski J., Praczyk T., "Influence of dose of flufenacet on its degradation on light soil." ("Wpływ wielkości dawki flufenacetu na jego trwałość w glebie lekkiej."); Progress in Plant Protection, 2007, 47 (3), 306 – 309.	Paper displays several deficiencies in analytical protocol and there are inconsistencies in the conclusions drawn.	Not applicable – the paper not identified by the Applicant as potentially relevant.
94	Włodarczyk M., Wybieralski J., Praczyk T., "Influence of adjuvants on flufenacet degradation in light soil in field condition." ("Wpływ adiuwantów na trwałość flufenacetu w glebie lekkiej w warunkach polowych."); Progress in Plant Protection, 2008, 48 (4), 1271 – 1275.	Paper displays several deficiencies in analytical protocol and there are inconsistencies in the conclusions drawn. Additionally the main focus is on the examination of the influence of adjuvant on the persistence of Flufenacet in soil under field conditions.	Not applicable – the paper not identified by the Applicant as potentially relevant.
95	Włodarczyk, M.; Wybieralski, J.; „Adsorption kinetics of atrazine and flufenacet and their water/soil partition coefficients <i>K_d</i> and <i>KOC</i> ”; Ekologia i Technika (2006), 14(1), 16-22	Paper displays several deficiencies in analytical protocol. It seems not to comply with the provisions of OECD 106 Guideline, mainly because the test compound – Flufenacet was applied as a formulated product containing another active substance – atrazine, what might have corrupted the results.	Yes , the Applicant also indicated that the deficiencies of the experimental protocol excluded the paper from the list of publications that may be used in the assessment.

No	Publication data	Reason(s) for considering the publication not relevant for the assessment	RMS' and Applicant's conclusions similar Yes/No
96	Włodarczyk M., "Influence of adjuvant Adpros 850 SL on adsorption of flufenacet on soils with different organic carbon content." ("Wpływ adiuwantu Adpros 850 SL na adsorpcję flufenacetu na glebach o różnej zawartości węgla organicznego."); Progress in Plant Protection, 2009, 49 (3), 1456 – 1460.	Paper displays several deficiencies in analytical protocol. It seems not to comply with the provisions of OECD 106 Guideline, mainly because the test compound – Flufenacet was applied as a formulated product, probably containing also another active substance – atrazine. Additionally, its main goal was to examine the influence of adjuvant on the adsorption of Flufenacet onto soil.	Yes , the Applicant also indicated that the deficiencies of the experimental protocol excluded the paper from the list of publications that may be used in the assessment.
97	Woudnech M. B., Ou Z., Sekela M., Tuominen T., Gledhik M., "Pesticide Multiresidues in Waters of the Lower Fraser Valley, British Columbia, Canada. Part I. Surface Water."; Journal of Environmental Quality, 2009, 38 , 940 – 947.	Flufenacet was among the compounds selected for determination, with reporting limits (LOD?) of 0.86 ng/L, but no measurable values were provided. As the use pattern on the examined area was not given, it cannot be stated what was the reason for the non-detection of Flufenacet in natural water samples.	Not applicable – the paper not identified by the Applicant as potentially relevant.
98	Xiang W., Xiang J., Zhang J. G., Wu F., Tang J. H., "Geochemical transformation of trichloroacetic acid to chloroform in fresh waters - The results based upon laboratory experiments."; Water, Air and Soil Pollution, 2005, 168 (1-4), 289 – 312.	Paper deals with reductive transformation of TCA to chloroform, so it does not concern the compound of interest – TFA.	Yes , Applicant also indicated that the paper did not contain the information related to the substance of concern.
99	Young C. J., Hurley M. D., Wallington T. J., Mabury S. A., "Atmospheric chemistry of CF ₃ CF ₂ H and CF ₃ CF ₂ CF ₂ H: Kinetics and products of gas-phase reactions with Cl atoms and OH radicals, infrared spectra, and formation of perfluorocarboxylic acids."; Chemical Physics Letters, 2009, 473 (4-6), 251 – 256.	Study does not contain any reference to the substances of concern, in particular TFA.	No , Applicant in his rationale pointed out that the paper reported chemical synthesis or the development of measurement methods with no application to natural samples.

Table B.8.6_CA-6: Results of the "Detailed assessment" stage of the literature search performed by the RMS – publications found relevant and included into the RAR.

No	SANCO Data Point	Publication data	Reason(s) for inclusion into RAR and status
1	KCA B.8.1.1.1.1.	Bloomberg A. M., Shadrick B. A., Arthur E. L., Clay V. E., "Outdoor soil metabolism of [Phenyl-U- ¹⁴ C] Flufenacet on California Soils."; ACS Symposium Series, 2002, vol. 813 – "Pesticide Environmental Fate" (chapter 12), 167 – 182 (book chapter); published (print) 2009.	Study presents the results of the examination of the degradation of Flufenacet in two soils under field, semi-controlled conditions – in open vessels placed outdoors and treated with radiolabelled Flufenacet. Status of the study: because the study enabled the identification and quantitation of the degradation products of Flufenacet, it should be considered as relevant and used to derive regulatory endpoints.

No	SANCO Data Point	Publication data	Reason(s) for inclusion into RAR and status
2	KCA B.8.1.1.1.1.1.	Lam C. K., McKinney M. K., Clay V. E., “ <i>Evaluation of Laboratory and Field Extraction Methods: Extraction of [Phenyl-¹⁴C] Flufenacet from Aged Soils.</i> ”; ACS Symposium Series, 2002, vol. 813 – “Pesticide Environmental Fate” (chapter 11), 153 – 166 (book chapter); published (print) 2009.	The study presents the performance parameters of two analytical procedures, one of which was used in the studies submitted by the Applicant. For that reason it can be used to conform the validity of the studies. Additionally it provides the information on the amounts of two major degradation products formed. Status of the study: supplementary, not to be used to derive regulatory endpoints.
3	KCA B.8.1.1.2.1.1. KCA B.8.1.2. KCA B.8.1.3.1.	Gupta S., Gajbhiye V. T., Agnihotri N. P., “ <i>Adsorption-Desorption, Persistence, and Leaching Behaviour of Flufenacet in Alluvial Soil of India.</i> ”; Bulletin of Environmental Contamination and Toxicology, 2001, 66 (1), 9 – 16.	Study provides numerical results of the determination of persistence, adsorption parameters and leaching in soil column for one soil. The test soil is a non-EU soil, what somehow limits the utility of the study, nevertheless it provides the data that can be considered supplementary to the Applicant’s ones. Status of the study: supplementary, not to be used to derive regulatory endpoints.
4	KCA B.8.1.1.2.1.1.	Gupta S., Gajbhiye V. J., “ <i>Effect of concentration, moisture and soil type on the dissipation of flufenacet from soil.</i> ”; Chemosphere, 2002, 47 (9), 901 – 906.	Study provides numerical results of the determination of persistence in three different soils and influence of different parameters on the process. The test soils were non-EU soils, what somehow limits the utility of the study, nevertheless it provides the data that can be considered supplementary to the Applicant’s ones. Status of the study: supplementary, not to be used to derive regulatory endpoints.
5	KCA B.8.1.1.2.2.	Rouchaud J., Neus O., Cools K., Bulcke R., “ <i>Flufenacet Soil Persistence and Mobility in Corn and Wheat Crops.</i> ”; Bulletin of Environmental Contamination and Toxicology, 1999, 63 (4), 406 – 466.	Study provides the numerical results of the examination of the dissipation Flufenacet in soil in field conditions. The test system was well characterised. Status of the study: supplementary, not to be used to derive regulatory endpoints.
6	KCA B.8.1.1.2.2.; KCA B.8.1.2.	Rouchaud J., Neus O., Cools K., Bulcke R., “ <i>Dissipation and mobility of the oxyacetamide flufenacet herbicide in corn and wheat crops.</i> ”; Mededelingen – Faculteit Landbouwkundige en Toegepaste Biologische Wetenschappen, Universiteit Gent, 1999, 64 (3b), 673 – 677.;	examination of the dissipation Flufenacet in soil in field conditions. The test system was well characterised. It provides also information on accumulation potential of Flufenacet in soil and the phytotoxicity of its residues for succeeding crops. Status of the study: supplementary, not to be used to derive regulatory endpoints.
7	KCA B.8.1.1.2.2.	Rouchaud J., Neus O., Eelen H., Bulcke R., “ <i>Persistence, Mobility, and Adsorption of the Herbicide Flufenacet in the Soil of Winter Wheat Crops.</i> ”; Bulletin of Environmental Contamination and Toxicology, 2001, 67 (4), 609 – 616.	Study provides the numerical results of the examination of the dissipation Flufenacet in soil in field conditions. The test system was well characterised. It provides a further insight into a test systems presented in the earlier study (Rouchaud et al; 1999). Status of the study: supplementary, not to be used to derive regulatory endpoints.
8	KCA B.8.1.2.	Gajbhiye V. T., Gupta S., “ <i>Adsorption-desorption behaviour of flufenacet in five different soils of India.</i> ”; Pest Management Science, 2001, 57 (7), 633 – 639.	Paper provides the numerical results of the examination of adsorption of flufenacet in five soils. Although the specific guidelines are not specified, study seemed to comply with OECD 106 Guideline, and the paper provides all data required in such cases. It shall however be pointed out that the test soils are non-EU soils, so the results are only supplementary ones. Status of the study: supplementary, not to be used to derive regulatory endpoints.

No	SANCO Data Point	Publication data	Reason(s) for inclusion into RAR and status
9	KCA B.8.1.3.1.	Campagna G., Paci F., Fabbri A., Rapparini G., “ <i>Percolation of acetochlor, dimethenamid, flufenacet and s-metolachlor applied in columns.</i> ” (“ <i>Studio in colonna della percolazione di alcuni dieserbanti residuali del mais.</i> ”); Giornate Fitopatologiche 2006, Riccione (RN), 27-29 Marzo 2009 Atti, volume primo (University of Bologna) 2006, 591 - 598, (book chapter, conference paper)	Paper provides the numerical results of the examination of leaching behaviour of flufenacet in soil columns. Although the specific guidelines are not specified, study seemed to comply with OECD 312 Guideline, and the paper provides all data required in such cases. Status of the study: supplementary, not to be used to derive regulatory endpoints.
10	KCA B.8.2.1.1.	Rani Sunita, Kumari Beena., Kathpal T. S., “ <i>Effect of pH on the dissipation behaviour of flufenacet (FOE-5043) in water.</i> ”; Pesticide Research Journal, 2006, 18 (2), 201 – 204.	Paper provides the results of the examination of the aqueous hydrolysis of Flufenacet. The experimental protocol seems to comply with OECD 111 Guideline, although the measurements were performed at ambient temperature and it was not indicated whether the buffer solutions were sterile throughout the experiment. Status of the study: supplementary, not to be used to derive regulatory endpoints.
11	KCA B.8.2.2.4.; KCP B.8.4.	Ellis D. A., Hanson M. L., Sibley P. K., Shahid T., Fineberg N. a., Solomon K. R., Muir D. C. G., Mabury S. A., “ <i>The fate and persistence of trifluoroacetic and chloroacetic acids in pond water.</i> ”; Chemosphere, 2001, 42 , 309 – 318	Paper describes the fate and behaviour of TFA in natural water body – a pond. It may be considered a special case of water/sediment study. Status of the study: supplementary, not to be used to derive regulatory endpoints.
12	KCA B.8.2.6	anon., “ <i>Final Report of Project WT1246- Understanding changes in pesticide usage to inform water company risk assessment.</i> ”, DEFRA 2013,	The reports provides the estimates of the concentrations of Flufenacet and its degradation products in drinking water and substrate for its abstraction. It also provides estimates for the removal of Flufenacet during the substrate treatment for drinking water. Status of the study: major, enabling the addressing the issue of the impact on water treatment procedures.
13	KCA B.8.2.6	Sinclair C. J., van Beinum W., Adams C., Bevan R., Levy L., Parsons S., et al., “ <i>A desk study on pesticide metabolites, degradation and reaction products to inform the Inspectorate’s position on monitoring requirements.</i> ”; Final Report for Drinking Water Inspectorate, York: Food and Environment Research Agency (FERA), 2010.	The reports provides the estimates of the concentrations of Flufenacet and its degradation products in drinking water and substrate for its abstraction. It also provides estimates for the removal of the degradation products Flufenacet during the substrate treatment for drinking water as well as their potential toxicity. Status of the study: major, enabling the addressing the issue of the impact on water treatment procedures.
14	KCA B.8.2.6	Manoj A. Lazar, Shaji Varghese, Santhosh S. Nair, “ <i>Photocatalytic Water Treatment by Titanium Dioxide: Recent Updates.</i> ”; Catalysis, 2012, 2 , 572 – 601.	Provides a general overview of AOP process using TiO ₂ . Status of the study: supplementary, in the area of the impact on water treatment procedures.
15	KCA B.8.2.6	Sakkas V. A., Calza P., Vlachou A. D., Medana C., Minero C, Albanis T., “ <i>Photocatalytic transformation of flufenacet over TiO₂ aqueous suspensions: Identification of intermediates and the mechanisms involved.</i> ”; Applied Catalysis, B: Environmental; 2011, 110 (complete), 238 – 250;	The paper describes the transformation of flufenacet in water during the process of UV-induced Advanced Oxidation Process (AOP) with TiO ₂ as catalyst, which is now commonly used step in purification of water abstracted for drinking purposes and specifically for elimination of pesticides from the substrate. Status of the study: major, enabling the addressing the issue of the impact on water treatment procedures.
16	KCA B.8.2.6	Verstraeten I. M., Thurman E. M., Lindsey M. E., Lee E. C., “ <i>Changes in concentrations of triazine and acetamide herbicides by bank filtration, ozonation, and chlorination in a public water supply.</i> ”, Journal of Hydrology, 2002, 266 (3-4), 190 – 208.	Paper presents the efficiency of the removal of Flufenacet in the typical drinking water abstraction plant. All steps of treatment are covered. Status of the study: major, enabling the addressing the issue of the impact on water treatment procedures.

No	SANCO Data Point	Publication data	Reason(s) for inclusion into RAR and status
17	KCA B.8.2.6	Dealtry S., Holmsgaard P. N., Dunon V., Jechalke S. Ding G.-C., Krögerrecklenfort E., Heuer H., Hansen L. H., Springael D., Zühlke S., Sørensen S. J., Smalla K., “ <i>Shifts in Abundance and Diversity of Mobile Genetic Elements after the Introduction of Diverse Pesticides into an On-Farm Biopurification System over a Course of a Year.</i> ”; Applied and Environmental Microbiology, 2014, 80 (13), 4012 – 4020.	Paper presents the performance of On-farm wastewater treatment plants in treasting wastewater containing the residues of plant protection products. Flufenacet was one of 7 major compounds of concern. The study, despite its limitations – it reports only the concentrations of flufenacet retained in BPS material without reporting its concentrations in water prior and after the treatment, it may be considered indicative with regard to the efficiency of the removal of Flufenacet by such installations. Status of the study: supplementary, in the area of the impact on water treatment procedures.
18	KCA B.8.2.6	Hollender J., Zimmermann S. G., Koepke S., Krauss M., McArdell C. S., Ort C., Singer H., von Gunten U., Siegrist H., “ <i>Elimination of Organic Micropollutants in a Municipal Wastewater Treatment Plant Upgraded with Full-Scale – Ozonation Followed by Sand Filtration.</i> ”; Environmental Science and Technology, 2009, 43 (20), 7862 – 7869;	Study examined the efficiency of the removal of 220 micropollutants present in secondary effluent of WWTP, by ozonation. Flufenacet and its OXA and ASA metabolites were listed among the compounds screened in secondary and post-ozonation effluents, but with no numerical results provided, most probably not detected in concentrations > 15 ng/L. There is no information about the initial concentrations of these compounds in treated wastewater. Status of the study: supplementary, in the area of the impact on water treatment procedures.
19	KCA B.8.2.6	Sinclair C. J., Boxall A. B. A., Parsons S. A., Thomas M. R., “ <i>Prioritization of Pesticide Environmental Transformation Products in Drinking Water Supplies.</i> ”; Environmental Science and Technology, 2006, 40 (23), 7283 – 7289.	Paper does not contain any specific reference to flufenacet or its degradation products, but it provides a clear methodology for assessing the importance of the degradation products for the processes of the abstraction of drinking water. From that point of view it may be considered useful with regard to the evaluation of the impact of the degradates of Flufenacet on weater treatment procedures. Status of the study: supplementary, in the area of the impact on water treatment procedures.
20	KCA B.8.3.1.	Hurley M. D., Sulbaek Andersen, M. P., Wallington T. J., Ellis D. A., Martin J. W., Mabury S. A., “ <i>Atmospheric Chemistry of Perfluorinated Carboxylic Acids: Reaction with OH Radicals and Atmospheric Lifetimes.</i> ”; Journal of Physical Chemistry, A, 2004, 108 (4), 615 – 620.	It provides the information relevant for elucidating the route and rate of degradation of TFA in the atmosphere. Status of the study: supplementary, not to be used to derive regulatory endpoints.
21	KCA B.8.3.1.	Oeberg, T. “ <i>A QSAR for the hydroxyl radical reaction rate constant: validation, domain of application, and prediction.</i> ”; Atmospheric Environment 2005, 39 (12), 2189 – 2200.	Paper provides the half life for TFA in atmosphere. Three calculations were in line with EU recommendations. Status of the study: supplementary, not to be used to derive regulatory endpoints.
22	KCA B.8.3.1.	Kutsuna S., Hori H., “ <i>Experimental determination of Henry's law constants of trifluoroacetic acid at 278-298 K.</i> ”; Atmospheric Environment, 2008, 42 (7), 1399 – 1412.	Paper provides the value of Henry's law constant for TFA and therefore addresses the issue of the would-be behaviour of the compound on the borderline between water and air, as well as possible implications for air pollution. Status of the study: supplementary, not to be used to derive regulatory endpoints.
23	KCA B.8.3.1.	Bowden D. J., Clegg S. L., Brimblecombe P. “ <i>The Henry's law constant of Trifluoroacetic acid and its partitioning into liquid water in the atmosphere.</i> ”; Chemosphere, 1996, 32 (2), 405 – 420;	Paper provides the value of Henry's law constant for TFA and therefore addresses the issue of the would-be behaviour of the compound on the borderline between water and air, as well as possible implications for air pollution. Status of the study: supplementary, not to be used to derive regulatory endpoints.

No	SANCO Data Point	Publication data	Reason(s) for inclusion into RAR and status
24	KCA B.8.3.2.; KCA B.8.5.	Capel P. D., McCarthy K. A., Barbash J. E., “ <i>National, Holistic, Watershed-Scale Approach to Understand the Sources, Transport, and Fate of Agricultural Chemicals.</i> ”; Journal of Environmental Quality, 2008, 37 , 983 – 993.	Paper provides the characterisation of the methodological approach as well as characteristic of the sampling locations used in several other studies aimed on the monitoring of Flufenacet and its degradation products across the USA. It was identified by cross-reference in the study by [Vogel et al.; 2008], used in this assessment as the relevant study in the area of the examination of transport of Flufenacet in the atmosphere. For that reason, although it contains no data directly related to the monitoring of Flufenacet, this publication was included as relevant into the Renewal Assessment Report. Status of the study: supplementary, not to be used to derive regulatory endpoints.
25	KCA B.8.3.2.; KCA B.8.5.	Vogel J. R., Majewski M. S., Capel P. D., “ <i>Pesticides in Rain in Four Agricultural Watersheds in the United States.</i> ”; Journal of Environmental Quality, 2008, 37 , 1101 – 1115.	Paper provides the measured concentrations of Flufenacet in rain water samples. Status of the study: relevant in the area of determination of the behaviour of Flufenacet in the air and its secondary deposition, however not to be used to derive regulatory endpoints.
26	KCA B.8.3.2.; KCA B.8.5.	Henne, S.; Shallcross, D. E.; Reimann, S.; Xiao, P.; Boulos, S.; Gerecke, A. C.; Brunner, D.; “ <i>Environmental impacts of HFO-1234yf and other HFOs.</i> ”; Moving Towards Sustainability, ASHRAE/NIST Refrigerants Conference, Gaithersburg, MD, United States, Oct. 29-30, 2012 (2012), 13/1-13/13.	The paper presents potential sources of TFA in environment. As such it may be used to demonstrate the contribution of flufenacet as source of TFA in environment as marginal. Additionally it provides the numerical data on concentrations of TFA in rain water. Status of the study: supplementary and conformatory in the areas of the assessment of fate and behaviour in air and monitoring.
27	KCA B.8.3.2.; KCA B.8.5.	Jordan A., Frank H., “ <i>Trifluoroacetate in the Environment. Evidence for Sources Other Than HFC/HCFCs.</i> ”; Environmental Science and Technology, 1999, 33 (4), 522 – 527;	The paper presents potential sources of TFA in environment. As such it may be used to demonstrate the contribution of flufenacet as source of TFA in environment as marginal. Additionally it provides the numerical data on concentrations of TFA in rain water. Status of the study: supplementary and conformatory in the areas of the assessment of fate and behaviour in air and monitoring.
28	KCA B.8.3.2.	Wilson S. R., Solomon K. R., Tang X., „ <i>Changes in tropospheric composition and air quality due to stratospheric ozone depletion and climate change.</i> ”; Photochemical and Photobiological Sciences, 2007, 6 (3), 301 – 310.	Paper provides the information on the sources of TFA as well as its removal from that compartment via wet deposition, as well as background concentrations in water. Status of the study: fully relevant with regard to fate and behaviour of TFA in the atmosphere, however not to be used to derive regulatory endpoints.
29	KCA B.8.5.	Baker N. T., Stone W. S., “ <i>Estimated Annual Agricultural Pesticide Use for Counties of the Conterminous United States, 2008 – 12.</i> ”; US Geological Survey Data Series 907, 2015.	Paper provides the background information on the methodology for the preparation of maps of use on pesticides in the US, including Flufenacet. It is relevant as the background information for the studies presenting the results of the monitoring for Flufenacet residues in GW and SW compartments. Status of the study: relevant in the area of monitoring of residues of Flufenacet in SW compartment.
30	KCA B.8.5.	Battaglin W. A., Kolpin D. A., Scribner E. A., Kuivila K. M., Sandstrom M. W., “ <i>Glyphosate, other herbicides, and transformation products in Midwestern streams, 2002.</i> ”; JAWRA Journal of the American Water Resources Association, 2005, 41 (2), 323 – 332.	Paper provides the measured concentrations of Flufenacet and its OXA and ASA degradation products in streams. Status of the study: relevant in the area of monitoring of residues of Flufenacet in SW compartment, however not to be used to derive regulatory endpoints.

No	SANCO Data Point	Publication data	Reason(s) for inclusion into RAR and status
31	KCA B.8.5.	Berg M., Müller S. R., Mühlemann J., Wiedmer A., Schwarzenbach R. P., „Concentrations and Mass Fluxes of Chloroacetic acids and Trifluoroacetic acid in Rain and Natural Waters in Switzerland.”; Environmental Science and Technology, 2000, 34 (13), 2675 – 2683;	Paper provides the data on the concentrations of TFA in precipitation and water samples collected in Switzerland. Status of the study: relevant in the area of monitoring of TFA in environment, however not to be used to derive regulatory endpoints.
32	KCA B.8.5.	Bishoff G., Pestmer W., Rodemann B.; “Entry of pesticides into surface waters – new results of Lamsprange run-off monitoring project 1999 – 2001.”; Pesticide in Air, Plant, Soil and Water System, Proceedings of the Symposium Pesticide Chemistry, 12 th , Piacenza, Italy, 2003, pp. 849 – 856.	Paper submitted by the Applicant, presents the results of the monitoring study carried out in an agricultural European catchment. Flufenacet was one of the compounds of concern. Status of the study: relevant in the area of monitoring of residues of Flufenacet in SW compartment, however not to be used to derive regulatory endpoints.
33	KCA B.8.5.	Durham L., Fisk A., Kannan K., Macdonald R. W., Miur D. C. G., Scott B. F., Spencer C., Witter A., Yamashita N., “Trifluoroacetate profiles in the Arctic, Atlantic, and Pacific Oceans.”; Environmental Science and Technology, 2005, 39 (17), 6555 – 6560.	Paper submitted by the Applicant, provides the data on the concentrations of TFA in marine environment. Status of the study: relevant in the area of monitoring of TFA in environment, however not to be used to derive regulatory endpoints.
34	KCA B.8.5.	Frank H., Christoph E. H., Holm-Hansen O., Bullister J. L., “Trifluoroacetate in Ocean Waters.”; Environmental Science and Technology, 2002, 36 (1), 12 – 15.	Paper submitted by the Applicant, provides the data on the concentrations of TFA in marine environment. Status of the study: relevant in the area of monitoring of TFA in environment, however not to be used to derive regulatory endpoints.
35	KCA B.8.5.;	Kern S., Singer H., Hollender J., Schwarzenbach R. P., Fenner K., “Assessing Exposure to Transformation Products of Soil-Applied Organic Contaminants in Surface Water: Comparison of Model Predictions and Field Data.”; Environmental Science and Technology, 2011, 45 (7), 2833 – 2841.	Paper provides the results of measuring and modelling assessment of the concentrations of Flufenacet, FOE OXA and FOE ASA in SW and GW compartments. It is therefore relevant for monitoring, may be also considered as indicative and conformatory for performed FOCUS GW and FOCUS SW modelling exposure assessment. Status of the study: relevant in the area of monitoring of residues of Flufenacet in GW and SW compartments, however not to be used to derive regulatory endpoints.
36	KCA B.8.5	Kolpin D. W., Schnoebelen D. J., Thurman M. E., “Degradates Provide Insight to Spatial and Temporal Trends of Herbicides in Ground Water.”; Groundwater, 2004, 42 (4), 601 – 608.	Paper provides the concentrations of Flufenacet, FOE ASA and FOE OXA in 86 GW wells used as the source of drinking water, measured in 2001. Status of the study: relevant in the area of monitoring of residues of Flufenacet in GW compartment, however not to be used to derive regulatory endpoints.
37	KCA B.8.5.	Kowal S. Balsaa P., Werres F., Schmidt T. C., “Fully automated standard addition method for the quantification of 29 polar pesticide metabolites in different water bodies using LC-MS/MS.”; Analytical and Bioanalytical Chemistry, 2013, 405 , 6337 – 6351.	Paper provides the measured concentrations of Flufenacet and its OXA and ASA degradation products in natural water and wastewater samples collected in North Rine-Westphal land of Gernany (regions of Rhine and Ruhr rivers). Status of the study: relevant in the area of monitoring of residues of Flufenacet in GW and SW compartments.
38	KCA B.8.5.	Mills P. C., Kolpin D. W., Scribner E. A., Thurman E. M., “Herbicides and degradates in shallow aquifers of Illinois: spatial and temporal trends.”; JAWRA Journal of the American Water Resources Association, 2005, 41 (3), 537 – 547.	Paper provides the measured concentrations of Flufenacet and its OXA and ASA degradation products in natural water samples. Status of the study: relevant in the area of monitoring of residues of Flufenacet in GW and SW compartments, however not to be used to derive regulatory endpoints.

No	SANCO Data Point	Publication data	Reason(s) for inclusion into RAR and status
	KCA B.8.5.	Moschet C., Götz C., Longrée P., Hollender J., Singer H., “ <i>Multi-Level Approach for the Integrated Assessment of Polar Organic Micropollutants in an International Lake Catchment: The Example of Lake Constance.</i> ”; Environmental Science and Technology, 2013, 47 (13), 7028 – 7036.	Flufenacet, FOE OXA and FOE ASA were listed among the compounds searched for in lake water, but not detected there. Status of the study: relevant in the area of monitoring of residues of Flufenacet in SW compartment, however not to be used to derive regulatory endpoints.
40	KCA B.8.5.	Moschet C., Wittmer I., Simovic J., Junghans M., Piazzoli A., Singer H., Stamm C., Leu C. Hollender J., “ <i>How a Complete Pesticide Screening Changes the Assessment of Surface Water Quality.</i> ”; Environmental Science and Technology, 2014, 48 (10), 5423 – 5432.	Paper provides the measured concentrations of Flufenacet and its OXA and ASA degradation products in rivers. Status of the study: relevant in the area of monitoring of residues of Flufenacet in SW compartment, however not to be used to derive regulatory endpoints.
41	KCA B.8.5.	Moschet C., Vermeirsser E. L. M., Singer H., Stamm C., Hollender J., “ <i>Evaluation of in-situ calibration of Chemcatcher passive samplers for 322 micropollutants in agricultural and urban affected rivers.</i> ”; Water Research, 2015, 71 , 306 – 317.	Paper provides the measured concentrations of Flufenacet and its OXA and ASA degradation products in rivers. Status of the study: relevant in the area of monitoring of residues of Flufenacet in SW compartment, however not to be used to derive regulatory endpoints.
42	KCA B.8.5.	Rebich R. A., Coupe R. H., Thurman E. M., “ <i>Herbicide concentrations in the Mississippi River Basin – the importance of chloroacetanilide herbicide degradates.</i> ”; Science of the Total Environment, 2004, 321 (1-3), 189 – 199.	Paper provides the measured concentrations of Flufenacet in riverine water. Status of the study: relevant in the area of monitoring of residues of Flufenacet in SW compartment, however not to be used to derive regulatory endpoints.
43	KCA B.8.5.	Scott B. F., MacTavish D., Spencer C., Strachan W. M. J., Muir D. C., “ <i>Haloacetic Acids in Canadian Lake Waters and Precipitation.</i> ”; Environmental Science and Technology, 2000, 34 (20), 1266 – 4272.	Paper submitted by the Applicant, provides the data on the concentrations of TFA in fresh surface water bodies and precipitation in Canada. Status of the study: relevant in the area of monitoring of TFA in environment, however not to be used to derive regulatory endpoints.
44	KCA B.8.5.	Scribner E. A., Battaglin W. A., Diez J. E., Thurman E. M., “ <i>Reconnaissance Data for Glyphosate, Other Selected Herbicides, Their Degradation Products, and Antibiotics in 51 Streams in Nine Mid-Western States 2002.</i> ”; US Geological Survey Open-File Report 03-217, 2003.	Paper provides the measured concentrations of Flufenacet and its OXA and ASA degradation products in natural water samples. Status of the study: relevant in the area of monitoring of residues of Flufenacet in SW compartment, however not to be used to derive regulatory endpoints.
45	KCA B.8.5.	Wujcik C., Cahill T. M., Seiber J. N., “ <i>Determination of Trifluoroacetic Acid in 1996 – 1997 Precipitation and Surface Waters in California and Nevada.</i> ”; Environmental Science and Technology, 1999, 33 (10), 1747 – 1751.	Paper submitted by the Applicant, provides the data on the concentrations of TFA in fresh surface water bodies and precipitation in the USA. Status of the study: relevant in the area of monitoring of TFA in environment, however not to be used to derive regulatory endpoints.
46	KCA B.8.5.	Zimmerman L. R., Schneider R. J., Thurman E. M., “ <i>Analysis and Detection of the Herbicides Dimethenamid and Flufenacet and Their Sulfonic and Oxalinic Acid Degradates in Natural Degradates in Natural Water.</i> ”; Journal of Agricultural and Food Chemistry, 2002, 50 (5), 1045 – 1052.	Paper provides the measured concentrations of Flufenacet and its OXA and ASA degradation products in natural water samples. Status of the study: relevant in the area of monitoring of residues of Flufenacet in SW compartments, however not to be used to derive regulatory endpoints.

The publications listed in the table B.8.6_CA-6 are summarized under the relevant points of the Renewal Assessment Report, indicated in the second column of the table.

Additionally, for the purpose of the assessment of the impact of water treatment procedures (drinking water abstraction) were used the following publications, dealing with the problem of the toxic by-products formed during the processing of the raw water for the drinking water:

- Bond T., Tempelton M. R., Graham N. “Precursors of nitrogenous disinfection byproducts in drinking water – A Critical review and analysis.”; Journal of Hazardous Materials 2012, **235-236**, 1 – 16.
- Boorman G. A., Dellarco V., Dunnick J. K., Chapin R. E., Hunter S., Hauchman F., Gardner H., Cox M., Sills R. C., “Drinking Water Disinfection Byproducts: Review and Approach to Toxicity Evaluation.”; Environmental Health Perspectives, 1999, **107 Supplement 1**, 207 – 217;
- Richardson S. D., Postigo C., “Drinking Water Disinfection By-products” in Barcelo D. (ed.) “Emerging Organic Contaminants and Human Health”, “Handbook of Environmental Chemistry”, 2012, Springer Verlag, 93 – 138;
- Toxicological data sheet for TFA published on TOXNET – Toxicology Data Network, site of US NIH National Library of Medicine; available on-line at <http://toxnet.nlm.nih.gov/index.html> as a record CASRN: 76-05-1;
- Le Roux J., Gallard H., Croué J.-P., “Chloramination of nitrogenous contaminants (pharmaceuticals and pesticides): NDMA and halogenated DBPs formation.”; Water Research, 2011, **45**, 3164 – 3174;
- Krasner S. W., Mitch W. A., McCurry D. L., Hanigan D., Westerhoff P., “Formation, precursors, control and occurrence of nitrosoamines in drinking water: a review.”; Water Research, 2013, **47**, 4433 – 4450;
- Kim J., Clevenger T. E., “Prediction of *N*-nitrosodimethylamine (NDMA) formation as a disinfection by-product.”; Journal of Hazardous Materials, 20007, **145**, 270 – 276;
- Nawrocki J., Andrzejewski P., “Nitrosoamines and water.”; Journal of Hazardous Materials 2011, **189**, 1 – 18;
- Mitch W. A., Sedlak D. L., “Factors controlling nitrosamine formation during wastewater chlorination.”; Water Science and Technology: Water Supply, 2002, **2** (3), 191 – 198;
- Rostkowska K., Zwierz K., Róžański A., Moniuszko-Jakoniuk J., Roszczenko A., „Formation and Metabolism of *N*-Nitrosamines.”; Polish Journal of Environmental Studies, 1998, **7** (6), 321 – 325;
- Anon.: “Report on Carcinogens, Thirteen Edition; *N*-Nitrosamines: 15 Listing.”; NIH National Toxicology Program, Department of Health and Human Services; document available on-line on: <http://ntp.niehs.nih.gov/go/roc13>

These publications were identified independently of the literature search performed for Flufenacet by both the Applicant and the RMS, therefore were not listed in any of the tables above. However, they were used as the reference papers in the evaluation and for that reason RMS decided to list them here. These publications will be also listed under the point B.8.7 presenting the references relied upon, under the letter-subpoint *b) Open- source literature used in the evaluation.*

B. 8.7 – References relied on**Literature search:**

The Applicant carried out literature search, summarising its results in the document MCA section 9 as a following study report:

Derpmann J., Teubner. L.; **2014**: “*Summary of the literature data for Flufenacet*”; Bayer CropScience; Document MCA: Section 9 Literature Data Flufenacet (unpublished document No. M-482180-01-1); issuing date: 2014. 03. 18.

According to the Applicant it was performed in line with the recommendations given in the EFSA guidance document “Submission of scientific peer-reviewed open literature for the approval of pesticide active substances under Regulation (EC) No 1107/2009”, published in *EFSA Journal*, 2011, **9** (2), 2092.

RMS having verified the report stated that it complied with the Guidelines referred to, therefore from formal point of view it may be considered acceptable. The report is summarised above under the point B.8.6 – Open literature review.

The thorough examination of the Applicant’s report performed by the RMS showed, that at the initial stage 369 publications were found for flufenacet and 3120 for its metabolites, of which 3089 for trifluoroacetic acid (TFA). Of them for the detailed assessment were qualified 91 publications for flufenacet and 62 for its degradation products, 53 of which for TFA.

The detailed assessment resulted in identification of only nine publications relevant for the assessment - two for flufenacet and seven for TFA. No relevant open source publication relevant for the assessment was found for any of the remaining degradation products of flufenacet.

Examining the results presented in the report cited above RMS stated that:

- 1) Initial stage of the literature search – selection of the data bases, key words and phrases, time window and the rapid assessment of the results, was performed fully in line with the recommendations given in the EFSA Guidelines referred to above.
- 2) For the detailed assessment alongside the applied selection criteria, the full list of evaluated publications was provided in form of two tables – one presenting the publications identified as relevant, the second listing those found not relevant with rationale for their rejection. However, only for the publications considered relevant the Applicant provided information enabling their appropriate placing in the Assessment Report, as well as summaries and full texts. In case of rejected publications they were neither attributed to the relevant sections of the Report nor, at least, their summaries were provided, what would enable the verification of the correctness of Applicant’s selection.

In light of the doubts related to the results of detailed assessment performed by the Applicant – Bayer CropSciences, RMS repeated the literature search, using the search criteria similar to those applied by the Applicant. The only difference was that the search was not limited to the last thirteen years predating the application (i. e. covering the period 2000 – 2013), but was broader, what enabled to find earlier or later publications, not found by the BCS.

The results of the literature search performed by the RMS are presented under the point 9.6., under the summary of the report on the literature search submitted by the Applicant – Bayer CropSciences.

Additionally all peer-reviewed publications found relevant for the current evaluation, either by the Applicant or by the RMS as a result of the repeated literature search, are listed in the table placed under the letter “b” of this data point.

a) studies submitted by the Notifier:

Data point (OECD-format)	Author(s)	Year	Title Company Report No. Source (where different from company) GLP or GEP status Published or not	Vertebrate study yes/no	Data protection claimed yes/no	Justification if data protection is claimed	Owner ^{*)}	Previous evaluation
KCA 7.1.1.1./01; KCA 7.1.2.1.1. (OECD Annex points KIIA 7.1.1, KIIA 7.2.1 and KIIA 7.2.3)	Kelley I. V., Wood S., McKinney M.	1995	“Degradation of [Phenyl-UL- ¹⁴ C]FOE 5043 in Three Soil Types.”; Bayer Corporation (formerly Miles Inc), Agriculture Division, P. O. Box 4913, Kansas City, Missouri 64120, USA; study No. F3042104; unpublished Bayer Report No. MR 106664; 31 August 1995; Study reference number: M-002146-01-1; GLP: yes; Unpublished study	No	Yes	Justification not provided by the Applicant. However apply the provisions of Article 59, § 1, subparagraph 7 of the Regulation (EC) 1107/2009, stating that “ <i>A study shall also be protected if it was necessary for renewal or review of authorisation. The period for data protection shall be 30 months. The first to fourth subparagraphs shall apply mutatis mutandis.</i> ”	BCS	The study submitted for the purpose of the previous authorisation of flufenacet in the EU.
KCA 7.1.1.1./02; KCA 7.1.2.1.1.1. (OECD Annex points KIIA 7.1.1, KIIA 7.2.1 and KIIA 7.2.3)	Pangilinan N. C., Smith D. M.,	1994	“Aerobic Soil Metabolism of [Phenyl-U- ¹⁴ C] FOE 5043”; Miles Inc., Agriculture Division, Research and Development Department, P. O. Box 4913, Kansas City, Missouri 64120-0013, USA; study No. F3042102; unpublished Miles Report No. MR 106408; 12 May 1994; Study reference number: M-002166-10-1; GLP: Yes Unpublished study	No	Yes	Justification not provided by the Applicant. However apply the provisions of Article 59, § 1, subparagraph 7 of the Regulation (EC) 1107/2009, stating that “ <i>A study shall also be protected if it was necessary for renewal or review of authorisation. The period for data protection shall be 30 months. The first to fourth subparagraphs shall apply mutatis mutandis.</i> ”	BCS	The study submitted for the purpose of the previous authorisation of flufenacet in the EU.

Data point (OECD-format)	Author(s)	Year	Title Company Report No. Source (where different from company) GLP or GEP status Published or not	Vertebrate study yes/no	Data protection claimed yes/no	Justification if data protection is claimed	Owner ^{*)}	Previous evaluation
KCA 7.1.1.1./03; (OECD Annex point KIIA 7.1.1)	Hellpointner E.,	1995	“Evolution of the microbial biomass in the biometer flask system (supportive to study no. F3042102, aerobic metabolism of FOE 5043).”; Bayer AG, Agrochemicals Division, Development, Institute for Metabolism Research & Residue Analysis, D51368 Leverkusen; Germany; unpublished Report No. PF 4066; 20 June 1995; Study reference number: M-002164-01-1; GLP: Yes; Unpublished study	No	Yes	Justification not provided by the Applicant. However apply the provisions of Article 59, § 1, subparagraph 7 of the Regulation (EC) 1107/2009, stating that “ <i>A study shall also be protected if it was necessary for renewal or review of authorisation. The period for data protection shall be 30 months. The first to fourth subparagraphs shall apply mutatis mutandis.</i> ”	BCS	The study submitted for the purpose of the previous authorisation of flufenacet in the EU.
KCA 7.1.1.1./04; KCA 7.1.2.1.1 (OECD Annex points KIIA 7.1.1, KIIA 7.2.1 and KIIA 7.2.3)	Pangilinan N. C., Smith D. M.,	1994a	“Aerobic Soil Metabolism of [Thiadiazole -2- ¹⁴ C] FOE 5043”; Miles Inc., Agriculture Division, Research and Development Department, P. O. Box 4913, Kansas City, Missouri 64120-0013, USA; study No. F3042103; unpublished Miles Report No. MR 106420; 30 June 1994; Study reference number: M-002165-01-1 GLP: Yes Unpublished study	No	Yes	Justification not provided by the Applicant. However apply the provisions of Article 59, § 1, subparagraph 7 of the Regulation (EC) 1107/2009, stating that “ <i>A study shall also be protected if it was necessary for renewal or review of authorisation. The period for data protection shall be 30 months. The first to fourth subparagraphs shall apply mutatis mutandis.</i> ”	BCS	The study submitted for the purpose of the previous authorisation of flufenacet in the EU.

Data point (OECD-format)	Author(s)	Year	Title Company Report No. Source (where different from company) GLP or GEP status Published or not	Vertebrate study yes/no	Data protection claimed yes/no	Justification if data protection is claimed	Owner ^{*)}	Previous evaluation
KCA 7.1.1.1./05; KCA 7.1.2.1.1./04 (OECD Annex points KIIA 7.1.1, KIIA 7.2.1 and KIIA 7.2.3)	Hein E.-M.	2012	“[Thiadiazole -5- ¹⁴ C] Flufenacet: Aerobic Degradation/Metabolism in One European Soil.”; Bayer CropScience AG, BCS-D-EnSa-Testing, 40789 Monheim, Germany, Study M1251994-1; unpublished Study Report No. MEF-11/937; 2012. 09. 19, amended (Amendment No 1) 2013. 04. 10; Study reference number: M-439105-02-1 GLP: Yes; Unpublished study	No	Yes	EU data requirement – further elucidation of the route of degradation of heterocycle	BCS	Study is submitted specifically for this evaluation.
KCA 7.1.1.1./06; KCA 7.1.2.1.1./05 (OECD Annex points KIIA 7.1.1, KIIA 7.2.1 and KIIA 7.2.3)	Hein E.-M.	2012a	“[Thiadiazole -5- ¹⁴ C] Flufenacet: Aerobic Degradation/Metabolism in Three European Soils.”; Bayer CropScience AG, BCS-D-EnSa-Testing, 40789 Monheim, Germany, Study M1252037-0; unpublished Study Report No. MEF-11/938; 2012. 10. 18, amended (Amendment No 1) 2013. 01. 28; Study reference number: M-440348-02-1 GLP: Yes; Unpublished study,	No	Yes	EU data requirement – further elucidation of the route of degradation of heterocycle	BCS	Study is submitted specifically for this evaluation.
KCA 7.1.1.2./01; KCA 7.1.2.1.2./01 (OECD Annex points KIIA 7.1.2, KIIA 7.2.4 and KIIA 7.2.5,)	Pangilinan N. C., Smith D. M.,	1995	“Anaerobic Soil Metabolism of [Phenyl-U- ¹⁴ C] FOE 5043”; Bayer Corporation (formerly Miles Inc.), Agriculture Division, P. O. Box 4913, Kansas City, Missouri 64120-0013, USA; study No. F3042106; unpublished Miles Report No. MR 106645; 20 June 1995; Study reference number: M-002162-01-1; GLP: Yes; Unpublished study;	No	Yes	EU data requirement – study originally conducted for US-EPA, so far not evaluated in the EU	BCS	Study is submitted specifically for this evaluation.

Data point (OECD-format)	Author(s)	Year	Title Company Report No. Source (where different from company) GLP or GEP status Published or not	Vertebrate study yes/no	Data protection claimed yes/no	Justification if data protection is claimed	Owner ^{*)}	Previous evaluation
KCA 7.1.1.2./02; KCA 7.1.2.1.2./02 (OECD Annex points KIIA 7.1.2, KIIA 7.2.4 and KIIA 7.2.5,)	Heinemann O.	2012	“[Thiadiazole-5- ¹⁴ C] FOE 5043: Anaerobic degradation/Metabolism in Two European Soils.”; Bayer CropScience AG, Development Environmental Safety-Testing, Alfred-Nobel-Str. 50, D-40789 Monheim am Rhein, Germany; Study M1262057-3; unpublished Study Report No. MEF-11/908; 2012. 08. 16; amended by the Amendment No 1 on 2013. 02. 28 and Amendment No 2 on 2013. 11. 27; Study reference number: M-437443-03-1; GLP: Yes; Unpublished study;	No	Yes	EU data requirement	BCS	Study is submitted specifically for this evaluation.
KCA 7.1.1.3./01; KCA 7.1.2.1.3. (OECD Annex points KIIA 7.1.3 and KIIA 7.2)	Kasper A. M., Shadrick B. A.,	1995	“Photolysis of [Phenyl-U- ¹⁴ C] FOE 5043 on Sandy Loam.”; Bayer Corporation (formerly Miles Inc.), Agriculture Division, P. O. Box 4913, Kansas City, Missouri 64120-0013, USA; study No. F3082101/F3082102 (Bayer); unpublished Miles Report No. MR 106247; 22 June 1995; Study reference number: M-002145-01-1; GLP: Yes; Unpublished study;	No	Yes	Justification not provided by the Applicant. However apply the provisions of Article 59, § 1, subparagraph 7 of the Regulation (EC) 1107/2009, stating that “ <i>A study shall also be protected if it was necessary for renewal or review of authorisation. The period for data protection shall be 30 months. The first to fourth subparagraphs shall apply mutatis mutandis.</i> ”	BCS	The study submitted for the purpose of the previous authorisation of flufenacet in the EU.

Data point (OECD-format)	Author(s)	Year	Title Company Report No. Source (where different from company) GLP or GEP status Published or not	Vertebrate study yes/no	Data protection claimed yes/no	Justification if data protection is claimed	Owner ^{*)}	Previous evaluation
KCA 7.1.1.3./02; KCA 7.1.2.1.3. (OECD Annex points KIIA 7.1.3 and KIIA 7.2)	Lentz N. R., Bloomberg A. M.,	2001	“Soil Photolysis of Thiadone on Loamy Sand (A Metabolite of FOE 5043).”; Ricerca LLC, Department of Environmental and Metabolic Fate, 7528 Auburn Road, Painesville, Ohio 44077, USA (performing laboratory) for Bayer Corporation, Agriculture Division, P. O. Box 4913, Kansas City, MO 64120, USA; Ricerca document No. 7410-0055-EF-001, study No. F3082103 (Bayer); Bayer Report No. 108721; 21 June 2001; Study reference number: M-106297-01-1 GLP: Yes; Unpublished study;	No	Yes	Study originally conducted for US-EPA, so far not evaluated in the EU	BCS	Study is submitted specifically for this evaluation.
KCA 7.1.2.1.1./01 (OECD Annex point KIIA 7.2.1)	Hellpointner E.,	1999	“Aerobic Degradation of Flufenacet in Lysimeter Soil Laacherhof AXXa.”; Bayer AG, Institute for Metabolism Research and Residue Analysis, D-513468 Leverkusen, Federal Republic of Germany; study No. M1250988-3, unpublished study Report No. MR-388/99; 23 July 1999; Study reference number: M-009592-01-1; GLP: Yes; Unpublished study;	No	Yes	Requested by EU-generation of paired data for modeling of lysimeter study	BCS	Study is submitted specifically for this evaluation.
KCA 7.1.2.1.1./02 (OECD Annex points KIIA 7.2.1 and KIIA 7.2.3)	Reinken G., Partsch S.,	2014	“Kinetic Evaluation of the Degradation of [phenyl-UL- ¹⁴ C] flufenacet and its Degradation Products under Aerobic Soil Conditions in Laboratory According to FOCUS Kinetics Using the KinGUI 2 Tool. Flufenacet (FOE 5043); FOE sulfonic acid; FOE oxalate; FOE methylsulfone.”; Bayer CropScience AG, Environmental Safety, Alfred-Nobel-Straße 50, 40789 Monheim, Germany; Study Report No. EnSa-12-0575; 2014. 02. 17; Study reference number: M-477878-01-1; GLP: no, not applicable (modelling study); Unpublished study;	No	Yes	New data/guideline requirement: Kinetic analysis of the degradation of flufenacet and its major degradation products FOE oxalate, FOE sulfonic acid and FOE methylsulfone for modelling purpose.	BCS	Study is submitted specifically for this evaluation.

Data point (OECD-format)	Author(s)	Year	Title Company Report No. Source (where different from company) GLP or GEP status Published or not	Vertebrate study yes/no	Data protection claimed yes/no	Justification if data protection is claimed	Owner ^{*)}	Previous evaluation
KCA 7.1.2.1.1./03 (OECD Annex points KIIA 7.2.1 and KIIA 7.2.3)	Reinken G., Maassen K.,	2014a	“Trigger evaluation for the Degradation of Flufenacet Degradation Product FOE oxalate under Aerobic Soil Conditions in Laboratory According to FOCUS Kinetics Using the KinGUI 2 Tool. FOE oxalate.”; Bayer CropScience AG, Environmental Safety, Alfred-Nobel-Strasse 50, 40789 Monheim, Germany; Study Report No. En-Sa-13-1009; 2014. 02. 18.; Study reference number: M-478440-01-1; GLP: no, not applicable (modelling study); Unpublished study;	No	Yes	New data/guideline requirement: Kinetic analysis of the degradation of flufenacet to derive half-lives for its major degradation product FOE oxalate for trigger evaluation.	BCS	Study is submitted specifically for this evaluation.
KCA 7.1.2.1.1./06 (OECD Annex points KIIA 7.2.1 and KIIA 7.2.3)	Reinken G., Partsch S.,	2014b	“Trigger evaluation for the Degradation of Flufenacet Degradation Product FOE 5043 trifluoroethane-sulfonic acid under Aerobic Conditions in Laboratory According to FOCUS Kinetics Using the KinGUI 2 Tool. FOE 5043-trifluoroethane sulfonic acid, Trifluoroacetic acid.”; Bayer Crop Science AG, Environmental Safety, Alfred-Nobel-Strasse 50, 40789 Monheim, Germany; Study Report No. En-Sa-13-1010; 2014. 02. 18.; Study reference number: M-478444-01-1; GLP: no, not applicable (modelling study); Unpublished study;	No	Yes	New data/guideline requirement: Kinetic analysis of the degradation of flufenacet to derive half-lives for its major degradation product FOE 5043-trifluoroethanesulfonic acid for trigger evaluation.	BCS	Study is submitted specifically for this evaluation.

Data point (OECD-format)	Author(s)	Year	Title Company Report No. Source (where different from company) GLP or GEP status Published or not	Vertebrate study yes/no	Data protection claimed yes/no	Justification if data protection is claimed	Owner ^{*)}	Previous evaluation
KCA 7.1.2.1.1./07 (OECD Annex points KIIA 7.2.1 and KIIA 7.2.3)	Reinken G., Partsch S.,	2014c	“Kinetic Evaluation of [thiadiazole-5- ¹⁴ C] flufenacet and its Degradation Products under Aerobic Conditions in Laboratory According to FOCUS Kinetics Using the KinGUI 2 Tool. Flufenacet (FOE 5043), FOE-thiadone, FOE 5043-trifluoroethane sulfonic acid, Trifluoroacetic acid.”; Bayer Crop Science AG, Environmental Safety, Alfred-Nobel-Strasse 50, 40789 Monheim, Germany; Study Report No. En-Sa-12-0577; 2014. 02. 17.; Study reference number: M-477835-01-1; GLP: no, not applicable (modelling study); Unpublished study;	No	Yes	New data/guideline requirement: Kinetic analysis of the degradation of flufenacet and its major degradation products FOE-thiadone, FOE 5043-trifluoroethanesulfonic acid and Trifluoroacetic acid for modelling purpose	BCS	Study is submitted specifically for this evaluation.
KCA 7.1.2.1.1./08 (OECD Annex points KIIA 7.2.1 and KIIA 7.2.3)	Reinken G., Partsch S.,	2014d	“Kinetic Evaluation of the Degradation of [thiadiazole-2- ¹⁴ C] flufenacet and its Degradation Product under Aerobic Soil Conditions in Laboratory According to FOCUS Kinetics using the KinGUI 2 Tool. Flufenacet (FOE 5043); FOE-thiadone.”; Bayer CropScience AG, Environmental Safety, Alfred-Nobel-Strasse 50, 40789 Monheim, Germany; Study Report No. EnSa-12-0576; 2014. 02.17; Study reference number: M-477885-01-1; GLP: no, not applicable (modelling study); Unpublished study;	No	Yes	New data/guideline requirement: Kinetic analysis of the degradation of flufenacet and its major degradation product FOE-thiadone for modelling purpose	BCS	Study is submitted specifically for this evaluation.

Data point (OECD-format)	Author(s)	Year	Title Company Report No. Source (where different from company) GLP or GEP status Published or not	Vertebrate study yes/no	Data protection claimed yes/no	Justification if data protection is claimed	Owner ^{*)}	Previous evaluation
KCA 7.1.2.1.1./09 (OECD Annex point KIIA 7.2.3)	Hellpointner E.,	1996	“Degradation of [Phenyl-UL- ¹⁴ C]FOE 5043-Sulfonic Acid in Three Soils.”; Bayer AG, Crop Protection Business Group, Crop-Protection Development, Agrochemicals Division, Development, Institute for Metabolism Research and Residue Analysis, D51368 Leverkusen; Germany for Bayer Corporation, Agriculture Division, P. O. Box 4913, Hawthorne Road, Kansas City, MO 64120-0013, USA; Study Report No. PF 4110 (Bayer Report Number 107515); 8 January 1996; Study reference number: M-004098-01-2; GLP: Yes; Unpublished study;	No	Yes	Justification not provided by the Applicant. However apply the provisions of Article 59, § 1, subparagraph 7 of the Regulation (EC) 1107/2009, stating that “A study shall also be protected if it was necessary for renewal or review of authorisation. The period for data protection shall be 30 months. The first to fourth subparagraphs shall apply mutatis mutandis.”	BCS	The study submitted for the purpose of the previous authorisation of flufenacet in the EU.
KCA 7.1.2.1.1./10; 7.1.3.2/01; (OECD Annex points KIIA, 7.2.3 and KIIA 7.4.2)	Hellpointner E.,	2003	“Time-Dependent Sorption of FOE5043-Sulfonic Acid in Soil.”; Bayer Crop Science AG, Development – Global Regulatory Affairs, D-40789 Monheim, Germany; Study Report No. MEF-229/03; 2003-10-13.; Study reference number: M-111445-01-1; GLP: Yes; Unpublished study;	No	Yes	Higher tier study for the refinement of risk assessment	BCS	Study is submitted specifically for this evaluation.
KCA 7.1.2.1.1./11; (OECD Annex point KIIA 7.2.3)	Hein E. M.	2013	“FOE sulfonic acid: Aerobic Degradation in Four European Soils.”; Bayer CropScience AG, BCS-D-EnSa-Testing, 40789 Monheim, Germany; unpublished Study Report No. EnSa-13-0442; 2013. 08. 05, updated by the Amendment No. 1 (Hein E. M. (2013): “Amendment No. 1 to: FOE Sulfonic Acid: Aerobic Degradation in Four European Soils.”; Bayer CropScience AG, BCS-D-EnSa-Testing, 40789 Monheim, Germany; 2013. 08. 22.; Study reference number: M-461413-02-1; GLP: Yes; Unpublished study;	No	Yes	EU Data requirement	BCS	Study is submitted specifically for this evaluation.

Data point (OECD-format)	Author(s)	Year	Title Company Report No. Source (where different from company) GLP or GEP status Published or not	Vertebrate study yes/no	Data protection claimed yes/no	Justification if data protection is claimed	Owner ^{*)}	Previous evaluation
KCA 7.1.2.1.1./12; (OECD Annex point KIIA 7.2.3)	Ströch K., Junge T.	2013	„FOE sulfonic acid: Degradation in Four Aerobic Soils.”; Bayer CropScience AG, BCS-D-EnSa-Testing, 40789 Monheim, Germany; unpublished Study Report No. EnSa-13-0618; 2013. 10. 24.; Study reference number: M-467862-01-1; GLP: Yes; Unpublished study;	No	Yes	Additional data: Rate of degradation in aerobic soil of major degradation product FOE sulfonic acid	BCS	Study is submitted specifically for this evaluation.
KCA 7.1.2.1.1./13; (OECD Annex point KIIA 7.2.3)	Reinken G., Parsch S.	2014e	“Kinetic Evaluation of the Degradation of Flufenacet Degradation Product FOE sulfonic acid under Aerobic Soil conditions in Laboratory according to FOCUS Kinetics Using the KinGUI 2 Tool. FOE sulfonic acid.”; Bayer CropScience AG, Environmental Safety, Alfred-Nobel-Strasse 50, 40789 Monheim, Germany; unpublished Study Report No. EnSa-12-0580; 2014. 02. 17.; Study reference number: M-477844-01-1; GLP: no, not applicable (modelling study); Unpublished study;	No	Yes	New data/guideline requirement: Kinetic analysis of the degradation of FOE sulfonic acid for modelling purpose	BCS	Study is submitted specifically for this evaluation.
KCA 7.1.2.1.1./14; (OECD Annex point KIIA 7.2.3)	Traub M.	2012	“FOE methylsulfone: Aerobic Degradation in Four European Soils.”; Eurofins Agroscience Services EcoChem GmbH, Eutingen Str. 24, 75223 Niefern-Öschelbronn, Germany, for Bayre Crop Science AG, 40789 Monheim; unpublished study No. S11-03808; 2012. 10.18; Study reference number:M-443658-01-1; GLP: Yes; Unpublished study;	No	Yes	EU Data requirement	BCS	Study is submitted specifically for this evaluation.
KCA 7.1.2.1.1./15; (OECD Annex point KIIA 7.2.3)	Ströch K., Junge T.	2013a	„FOE methylsulfone: Degradation in Four Aerobic Soils.”; Bayer CropScience AG, BCS-D-EnSa-Testing, 40789 Monheim, Germany; unpublished Study Report No. EnSa-13-0617; 2013. 10. 24.; Study reference number: M-467858-01-1; GLP: Yes; Unpublished study;	No	Yes	New data/guideline requirement: Rate of degradation for the newly identified major degradation product FOE methylsulfone	BCS	Study is submitted specifically for this evaluation.

Data point (OECD-format)	Author(s)	Year	Title Company Report No. Source (where different from company) GLP or GEP status Published or not	Vertebrate study yes/no	Data protection claimed yes/no	Justification if data protection is claimed	Owner ^{*)}	Previous evaluation
KCA 7.1.2.1.1./16; (OECD Annex point KIIA 7.2.3)	Reinken G., Partsch S.	2014f	“Kinetic Evaluation of the Degradation of Flufenacet Degradation Product FOE methylsulfone under Aerobic Soil conditions in Laboratory according to FOCUS Kinetics Using the KinGUI 2 Tool. FOE methylsulfone acid.”; Bayer CropScience AG, Environmental Safety, Alfred-Nobel-Strasse 50, 40789 Monheim, Germany; unpublished Study Report No. EnSa-12-0578; 2014. 02. 17.; Study reference number: M-477839-01-1; GLP: no, not applicable (modelling study); Unpublished study;	No	Yes	New data/guideline requirement: Kinetic analysis of the degradation of FOE methylsulfone for modelling purpose	BCS	Study is submitted specifically for this evaluation.
KCA 7.1.2.1.1./17; (OECD Annex point KIIA 7.2.3)	Lentz N. R., Bloomberg A. M.	1999	“Rate of Aerobic Soil Degradation for Thiadone (A Metabolite of FOE 5043).”; Ricerca LLC, Department of Environmental and Metabolic Fate, 7528 Auburn Road, Painesville, Ohio 44077, USA (performing laboratory) for Bayer Corporation, Agriculture Division, P. O. Box 4913, Kansas City, MO 64120, USA; Ricerca document No. 7410-0055-EF-001, study No. F3082103 (Bayer); Bayer Report No. 108722; 16 February 1999, amended on 24 March 1999; Study reference number: M-009828-01-1; GLP: Yes; Unpublished study;	No	Yes	EU data requirement	BCS	Study is submitted specifically for this evaluation.

Data point (OECD-format)	Author(s)	Year	Title Company Report No. Source (where different from company) GLP or GEP status Published or not	Vertebrate study yes/no	Data protection claimed yes/no	Justification if data protection is claimed	Owner ^{*)}	Previous evaluation
KCA 7.1.2.1.1./18; (OECD Annex point KIIA 7.2.3)	Reinken G., Partsch S.	2014g	“Kinetic Evaluation of the Degradation of Flufenacet Degradation Product FOE-thiadone under Aerobic Soil conditions in Laboratory according to FOCUS Kinetics Using the KinGUI 2 Tool. FOE-thiadone.”; Bayer CropScience AG, Environmental Safety, Alfred-Nobel-Strasse 50, 40789 Monheim, Germany; unpublished Study Report No. EnSa-12-0579; 2014. 02. 17.; Study reference number: M-477840-01-1; GLP: no, not applicable (modelling study); Unpublished study;	No	Yes	New data/guideline requirement: Kinetic analysis of the degradation of FOE-thiadone for modelling purpose	BCS	Study is submitted specifically for this evaluation.
KCA 7.1.2.1.1./19; (OECD Annex point KIIA 7.2.3)	Eckermann N.	2012	“[1- ¹⁴ C]Trifluoroacetate: Aerobic Degradation in Four European Soils.”; Bayer CropScience AG, BCS-D-EnSa-Testing, 40789 Monheim, Germany; unpublished Study Report No. EnSa-12-0393; 2012. 09. 26.; Study reference number: M-439283-01-1; GLP: Yes; Unpublished study;	No	Yes	New data requirements	BCS	Study is submitted specifically for this evaluation.
KCA 7.1.2.1.1./20; (OECD Annex point KIIA 7.2.3)	Eckermann N.	2012a	“[1- ¹⁴ C]Trifluoroacetate: Concentration dependent Mineralization under Aerobic Conditions.”; Bayer CropScience AG, BCS-D-EnSa-Testing, 40789 Monheim, Germany; unpublished Study Report No. EnSa-12-0445; 2012. 10. 11.; Study reference number: M-441101-01-1; GLP: Yes; Unpublished study;	No	Yes	Additional data for refinement of risk assessment	BCS	Study is submitted specifically for this evaluation.

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KCA 7.1.2.1.1./21; (OECD Annex points KIIA 7.2.1 and KIIA 7.2.3)	Reinken G. Porschewski R.,	2014g	“Flufenacet Core PECsoil and Accumulation: Modelling Core Info Document for Soil Exposure Assessment in Europe.”; Bayer CropScienceAG, Environmental Safety, Alfred-Nobel-Straße 50, 40789 Monheim, Germany, unpublished Report No. EnSa-13-1007; 2014. 02. 25.; Study reference number: M-478418-01-1; GLP: no, not applicable (modelling study); Unpublished study;	No	Yes	Justification not provided by the Applicant, however should apply the provisions of the of Article 59, § 1, subparagraph 7 of the Regulation (EC) 1107/2009, stating that “ <i>A study shall also be protected if it was necessary for renewal or review of authorisation.</i> As this is a new study, should apply the rules set for the new/newly submitted studies.	BCS	Study is submitted specifically for this evaluation.
KCA 7.1.2.1.1./21; (OECD Annex points KIIA 7.2.1 and KIIA 7.2.3)	Reinken G. Porschewski R.,	2014h	“Flufenacet Core PECgw FOCUS EU: Modelling Core Info Document for Groundwater Risk Assessment in Europe.”; Bayer CropScienceAG, Environmental Safety, Alfred-Nobel-Straße 50, 40789 Monheim, Germany, unpublished Report No. EnSa-13-1006; 2014. 02. 25.; Study reference number: M-478214-01-1; GLP: no, not applicable (modelling study); Unpublished study;	No	Yes	Justification not provided by the Applicant, however should apply the provisions of the of Article 59, § 1, subparagraph 7 of the Regulation (EC) 1107/2009, stating that “ <i>A study shall also be protected if it was necessary for renewal or review of authorisation.</i> As this is a new study, should apply the rules set for the new/newly submitted studies.	BCS	Study is submitted specifically for this evaluation.

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KCA 7.1.2.1.2./01; (OECD Annex points KIIA 7.2.4 and KIIA 7.2.5)	Reinken G., Partsch S., Bolekhan A.,	2014	“Kinetic evaluation of the Degradation of Flufenacet and its Degradation Products under Anaerobic Soil Conditions in Laboratory According to FOCUS Kinetics Using the KinGUI 2 Tool.”; Bayer CropScience AG, Environmental Safety, Alfred-Nobel-Strasse 50, 40789 Monheim, Germany; unpublished study Report No. EnSa-13-0971; 2014. 02. 28.; Study reference number: M-478213-02-1; GLP: no, not applicable (modelling study); Unpublished study;	No	Yes	New data/guideline requirement: Kinetic analysis of degradation of FOE oxalate, FOE sulfonic acid, FOE-thiadone, FOE 5043-trifluoroethanesulfonic acid and trifluoroacetic acid under anaerobic conditions for modelling purpose and trigger evaluation	BCS	Study is submitted specifically for this evaluation.
KCA 7.1.2.1.2./01; (OECD Annex point KIIA 7.3.1.)	Sommer H.	1995	“Dissipation of FOE 5043 in Soil under Field Conditions (Germany, France).”; Bayer AG, Crop Protection Business Group, Crop Protection-Development, Institute for Metabolism Research & Residue Analysis, D-51368 Leverkusen-Baywerk, Germany (performing laboratory) for Bayer Corporation, Agriculture Division, P. O. Box 4913, Hawthorne Road, Kansas City, MO 64120-0013, USA; Study Report RA-2112/93; Bayer Report No. 107724; 1 September 1995; Study reference number: M-002172-01-2; GLP: Yes; Unpublished study;	No	Yes	Justification not provided by the Applicant, however should apply the provisions of the of Article 59, § 1, subparagraph 7 of the Regulation (EC) 1107/2009, stating that “ <i>A study shall also be protected if it was necessary for renewal or review of authorisation.</i> As this is a new study, should apply the rules set for the new/newly submitted studies.	BCS	The study submitted for the purpose of the previous authorisation of flufenacet in the EU.

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KCA 7.1.2.2.1./02; (OECD Annex point KIIA 7.3.1.)	Sommer H.	1995a	“Dissipation of FOE 5043 in Soil under Field Conditions (Germany).”; Bayer AG, Crop Protection Business Group, Crop Protection-Development, Institute for Metabolism Research & Residue Analysis, D-51368 Leverkusen-Baywerk, Germany (performing laboratory) for Bayer Corporation, Agriculture Division, P. O. Box 4913, Hawthorne Road, Kansas City, MO 64120-0013, USA; Study Report RA-2116/93; Bayer Report No. 107722; 5 October 1995; Study reference number: M-02171-01-2; GLP: Yes; Unpublished study;	No	Yes	Justification not provided by the Applicant, however should apply the provisions of the of Article 59, § 1, subparagraph 7 of the Regulation (EC) 1107/2009, stating that “ <i>A study shall also be protected if it was necessary for renewal or review of authorisation.</i> As this is a new study, should apply the rules set for the new/newly submitted studies.	BCS	The study submitted for the purpose of the previous authorisation of flufenacet in the EU.
KCA 7.1.2.2.1./03; (OECD Annex point KIIA 7.3.1.)	Sommer H.	1995b	“Dissipation of FOE 5043 in Soil under Field Conditions (France).”; Bayer AG, Crop Protection Business Group, Crop Protection-Development, Institute for Metabolism Research & Residue Analysis, D-51368 Leverkusen-Baywerk, Germany (performing laboratory) for Bayer Corporation, Agriculture Division, P. O. Box 4913, Hawthorne Road, Kansas City, MO 64120-0013, USA; Study Report RA-2051/93; Bayer Report No. 107723; 6 October 1995; Study reference number: M-002169-01-2; GLP: Yes; Unpublished study;	No	Yes	Justification not provided by the Applicant, however should apply the provisions of the of Article 59, § 1, subparagraph 7 of the Regulation (EC) 1107/2009, stating that “ <i>A study shall also be protected if it was necessary for renewal or review of authorisation.</i> As this is a new study, should apply the rules set for the new/newly submitted studies.	BCS	The study submitted for the purpose of the previous authorisation of flufenacet in the EU.

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KCA 7.1.2.2.1./04; (OECD Annex point KIIA 7.3.1.)	Sommer H.,	1995c	“Dissipation of FOE 5043 in Soil under Field Conditions (France, Italy).”; Bayer AG, Crop Protection Business Group, Crop Protection-Development, Institute for Metabolism Research & Residue Analysis, D-51368 Leverkusen-Baywerk, Germany (performing laboratory) for Bayer Corporation, Agriculture Division, P. O. Box 4913, Hawthorne Road, Kansas City, MO 64120-0013, USA; Study Report RA-2019/94; Bayer Report No. 107721; 23 November 1995; Study reference number: M-002175-01-2; GLP: Yes; Unpublished study;	No	Yes	Justification not provided by the Applicant, however should apply the provisions of the of Article 59, § 1, subparagraph 7 of the Regulation (EC) 1107/2009, stating that “ <i>A study shall also be protected if it was necessary for renewal or review of authorisation.</i> As this is a new study, should apply the rules set for the new/newly submitted studies.	BCS	The study submitted for the purpose of the previous authorisation of flufenacet in the EU.
KCA 7.1.2.2.1./05; (OECD Annex point KIIA 7.3.1.)	Lin H, Green D. L., Fig P. S,	1995	“Freezer stability of [Phenyl-UL- ¹⁴ C]FOE 5043 in Soil.”; Agriculture Division, Miles Inc., Research and Development Department, P. O. Box 4913, Kansas City, Missouri 64120, USA; Miles Study No. F3132101, Miles Report No. 106231; 23 February 1995; Study reference number: M-002201-01-1; GLP: Yes; Unpublished study;	No	Yes	Justification not provided by the Applicant, however should apply the provisions of the of Article 59, § 1, subparagraph 7 of the Regulation (EC) 1107/2009, stating that “ <i>A study shall also be protected if it was necessary for renewal or review of authorisation.</i> As this is a new study, should apply the rules set for the new/newly submitted studies.	BCS	The study submitted for the purpose of the previous authorisation of flufenacet in the EU.

Data point (OECD-format)	Author(s)	Year	Title Company Report No. Source (where different from company) GLP or GEP status Published or not	Vertebrate study yes/no	Data protection claimed yes/no	Justification if data protection is claimed	Owner ^{*)}	Previous evaluation
KCA 7.1.2.2.1./06; (OECD Annex point KIIA 7.3.1.)	Lin H, Green D. L.,	1995	“Freezer stability of seven metabolites of [¹⁴ C]FOE 5043 in Soil.”; Agriculture Division, Miles Inc., Research and Development Department, P. O. Box 4913, Kansas City, Missouri 64120, USA; Miles Study No. F3132102, Miles Report No. 106640; 26 June 1995; Study reference number: M-002199-01-1; GLP: Yes; Unpublished study;	No	Yes	Justification not provided by the Applicant, however should apply the provisions of the of Article 59, § 1, subparagraph 7 of the Regulation (EC) 1107/2009, stating that “ <i>A study shall also be protected if it was necessary for renewal or review of authorisation.</i> As this is a new study, should apply the rules set for the new/newly submitted studies.	BCS	The study submitted for the purpose of the previous authorisation of flufenacet in the EU.
KCA 7.1.2.2.1./07; (OECD Annex point KIIA 7.3.1.)	Hammel K.,	2008	“Kinetic Evaluation of the Dissipation of Flufenacet and its Metabolite Flufenacet-sulfonic acid in soil based on Field Studies.”; Bayer CropScience AG, Institute for Metabolism and Environmental Fate, Alfred-Nobel-Strasse 50, 40789 Monheim, Germany; study Report MEF-08/266; 2008. 08. 25.; Study reference number: M-306683-01-1; GLP: no, not applicable (modelling study); Unpublished study;	No	Yes	The Applicant provided following justification: “ <i>New kinetic evaluation.</i> ”	BCS	Study is submitted specifically for this evaluation.

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KCA 7.1.3.1.1./01 (OECD Annex point KIIA 7.4.1)	Kelley I., Wood S.,	1992	“Adsorption/Desorption of FOE 5043 to Soil.”; Miles Inc., Agriculture Division, Research and Development Department, P. O. Box 4913, Kansas City, Missouri 64120, USA; Miles Study No. F3182101, Miles Report No. 103903; 30 September 1992; <i>updated by study report:</i> Kelley I., Wood S., (1993): Addendum to Miles Report No. 103903: Adsorption/Desorption of FOE 5043 to Soil.”; Miles Report No.103903-1; 13 September 1993; Study reference number: M-002202-01-1; GLP: Yes; Unpublished study;	No	Yes	Justification not provided by the Applicant, however should apply the provisions of the of Article 59, § 1, subparagraph 7 of the Regulation (EC) 1107/2009, stating that “ <i>A study shall also be protected if it was necessary for renewal or review of authorisation.</i> As this is a new study, should apply the rules set for the new/newly submitted studies.	BCS	The study submitted for the purpose of the previous authorisation of flufenacet in the EU.
KCA 7.1.3.1.1./02 (OECD Annex point KIIA 7.4.1)	Hein E.-M.,	2012	“[Thiadiazole-5- ¹⁴ C] FOE 5043 (Flufenacet): Adsorption/Desorption on Five Soils.”; Bayer CropScience AG, BCS-D-EnSa-Testing, 40789 Monheim, Germany; study ID M1312069-2, Report No. EnSa-12-0517; 01 October 2012; Study reference number: M-439282-01-1; GLP: Yes; Unpublished study;	No	Yes	Additional data for refinement of risk assessment.	BCS	Study is submitted specifically for this evaluation.

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KCA 7.1.3.1.1./03 (OECD Annex point KIIA 7.4.1)	Stupp H. P.	2010	“[Phenyl-UL- ¹⁴ C] Flufenacet: Adsorption on Two Japanese Soils.”; Bayer CropScience AG – Development, Environmental Safety Metabolism/ADME and Environmental Fate, Alfred-Nobel-Str. 50, D-40789 Monheim am Rhein, Germany (performing laboratory) for Bayer CropScience K. K, 6-5 Marunouchi 1-chome, Chiyoda-ku, 100-8262 Tokyo, Japan; Study No. M1311954-4; Bayer Report MEF-10/534; 04. 08. 2010.; Study reference number: M-387572-01-1; GLP: Yes; Unpublished study;	No	Yes	Study originally conducted for FAMIC (Japan) – so far not evaluated in EU.	BCS	Study is submitted specifically for this evaluation.
KCA 7.1.3.1.2./01 (OECD Annex point KIIA 7.4.2)	Blumhorst M. R., Yen P. Y., Marlow V. A.	1994	“Soil Adsorption/ Desorption of FOE 5043 Degradates: FOE Sulfonic acid, FOE Methyl Sulfoxide, FOE Oxalate, FOE Alcohol and Thiadone.”; EPL Bio-analytical Services, Inc. (EPL-BAS), P. O. Box 109, 395N. Memorial Parkway, Harristown IL 62537, USA (performing laboratory) for Miles Inc., Agriculture Division, Research and Development Department, P. O. Box 4913, Kansas City, MO 64120- 0013, USA; EPL-BAS study No. 122S19, study report (Miles) No. MR 106598; 26 September 1994; study reference number: M-002185-01-1; GLP: Yes; Unpublished study;	No	Yes	Justification not provided by the Applicant, however should apply the provisions of the of Article 59, § 1, subparagraph 7 of the Regulation (EC) 1107/2009, stating that “ <i>A study shall also be protected if it was necessary for renewal or review of authorisation. As this is a new study, should apply the rules set for the new/newly submitted studies.</i> ”	BCS	The study submitted for the purpose of the previous authorisation of flufenacet in the EU.

Data point (OECD-format)	Author(s)	Year	Title Company Report No. Source (where different from company) GLP or GEP status Published or not	Vertebrate study yes/no	Data protection claimed yes/no	Justification if data protection is claimed	Owner ^{*)}	Previous evaluation
KCA 7.1.3.1.2./02 (OECD Annex point KIIA 7.4.2)	Hein W.,	2011	“[Phenyl-UL- ¹⁴ C] BCS-CO62475: Adsorption/Desorption in Five Different Soils.”; RLP AgroScience GmbH, Breitenweg 71, 67435 Neustadt a. d. Weinstrasse, Germany (performing laboratory) for Bayer CropScience Aktiengesellschaft, Development, Environmental Safety Metabolism/ADME and Environmental Fate, Alfred Nobel Str. 50, D-40789 Monheim, Germany; Study number (RLP AgroSciences GmbH) AS158; Bayer Report No. M-411141-01-1; 30 June 2011; study reference number: M-411141-01-1. GLP: Yes; Unpublished study;	No	Yes	New data requirements	BCS	Study is submitted specifically for this evaluation.
KCA 7.1.3.1.2./03 (OECD Annex point KIIA 7.4.2)	Moendel M., Hein W.	2011	“[1- ¹⁴ C] BCS-AZ56567: Adsorption/Desorption in Five Different Soils.”; RLP AgroScience GmbH, Breitenweg 71, 67435 Neustadt a. d. Weinstrasse, Germany (performing laboratory) for Bayer CropScience Aktiengesellschaft, Development, Environmental Safety Metabolism/ADME and Environmental Fate, Alfred Nobel Str. 50, D-40789 Monheim, Germany; Study number (RLP AgroSciences GmbH) AS155; Bayer Report No. M-406740-01-1; 07 April 2011; study reference number: M-406740-01-1. GLP: Yes; Unpublished study;	No	Yes	EU data requirements	BCS	Study is submitted specifically for this evaluation.

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KCA 7.1.3.1.2./04 (OECD Annex point KIIA 7.4.2)	Traub M.,	2013	“Determination of the Adsorption/Desorption behaviour of FOE 5043-trifluoroethanesulfonic acid in five Soils.”; Eurofins Agroscience Services EcoChem GmbH, Eutinger Strasse 24, 75223 Niefern-Öschelbronn, Germany (performing laboratory) for Bayer CropScience AG, 40789 Monheim, Germany; Study number (Eurofins) S11-03923; Report No. MEFOP017; 18. 02. 2013; study reference number: M-449893-01-1. GLP: Yes; Unpublished study;	No	Yes	New data requirements	BCS	Study is submitted specifically for this evaluation.
KCA 7.1.4.1.2/01 (OECD Annex point KIIA 7.4.4:)	Hein E. –M.	2014	“[1- ¹⁴ C]trifluoroacetate: Soil column Leaching”; Bayer CropScience AG, BCS-D-EnSa Testing, 40789 Monheim, Germany; Study No. M1212045-5; Report No. EnSa-14-0050; 2014-02-20; study reference number: M-477737-01-1; GLP: Yes; Unpublished study;	No	Yes	New data requirement; higher tier study for investigation of the soil adsorption behaviour trifluoroacetic acid	BCS	Study is submitted specifically for this evaluation.
KCA 7.1.4.2/01 (OECD Annex point KIIA 7.4.7.)	Hellpointner E.,	1997	“Lysimeter study on the translocation of FOE 5043 into the subsoil after 2-year use as pre-emergence herbicide in corn.”; Bayer AG, Agrochemical Division, Development, Institute for Metabolism Research and Residue analysis; D-51368 Leverkusen, Germany; report No. PF-4188 (MR-074/97); 19 September 1997; study reference number: M-002187-01-1; GLP: Yes; Unpublished study;	No	Yes	Justification not provided by the Applicant, however should apply the provisions of the of Article 59, § 1, subparagraph 7 of the Regulation (EC) 1107/2009, stating that “A study shall also be protected if it was necessary for renewal or review of authorisation. As this is a new study, should apply the rules set for the new/newly submitted studies.	BCS	The study submitted for the purpose of the previous authorisation of flufenacet in the EU.

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KCA 7.1.4.2/02 (OECD Annex point KIIA 7.4.7.)	Hellpointner E.,	1996	“Lysimeter study on the translocation of <i>FOE 5043</i> into the subsoil after use as pre-emergence herbicide in a maize/winter wheat crop rotation.”; Bayer AG, Agrochemical Division, Development, Institute for Metabolism Research and Residue analysis; D-51368 Leverkusen, Germany; report No. PF-4184 (107688); 18 November 1996; study reference number: M-002190-01-2; GLP: Yes; Unpublished study;	No	Yes	Justification not provided by the Applicant, however should apply the provisions of the of Article 59, § 1, subparagraph 7 of the Regulation (EC) 1107/2009, stating that “ <i>A study shall also be protected if it was necessary for renewal or review of authorisation.</i> As this is a new study, should apply the rules set for the new/newly submitted studies.	BCS	The study submitted for the purpose of the previous authorisation of flufenacet in the EU.
KCA 7.1.4./01 (OECD Annex point not defined)	Schmeling S., Bongartz R.,	2012	“Determination of the Plant Uptake Factor of FOE Methylsulfone, FOE Sulfonic acid and Trifluoroethanesulfonic acid in Wheat.”; Bayer Crop Science AG, Development-Environmental Safety-Metabolism/ADME and Environmental Fate, 40789 Monheim am Rhein, Germany; Study ID: M9992073-9, Report No. EnSa-12-260; 2012. 06. 28, updated with Amendment No. 1 on 2013. 02. 19; study reference number: M-434257-02-1; GLP: Yes; Unpublished study;	No	Yes	New data for refinement of risk assessment	BCS	Study is submitted specifically for this evaluation.

Data point (OECD-format)	Author(s)	Year	Title Company Report No. Source (where different from company) GLP or GEP status Published or not	Vertebrate study yes/no	Data protection claimed yes/no	Justification if data protection is claimed	Owner ^{*)}	Previous evaluation
KCA 7.1.4./02 (OECD Annex point not defined)	Bongartz R.,	2013	“Determination of the Plant Uptake Factor of Trifluoroacetic acid (TFA) in Wheat.”; Bayer Crop Science AG, BCS-D-EnSA-Testing, Monheim, Germany; Study ID: M9992182-0, Report No. EnSa-13-0357; 2013. 06. 05, updated with Amendment No. 1 on 2013. 06. 24 and with Amendment No. 2 on 2013. 07. 25; study reference number: M-456754-03-1; GLP: Yes; Unpublished study;	No	Yes	New data for refinement of risk assessment	BCS	Study is submitted specifically for this evaluation.
KCA 7.1.4./03 (OECD Annex point not defined)	Bongartz R.,	2013a	“Determination of the Plant Uptake Factor of Trifluoroacetic acid (TFA) in Wheat, Corn and Tomatoes.”; Bayer Crop Science AG, BCS-D-EnSA-Testing, Monheim, Germany; Study ID: M9992182-0, Report No. EnSa-12-0581; 2012. 10. 18; study reference number: M-440106-01-1; GLP: Yes; Unpublished study;	No	Yes	New data for refinement of risk assessment	BCS	Study is submitted specifically for this evaluation.
KCA 7.1.4./04 (OECD Annex point not defined)	Roepke B.,	2013	“Determination of a suitable Plant Uptake Factor (PUF) of Trifluoroacetic acid (TFA) for use in Environmental Fate Models in the Target Crop Wheat.”; Bayer Crop Science AG, Environmental Safety, Alfred Nobel Str. 50, D-40789 Monheim am Rhein, Germany; Report No. EnSa-13-0545; 24. 10. 2013; study reference number: M-468684-01-1; GLP: No, not applicable – position paper; Unpublished study;	No	No	Not applicable	BCS	Study is submitted specifically for this evaluation.

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KCA 7.2.1.1./01 (OECD Annex point KIIA 2.9.1 and KIIA 7.5.)	Zeng Z., Wood S.,	1992	“Stability of FOE 5043 in Sterile Aqueous Buffer Solution.”; Miles Inc., Agriculture Division, Research and Development Department, P. O. box 4913, Kansas City, MO 64120, USA; study No. F3072401 (Miles Inc.); Report No. 102623 (Miles Inc.); 12 March 1992; study reference number: M-002203-01-1; GLP: Yes; Unpublished study;	No	Yes	Justification not provided by the Applicant, however should apply the provisions of the of Article 59, § 1, subparagraph 7 of the Regulation (EC) 1107/2009, stating that “ <i>A study shall also be protected if it was necessary for renewal or review of authorisation.</i> As this is a new study, should apply the rules set for the new/newly submitted studies.	BCS	The study submitted for the purpose of the previous authorisation of flufenacet in the EU.
KCA 7.2.1.1./02 (OECD Annex point KIIA 2.9.1 and KIIA 7.5.)	Shah J. F., Bloomberg A. M.,	1999	“Hydrolysis study of Thiadone (A Metabolite of FOE 5043).”; Ricerca LLC, Department of Environmental and Metabolic Fate, 7528 Auburn Road, Painesville, Ohio 44077, USA (performing laboratory) for Bayer Corporation, Agriculture Division, P. O. Box 4913, Kansas City, MO 64120, USA; Ricerca document No. 7410-0058-EF-001, study No. F3082402 (Bayer); Bayer Report No. 108719; 22 February 1999; study reference number: M-009620-01-1; GLP: Yes; Unpublished study;	No	Yes	Additional data: Requested by the US Environmental Protection Agency (EPA)	BCS	Study is submitted specifically for this evaluation.

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KCA 7.2.1.1./03 (OECD Annex point KIIA 2.9.1 and KIIA 7.5.)	Babczinski P., Jantzen T.,	2009	“[Thiadiazole-2- ¹⁴ C]FOE5043-Thiadone (BCS-AA41715): Hydrolytic degradation.”; Bayer Crop Science AG, Alfred-Nobel-Str. 50, D-40789 Monheim am Rhein, Germany; study No. M1111833-8, Report No. MEF-009/308; 2009. 10. 26; study reference number M-358419-01-1; GLP: Yes; Unpublished study;	No	Yes	Study originally requested by US EPA – so far not evaluated in EU	BCS	Study is submitted specifically for this evaluation.
KCA 7.2.1.2/01; KCA 7.2.1.3./01 (OECD Annex points: KIIA 2.9.2. and KIIA 7.6)	Kasper A. M., Shadrick B. A.,	1995	“Aqueous Photolysis of [Phenyl-U- ¹⁴ C] FOE 5043.”; Bayer Corporation (formerly Miles Inc.), Agriculture Division, P. O. Box 4913, Kansas City, Missouri 64120-0013, USA; study No. F3082401 (Bayer); unpublished Miles Report No. MR 106246; 30 May 1995; study reference number: M-002206-01-1; GLP: Yes, but only for the part of the experiment that examined the direct photolysis of Flufenacet; Unpublished study;	No	Yes	Justification not provided by the Applicant, however should apply the provisions of the of Article 59, § 1, subparagraph 7 of the Regulation (EC) 1107/2009, stating that “ <i>A study shall also be protected if it was necessary for renewal or review of authorisation. As this is a new study, should apply the rules set for the new/newly submitted studies.</i> ”	BCS	The study submitted for the purpose of the previous authorisation of flufenacet in the EU.

Data point (OECD-format)	Author(s)	Year	Title Company Report No. Source (where different from company) GLP or GEP status Published or not	Vertebrate study yes/no	Data protection claimed yes/no	Justification if data protection is claimed	Owner ^{*)}	Previous evaluation
KCA 7.2.1.2/02 (OECD Annex points: KIIA 2.9.2. and KIIA 7.6)	Hellpointner E.,	1993	“Determination of the Quantum Yield and Assessment of the Environmental Half-life of the Direct Photodegradation of FOE 5043 in Water.”; Bayer AG, Crop Protection, Development, Institute for Metabolism Research, 51368 Leverkusen, Germany; Study No. M 112 0566-1, Report No. PF-3919 (HPO-103); 27 September 1993; study reference number M-002206-01-1; GLP: Yes; Unpublished study;	No	Yes	Justification not provided by the Applicant, however should apply the provisions of the of Article 59, § 1, subparagraph 7 of the Regulation (EC) 1107/2009, stating that “ <i>A study shall also be protected if it was necessary for renewal or review of authorisation.</i> As this is a new study, should apply the rules set for the new/newly submitted studies.	BCS	The study submitted for the purpose of the previous authorisation of flufenacet in the EU.
KCA 7.2.1.2/03 (OECD Annex points: KIIA 2.9.2. and KIIA 7.6)	Lentz N. R., Bloomberg A. M.,	1999	“Aqueous Photolysis of Thiadone (A Metabolite of FOE 5043).”; Ricerca Inc., Department of Environmental and Metabolic Fate, 7528 Auburn Road, Painesville, Ohio 44077, USA (performing laboratory) for Bayer Corporation, Agriculture Division, P. O. Box 4913, Kansas City, MO 64120, USA; Ricerca document No. 7410-98-0056-EF-001, study No. F3082402 (Bayer); Bayer Report No. 108720; 1 9 August 1999; study reference number: M-017985-01-1; GLP: Yes; Unpublished study;	No	Yes	Study originally requested by US EPA – so far not evaluated in EU	BCS	Study is submitted specifically for this evaluation.

Data point (OECD-format)	Author(s)	Year	Title Company Report No. Source (where different from company) GLP or GEP status Published or not	Vertebrate study yes/no	Data protection claimed yes/no	Justification if data protection is claimed	Owner ^{*)}	Previous evaluation
KCA 7.2.1.3/02 (OECD Annex points: KIIA 2.9.2. and KIIA 7.6)	Stupp H.-P., Unold M.,	2011	“[Thiadiazole-2- ¹⁴ C] BCS-AA41715 (FOE 5043-thiadone). Phototransformation in Natural Water.”; Bayer CropScience AG, Development, Environmental Safety, Metabolism /ADME and Environmental Fate, BCS-D-EnSDa-MeA/Efate, Alfred-Nobel-Str. 50, D-40789 Monheim am Rhein, Germany; study No. M 1121843-0, Report No. MEF-09/506; 21. 03. 2011; study reference number: M-404931-01-1; GLP: Yes; Unpublished study;	No	Yes	Study originally requested by US EPA – so far not evaluated in EU	BCS	Study is submitted specifically for this evaluation.
KCA 7.2.2.2/01 (OECD Annex point KIIA 7.8.1.)	Schocken M. J., Yen P. Y., Widmer S. L.,	1995	“[Phenyl-U- ¹⁴ C]FOE 5043 – Determination of Aerobic Aquatic Biotransformation at 25°C.”; Springborn Laboratories Inc., Environmental Sciences Division, 790 Main Street, Wareham, Massachusetts 02571-1075, USA (performing laboratory) for Bayer Corporation (formerly Miles Inc.), Agriculture Division, Research and Development Department, P. O. Box 4913, Kansas City, MO 64120, USA; Springborn Laboratories Report No. 95-4-5785; study No. F3042404 (Bayer); Bayer Report No. BR106961; 27 December 1995; study reference number: M-002210-01-1; GLP: Yes; Unpublished study;	No	Yes	Study originally conducted for PMRA – will be used as surrogate for OECD 309 to fulfil current EU data requirements. So far not yet evaluated in EU	BCS	Study is submitted specifically for this evaluation.

Data point (OECD-format)	Author(s)	Year	Title Company Report No. Source (where different from company) GLP or GEP status Published or not	Vertebrate study yes/no	Data protection claimed yes/no	Justification if data protection is claimed	Owner ^{*)}	Previous evaluation
KCA 7.2.2.2/02 (OECD Annex point KIIA 7.8.1.)	Hein E. – M.,	2013	“Evaluation of the Study: [Phenyl- $U-^{14}C$] FOE 5043 – Determination of Aerobic Aquatic Biotransformation at 25°C.”; Bayer CropScience AG, Environmental Fate, BCS AG – R&D-D-EnSa-Efate, Alfred-Nobel-Str. 50, D-40789 Monheim, Germany; unpublished report No. EnSa-13-0268; 03. 04. 2013; study reference number: M-450131-01-1; GLP: No, not applicable – position paper; Unpublished study;	No	No	Not applicable	BCS	Study is submitted specifically for this evaluation.
KCA 7.2.2.3/01 (OECD Annex point KIIA 7.8.3.)	Kelley I., Wood S., McKinney M.	1995	“Degradability and Fate of [Phenyl- $UL-^{14}C$]FOE 5043 in Two Sediment/Water Systems.”; Bayer Corporation (formerly Miles Inc), Agriculture Division, Research and Development Department, 17745 S. Metcalf, Stilwell, Kansas 66085, USA (performing laboratory) for Bayer Corporation, Agriculture Division, P. O. Box 4913, Kansas City, Missouri 64120, USA; unpublished study No. F3042405; Report No. MR106928; 01 November 1995; study reference number: M-002213-01-1; GLP: Yes; Unpublished study;	No	Yes	Justification not provided by the Applicant, however should apply the provisions of the of Article 59, § 1, subparagraph 7 of the Regulation (EC) 1107/2009, stating that “A study shall also be protected if it was necessary for renewal or review of authorisation. As this is a new study, should apply the rules set for the new/newly submitted studies.	BCS	The study submitted for the purpose of the previous authorisation of flufenacet in the EU.

Data point (OECD-format)	Author(s)	Year	Title Company Report No. Source (where different from company) GLP or GEP status Published or not	Vertebrate study yes/no	Data protection claimed yes/no	Justification if data protection is claimed	Owner ^{*)}	Previous evaluation
KCA 7.2.2.3/02 (OECD Annex point KIIA 7.8.3.)	Halarnkar P. P., Irwin D. W.,	1997	“Degradability and Fate of [Thiadiazole-2- ¹⁴ C]FOE 5043 in Two Water/Sediment Systems.”; Bayer Corporation, Agriculture Division, Environmental Research, 17745 S. Metcalf, Stilwell, Kansas 66085, USA (performing laboratory) for Bayer Corporation, Agriculture Division, Research and Development Department, P. O. Box 4913, Kansas City, Missouri 64120, USA; unpublished study No. F3042406; unpublished Report No. 107822; 06 October 1997; study reference number: M-004595-01-1; GLP: Yes; Unpublished study;	No	Yes	Justification not provided by the Applicant, however should apply the provisions of the of Article 59, § 1, subparagraph 7 of the Regulation (EC) 1107/2009, stating that “ <i>A study shall also be protected if it was necessary for renewal or review of authorisation.</i> As this is a new study, should apply the rules set for the new/newly submitted studies.	BCS	The study submitted for the purpose of the previous authorisation of flufenacet in the EU.
KCA 7.2.2.3/03 (OECD Annex point KIIA 7.8.3.)	Reinken G., Maassen K.,	2014	“Kinetic Evaluation of Degradation and Dissipation Behaviour of Flufenacet and its Degradation Products in Water/Sediment Systems According to FOCUS Kinetics Using the KinGUI 2 Tool. Flufenacet (FOE 5043); FOE Methylsulfide; FOE-thiadone.”; Bayer CropScience AG, Environmental Safety, Alfred-Nobel-Strasse 50, 40789 Monheim, Germany; unpublished Study report No. En-Sa-13-0973; 17. 02. 2014; study reference number: M-477845-01-1. GLP: no, not applicable (modelling study); Unpublished study;	No	Yes	New data/guideline requirement: Kinetic analysis of the degradation of flufenacet and its major degradation products FOE methylsulfide and FOE-thiadone for modelling purpose.	BCS	Study is submitted specifically for this evaluation.

Data point (OECD-format)	Author(s)	Year	Title Company Report No. Source (where different from company) GLP or GEP status Published or not	Vertebrate study yes/no	Data protection claimed yes/no	Justification if data protection is claimed	Owner ^{*)}	Previous evaluation
KCA 7.3.1/01 (OECD Annex IIA point 7.10)	Hellpointner E.,	1995	“Determination of the Volatilisation Behavior of FOE 5043 (60WG) in a Field Trial.”; Bayer AG, Crop Protection-Development, Institute for Metabolism Research and Residue Analysis, D-51368 Leverkusen, Germany (performing laboratory) for Bayer Corporation, Agriculture Division, P. O. Box 4913, Kansas City, MO 64120, USA; Bayer Report No. 107281 (PF-4091); 12 September 1995; study reference number: M-002237-01-2.; GLP: Yes; Unpublished study;	No	Yes	Justification not provided by the Applicant, however should apply the provisions of the of Article 59, § 1, subparagraph 7 of the Regulation (EC) 1107/2009, stating that “A study shall also be protected if it was necessary for renewal or review of authorisation. As this is a new study, should apply the rules set for the new/newly submitted studies.	BCS	The study submitted for the purpose of the previous authorisation of flufenacet in the EU.
IIA 7.3.1./02 (OECD Annex IIA point 7.10)	Hellpointner E.,	1995	“Calculation of the Chemical Lifetime of Thiafluamide (FOE 5043) I the Troposphere.”; Bayer AG, Crop Protection-Development, Institute for Metabolism Research and Residue Analysis, D-51368 Leverkusen, Germany; Report No. PF-4069 (HPO-123); 07 July 1995; study reference number: M-002236-01-1; GLP: no, not applicable (modelling study); Unpublished study;	No	Yes	Justification not provided by the Applicant,	BCS	The study submitted for the purpose of the previous authorisation of flufenacet in the EU.
KCA 9; (OECD Annex point not defined)	Derpmann J., Teubner L.,	2014	“Summary of the literature data for Flufenacet”; Bayer Crop Science; BCS report No. M-482180-01-1; GLP: no, not required; Unpublished Report;	No	Yes	Justification not provided by the Applicant,	BCS	Report submitted specifically for this evaluation, to meet the requirement set by the Article 8(5) of the EU Regulation 1107/2009

b) Open- source literature used in the evaluation:

Annex point/ reference number	Author(s)	Year	Title of publication; Reference data (source's name, publication date)	Status of the publication	Submitted by:	Submitted – Original dossier (1 st inclusion) / Supplementary dossier (renewal of the inclusion)
KCA 7.1.1.1./07;	Bloomberg A. M., Shadrick B. A., Ellen A. L., Clay V. E.	2002	„Outdoor Soil Metabolism of [Phenyl-U- ¹⁴ C] Flufenacet on California Soils.”; published in: Phelps W. (ed.) “ ACS Symposium Series, vol. 813: Pesticide Environmental Fate ”, chapter 12, pp 167 – 182 ; American Chemical Society, Washington, DC, 2002, publication date March 1, 2002;	Study considered as relevant and used to derive regulatory endpoints, because it enabled the identification and quantitation of the degradation products of Flufenacet, in particular FOE alcohol as major metabolite.	Listed by RMS, submitted by Applicant on the request by RMS	Submitted in the supplementary dossier (renewal of the inclusion).
KCA 7.1.1.1./08;	Lam C. K., McKinney M. K., Clay V. E.,	2002	“Evaluation of Laboratory and Field Extraction Methods: Extraction of [Phenyl-U- ¹⁴ C] Flufenacet from Aged Soils.”; published in: Phelps W. (ed.) “ ACS Symposium Series, vol. 813: Pesticide Environmental Fate ”, chapter 11, pp 153 – 166 ; American Chemical Society, Washington, DC, 2002, publication date March 1, 2002;	Supplementary study, not to be used to derive regulatory endpoints.	Listed by both Applicant and RMS, submitted by Applicant on the request by RMS	Submitted in the supplementary dossier (renewal of the inclusion).
KCA 7.1.2.1.1./26; KCA 7.1.2.1.2; KCA 7.1.3.1.1/05; KCA 7.1.4.1./02	Gupta S., Gajbhiye V. T., Agnihotri N. P.	2001	“Adsorption-Desorption, Persistence, and Leaching Behaviour of Flufenacet in Alluvial Soil of India.”; published in: Bulletin of Environmental Contamination and Toxicology , 2001, 66 (1) , 9 – 16.	Supplementary study, not to be used to derive regulatory endpoints.	Listed by RMS,	No - the Applicant has not identified the paper as a potentially relevant, most probably because it was beyond the temporal limits set for the literature search (the paper was issued in 2001, a year before the Applicant's search began).
KCA 7.1.2.1.1./27; KCA 7.1.2.1.2;	Gupta S., Gajbhiye V. J.,	2002	“Effect of concentration, moisture and soil type on the dissipation of flufenacet from soil.”; Published in: Chemosphere , 2002, 47(9) , 901 – 906.	Supplementary study, not to be used to derive regulatory endpoints.	Listed by both Applicant and RMS, submitted by Applicant on the request by RMS	Submitted in the supplementary dossier (renewal of the inclusion).

Annex point/ reference number	Author(s)	Year	Title of publication; Reference data (source's name, publication date)	Status of the publication	Submitted by:	Submitted – Original dossier (1 st inclusion) / Supplementary dossier (renewal of the inclusion)
KCA 7.1.2.2.1./08;	Rouchaud J., Neus O., Cools K., Bulcke R.	1999	“Dissipation and mobility of the oxyacetamide flufenacet herbicide in corn and wheat crops.”; Published in: Mededlingen – Faculteit Landbouwkundige en Toegepaste Biologische Wetenschappen, Universiteit Gent , 1999, 64 , (3b), 673 – 677.	Supplementary study, not to be used to derive regulatory endpoints.	Listed by RMS,	No - the Applicant has not identified the paper as a potentially relevant, most probably because it was beyond the temporal limits set for the literature search (the paper was issued in 1999, two years before the Applicant's search began).
KCA 7.1.2.2.1./09;	Rouchaud J., Neus O., Cools K., Bulcke R.	1999	“Flufenacet Soil Persistence and Mobility in Corn and Wheat Crops.”; Published in: The Bulletin of Environmental Contamination and Toxicology , 1999, 63 , 460 – 466.	Supplementary study, not to be used to derive regulatory endpoints.	Listed by RMS,	No - the Applicant has not identified the paper as a potentially relevant, most probably because it was beyond the temporal limits set for the literature search (the paper was issued in 1999, two years before the Applicant's search began).
KCA 7.1.2.2.1./10; KCA 7.1.3.1.1./07	Rouchaud J., Neus O., Eelen H., Bulcke R.	2001	“Persistence, Mobility and Adsorption of the Herbicide Flufenacet in the Soil of Winter Wheat Crops.”; Published in: “ The Bulletin of Environmental Contamination and Toxicology ”, 2001, 67 , 609 – 616.	Supplementary study, not to be used to derive regulatory endpoints.	Listed by both Applicant and RMS, submitted by Applicant on the request by RMS	Submitted in the supplementary dossier (renewal of the inclusion).
KCA 7.1.3.1.1./06	Gajbhiye V. T., Gupta S.	2001	“Adsorption-desorption behaviour of flufenacet in five different soils of India.”; Published in: Pest Management Science , 2001, 57 , 633 – 639.	Supplementary study, not to be used to derive regulatory endpoints.	Listed by RMS,	No - the Applicant has not identified the paper as a potentially relevant, most probably because it was beyond the temporal limits set for the literature search (the paper was issued in 2001, a year before the Applicant's search began).
KCA 7.1.4.1./03	Campagna G. Paci F., Fabbi A., Rapparini G.,	2006	“Studio in colonna della percolazione di alcuni diserbanti residuali del mais.” (<i>title in English</i> : “Percolation of acetochlor, dimethenamid, flufenacet and s-metolachlor applied in columns.”); Published in: Giornate Fitopatologiche , 2006, I , 591 – 598;	Supplementary study, not to be used to derive regulatory endpoints.	Listed by both Applicant and RMS, submitted by Applicant on the request by RMS	Submitted in the supplementary dossier (renewal of the inclusion).
KCA 7.2.1.1./04	Sunita Rani, Beena Kumari, TS Kathpal,	2006	“Effect of pH on the Dissipation Behaviour of Flufenacet (FOE- 5043) in Water.”; Published in: Pesticide Research Journal , 2006, 18 (2), 201 – 204;	Supplementary study, not to be used to derive regulatory endpoints.	Listed by both Applicant and RMS, submitted by Applicant on the request by RMS	Submitted in the supplementary dossier (renewal of the inclusion).

Annex point/ reference number	Author(s)	Year	Title of publication; Reference data (source's name, publication date)	Status of the publication	Submitted by:	Submitted – Original dossier (1 st inclusion) / Supplementary dossier (renewal of the inclusion)
KCA 7.2.2.2.3./05	Ellis D. A., Hanson M. L., Sibley P. K., Shahid T., Fineberg N. A., Solomon K. R., Muir D. C. G., Mabury S. A.,	2001	“The fate and persistence of trifluoroacetic and chloroacetic acids in pond water.”; published in: “ Chemosphere ”, 2001, 42 , 309-318.	Supplementary study, not to be used to derive regulatory endpoints.	Listed by RMS,	No - the Applicant has not identified the paper as a potentially relevant, most probably because it was beyond the temporal limits set for the literature search (the paper was issued in 2001, a year before the Applicant's search began).
KCA 7.2	Anon.	2013	“Final Report of Project WT1246- Understanding changes in pesticide usage to inform water company risk assessment.”; DEFRA 2013, available on-line: http://dwi.defra.gov.uk/research/completed-research/2000todate.htm	One of the key studies used in the evaluation of the impact on water treatment processes	Listed by RMS,	No - the Applicant has not identified the paper as a potentially relevant, most probably because it was beyond the temporal limits set for the literature search.
KCA 7.2	Dealtry S., Holmsgaard P. N, Dunon V., Jechalke S., Ding G- C. Krögerreckl enfort E., Heuer H., Hansen L. H., Springael D., Zühlke S., Sørensen S., Smalla K.,	2014	“Shifts in abundance and Diversity of Mobile Genetic Elements after the Introduction of Diverse Pesticides into an On- Farm Biopurification System over the Course of a Year.”; Published in: Applied and Environmental Microbiology , 2014, 80 (13), 4012 – 4020.	One of the key studies used in the evaluation of the impact on water treatment processes	Listed by RMS,	No - the Applicant has not identified the paper as a potentially relevant, most probably because it was beyond the temporal limits set for the literature search.
KCA 7.2	Hollender J., Zimmerman n S. G., Koepke S., Krauss M., McArdell C. S., Ort C., Singer H., von Gunten U., Siegrist H.,	2009	“Elimination of Organic Micropollutants in a Municipal Wastewater Treatment Plant Upgraded with a Full-Scale Post- Ozonation Followed by Sand Filtration.”; Published in: Environmental Science and Technology , 2009, 43 (20), 7862 – 7869.	One of the key studies used in the evaluation of the impact on water treatment processes	Listed by RMS,	No - the Applicant has not identified the paper as a potentially relevant.
KCA 7.2	Sakkas V. A., Calza P., Vlachou A. D., Medana C., Minero C., Albanis T.,	2011	“Photocatalytic transformation of flufenacet over TiO ₂ aqueous suspension: Identification of intermediates and the mechanisms involved.”; Published in: Applied Catalysis B: Environmental , 2011, 110 , 238 – 250;	One of the key studies used in the evaluation of the impact on water treatment processes	Listed by both Applicant and RMS, submitted by Applicant on the request by RMS	Submitted in the supplementary dossier (renewal of the inclusion).

Annex point/ reference number	Author(s)	Year	Title of publication; Reference data (source's name, publication date)	Status of the publication	Submitted by:	Submitted – Original dossier (1 st inclusion) / Supplementary dossier (renewal of the inclusion)
KCA 7.2	Sinclair C., van Beinum W., Adams C., Bevan R., Levy L., Parsons S., Goslan E., Baumann G.,	2010	“A Desk Study on Pesticide Metabolites, Degradation and Reaction Products to Inform the Inspectorate’s Position on Monitoring Requirements. Final Report for Drinking Water Inspectorate.”; The Food and Environment Research Agency (FERA), Sand Hutton, York, UK, FERA Project S3VB, DEFRA Project WT1221, DWI Project 70/2/232, February 2010, report available on-line on DEFRA web-site.	One of the key studies used in the evaluation of the impact on water treatment processes	Listed by RMS,	No - the Applicant has not identified the paper as a potentially relevant.
KCA 7.2	Sinclair C. J., Boxall A. B. A., Parsons S. A., Thomas M. R.,	2006	“Prioritization of Pesticide Environmental Transformation Products in Drinking Water Supplies.”; Published in: Environmental Science and Technology , 2006, 40 (23), 7283 – 7289;	One of the key studies used in the evaluation of the impact on water treatment processes	Listed by RMS,	No - the Applicant has not identified the paper as a potentially relevant.
KCA 7.2	Verstraeten I. M., Thurman E. M., Lindsey M. E., Lee E. C., Smith R. D.,	2002	“Changes in concentrations of triazine and acetamide herbicides by bank filtration, ozonation and chlorination in a public water supply.”; Published in: Journal of Hydrology , 2002, 266 , 190 – 208	One of the key studies used in the evaluation of the impact on water treatment processes	Listed by RMS,	No - the Applicant has not identified the paper as a potentially relevant.
KCA 7.2	Bond T., Tempelton M. R., Graham N.	2012	“Precursors of nitrogenous disinfection byproducts in drinking water – A Critical review and analysis.”; Published in: Journal of Hazardous Materials , 2012, 235-236 , 1 – 16.	Supplementary study used in the evaluation of the impact on water treatment processes	Listed by RMS,	No - the Applicant has not identified the paper as a potentially relevant.
KCA 7.2	Anon.	----	“Report on Carcinogens, Thirteenth Edition; N-Nitrosamines: 15 Listing.”; NIH National Toxicology Program, Department of Health and Human Services; document available on-line on: http://ntp.niehs.nih.gov/go/roc13	Supplementary study used in the evaluation of the impact on water treatment processes	Listed by RMS,	No - the Applicant has not identified the paper as a potentially relevant.
KCA 7.2	Anon.	----	Toxicological data sheet for TFA published on TOXNET – Toxicology Data Network, site of US NIH National Library of Medicine; available on-line at http://toxnet.nlm.nih.gov/index.html as a record CASRN: 76-05-1;	Supplementary study used in the evaluation of the impact on water treatment processes	Listed by RMS,	No - the Applicant has not identified the paper as a potentially relevant.
KCA 7.2	Boorman G. A., Dellarco V., Dunnick J. K., Chapin R. E., Hunter S., Hauchman F., Gardner H., Cox M., Sills R. C.,	1999	“Drinking Water Disinfection Byproducts: Review and Approach to Toxicity Evaluation.”; Published in: Environmental Health Perspectives , 1999, 107 Supplement 1 , 207 – 217;	Supplementary study used in the evaluation of the impact on water treatment processes	Listed by RMS,	No - the Applicant has not identified the paper as a potentially relevant.

Annex point/ reference number	Author(s)	Year	Title of publication; Reference data (source's name, publication date)	Status of the publication	Submitted by:	Submitted – Original dossier (1 st inclusion) / Supplementary dossier (renewal of the inclusion)
KCA 7.2	Kim J., Clevenger T. E.,	2007	"Prediction of N-nitrosodimethylamine (NDMA) formation as a disinfection by-product."; Published in: Journal of Hazardous Materials , 20007, 145 , 270 – 276;	Supplementary study used in the evaluation of the impact on water treatment processes	Listed by RMS,	No - the Applicant has not identified the paper as a potentially relevant.
KCA 7.2	Krasner S. W., Mitch W. A., McCurry D. L., Hanigan D., Westerhoff P.,	2013	"Formation, precursors, control and occurrence of nitrosoamines in drinking water: a review."; Published in: Water Research , 2013, 47 , 4433 – 4450;	Supplementary study used in the evaluation of the impact on water treatment processes	Listed by RMS,	No - the Applicant has not identified the paper as a potentially relevant.
KCA 7.2	Le Roux J., Gallard H., Croué J.-P.,	2011	"Chloramination of nitrogenous contaminants (pharmaceuticals and pesticides): NDMA and halogenated DBPs formation."; Published in: Water Research , 2011, 45 , 3164 – 3174;	Supplementary study used in the evaluation of the impact on water treatment processes	Listed by RMS,	No - the Applicant has not identified the paper as a potentially relevant.
KCA 7.2	Manoj A. Lazar, Shaji Varghese, Santosh S. Nair	2012	"Photocatalytic Water Treatment by Titanium Dioxide: Recent Updates."; Published in: Catalyst , 2012, 2 , 572 – 601	Supplementary study used in the evaluation of the impact on water treatment processes	Listed by RMS,	No - the Applicant has not identified the paper as a potentially relevant.
KCA 7.2	Mitch W. A., Sedlak D. L.,	2002	"Factors controlling nitrosamine formation during wastewater chlorination."; Published in: Water Science and Technology: Water Supply , 2002, 2 (3), 191 – 198;	Supplementary study used in the evaluation of the impact on water treatment processes	Listed by RMS,	No - the Applicant has not identified the paper as a potentially relevant.
KCA 7.2	Nawrocki J., Andrzejewski P.,	2011	"Nitrosoamines and water."; Published in: Journal of Hazardous Materials , 2011, 189 , 1 – 18;	Supplementary study used in the evaluation of the impact on water treatment processes	Listed by RMS,	No - the Applicant has not identified the paper as a potentially relevant.
KCA 7.2	Richardson S. D., Postigo C.,	2012	"Drinking Water Disinfection By-products"; Published in <i>Barcelo D. (ed.) "Emerging Organic Contaminants and Human Health", "Handbook of Environmental Chemistry"</i> , 2012, Springer Verlag, 93 – 138;	Supplementary study used in the evaluation of the impact on water treatment processes	Listed by RMS,	No - the Applicant has not identified the paper as a potentially relevant.
KCA 7.2	Rostkowska K., Zwierz K., Róžański A., Moniuszko-Jakoniuk J., Roszczenko A.,	1998	"Formation and Metabolism of N-Nitrosamines."; Published in: Polish Journal of Environmental Studies , 1998, 7 (6), 321 – 325;	Supplementary study used in the evaluation of the impact on water treatment processes	Listed by RMS,	No - the Applicant has not identified the paper as a potentially relevant.

Annex point/ reference number	Author(s)	Year	Title of publication; Reference data (source's name, publication date)	Status of the publication	Submitted by:	Submitted – Original dossier (1 st inclusion) / Supplementary dossier (renewal of the inclusion)
KCA 7.3.1.	Hurley M. D., Sulbaek Andersen, M. P., Wallington T. J., Ellis D. A., Martin J. W., Mabury S. A.,	2004	“Atmospheric Chemistry of Perfluorinated Carboxylic Acids: Reaction with OH Radicals and Atmospheric Lifetimes.”; Published in: Journal of Physical Chemistry, A , 2004, 108 (4), 615 – 620.	Supplementary study, not to be used to derive regulatory endpoints.	Listed by both Applicant and RMS, submitted by Applicant on the request by RMS	Submitted in the supplementary dossier (renewal of the inclusion).
KCA 7.3.1.	Oeberg. T.	2005	“A QSAR for the hydroxyl radical reaction rate constant: validation, domain of application, and prediction.”; Published in: Atmospheric Environment , 2005, 39 (12), 2189 – 2200.	Supplementary study, not to be used to derive regulatory endpoints.	Listed by both Applicant and RMS, submitted by Applicant on the request by RMS	Submitted in the supplementary dossier (renewal of the inclusion).
KCA 7.3.1.	Kutsuna S., Hori H.,	2008	“Experimental determination of Henry's law constants of trifluoroacetic acid at 278-298 K.”; Published in: Atmospheric Environment , 2008, 42 (7), 1399 – 1412.	Supplementary study, not to be used to derive regulatory endpoints.	Listed by both Applicant and RMS, submitted by Applicant on the request by RMS	Submitted in the supplementary dossier (renewal of the inclusion).
KCA 7.3.1.	Bowden D. J., Clegg S. L., Brimblecom be P.	1996	“The Henry's law constant of Trifluoroacetic acid and its partitioning into liquid water in the atmosphere.”; Published in: Chemosphere , 1996, 32 (2), 405 – 420;	Supplementary study, not to be used to derive regulatory endpoints.	Listed by RMS,	No - the Applicant has not identified the paper as a potentially relevant, most probably because it was beyond the temporal limits set for the literature search.
KCA 7.3.2.; KCA 7.5;	Capel P. D., McCarthy K. A., Barbash J. E.,	2008	“National, Holistic, Watershed- Scale Approach to Understand the Sources, Transport, and Fate of Agricultural Chemicals.”; Published in: Journal of Environmental Quality , 2008, 37, 983 – 993.	Supplementary study, not to be used to derive regulatory endpoints.	Listed by RMS,	No - the Applicant has not identified the paper as a potentially relevant.
KCA 7.3.2.; KCA 7.5;	Vogel J. R., Majewski M. S., Capel P. D.,	2008	“Pesticides in Rain in Four Agricultural Watersheds in the United States.”; Published in: Journal of Environmental Quality , 2008, 37, 1101 – 1115.	Supplementary study, not to be used to derive regulatory endpoints.	Listed by RMS,	No - the Applicant has not identified the paper as a potentially relevant.
KCA 7.3.2.; KCA 7.5;	Henne, S.; Shallcross, D. E.; Reimann, S.; Xiao, P.; Boulos, S.; Gerecke, A. C.; Brunner, D.	2012	“Environmental impacts of HFO-1234yf and other HFOs.”; Published in : Moving Towards Sustainability, ASHRAE/NIST Refrigerants Conference, Gaithersburg, MD, United States, Oct. 29-30, 2012 (2012), 13/1-13/13.	Supplementary study, not to be used to derive regulatory endpoints.	Listed by both Applicant and RMS, submitted by Applicant on the request by RMS	Submitted in the supplementary dossier (renewal of the inclusion).
KCA 7.3.2.; KCA 7.5;	Jordan A., Frank H.,	1999	“Trifluoroacetate in the Environment. Evidence for Sources Other Than HFC/HCFCs.”; Published in: Environmental Science and Technology , 1999, 33 (4), 522 – 527;	Supplementary study, not to be used to derive regulatory endpoints.	Listed by RMS,	No - the Applicant has not identified the paper as a potentially relevant.

Annex point/ reference number	Author(s)	Year	Title of publication; Reference data (source's name, publication date)	Status of the publication	Submitted by:	Submitted – Original dossier (1 st inclusion) / Supplementary dossier (renewal of the inclusion)
KCA 7.3.2.;	Wilson S. R., Solomon K. R., Tang X.,	2007	“Changes in tropospheric composition and air quality due to stratospheric ozone depletion and climate change.”; Published in: Photochemical and Photobiological Sciences , 2007, 6 (3), 301 – 310.	Supplementary study, not to be used to derive regulatory endpoints.	Listed by both Applicant and RMS, submitted by Applicant on the request by RMS	Submitted in the supplementary dossier (renewal of the inclusion).
KCA 7.5.;	Baker N. T., Stone W. S.,	2015	“Estimated Annual Agricultural Pesticide Use for Counties of the Conterminous United States, 2008 – 12.”; US Geological Survey Data Series 907 , 2015.	Supplementary study, not to be used to derive regulatory endpoints.	Listed by RMS,	No - the Applicant has not identified the paper as a potentially relevant.
KCA 7.5.;	Battaglin W. A., Kolpin D. A., Scribner E. A., Kuivila K. M., Sandstrom M. W.,	2005	“Glyphosate, other herbicides, and transformation products in Midwestern streams, 2002.”; Published in: JAWRA Journal of the American Water Resources Association , 2005, 41 (2), 323 – 332.	Supplementary study, not to be used to derive regulatory endpoints.	Listed by RMS,	No - the Applicant has not identified the paper as a potentially relevant.
KCA 7.5.;	Berg M., Müller S. R., Mühlemann J., Wiedmer A., Schwarzenbach R. P.,	2000	“Concentrations and Mass Fluxes of Chloroacetic acids and Trifluoroacetic acid in Rain and Natural Waters in Switzerland.”; Published in: Environmental Science and Technology , 2000, 34 (13), 2675 – 2683;	Supplementary study, not to be used to derive regulatory endpoints.	Listed by RMS,	No - the Applicant has not identified the paper as a potentially relevant.
KCA 7.5.;	Bishoff G., Pestmer W., Rodemann B.;	2003	“Entry of pesticides into surface waters – new results of Lamspringe run-off monitoring project 1999 – 2001.”; Published in: Pesticide in Air, Plant, Soil and Water System, Proceedings of the Symposium Pesticide Chemistry, 12th, Piacenza, Italy , 2003, pp. 849 – 856.	Supplementary study, not to be used to derive regulatory endpoints.	Listed by the Applicant,	Submitted in the supplementary dossier (renewal of the inclusion).
KCA 7.5.;	Durham L., Fisk A., Kannan K., Macdonald R. W., Muir D. C. G., Scott B. F., Spencer C., Witter A., Yamashita N.,	2005	“Trifluoroacetate profiles in the Arctic, Atlantic, and Pacific Oceans.”; Published in: Environmental Science and Technology , 2005, 39 (17), 6555 – 6560.	Supplementary study, not to be used to derive regulatory endpoints.	Listed by the Applicant,	Submitted in the supplementary dossier (renewal of the inclusion).
KCA 7.5.;	Frank H., Christoph E. H., Holm- Hansen O., Bullister J. L.,	2002	“Trifluoroacetate in Ocean Waters.”; Published in: Environmental Science and Technology , 2002, 36 (1), 12 – 15.	Supplementary study, not to be used to derive regulatory endpoints.	Listed by the Applicant,	Submitted in the supplementary dossier (renewal of the inclusion).
KCA 7.5.;	Kern S., Singer H., Hollender J., Schwarzenbach R. P., Fenner K.,	2011	“Assessing Exposure to Transformation Products of Soil- Applied Organic Contaminants in Surface Water: Comparison of Model Predictions and Field Data.”; Published in: Environmental Science and Technology , 2011, 45 (7), 2833 – 2841.	Supplementary study, not to be used to derive regulatory endpoints.	Listed by both Applicant and RMS, submitted by Applicant on the request by RMS	Submitted in the supplementary dossier (renewal of the inclusion).

Annex point/ reference number	Author(s)	Year	Title of publication; Reference data (source's name, publication date)	Status of the publication	Submitted by:	Submitted – Original dossier (1 st inclusion) / Supplementary dossier (renewal of the inclusion)
KCA 7.5.;	Kolpin D. W., Schnoebele n D. J., Thurman M. E.,	2004	“Degradates Provide Insight to Spatial and Temporal Trends of Herbicides in Ground Water.”; Published in: Groundwater , 2004, 42 (4), 601 – 608.	Supplementary study, not to be used to derive regulatory endpoints.	Listed by RMS,	No - the Applicant has not identified the paper as a potentially relevant.
KCA 7.5.;	Kowal S. Balsaa P., Werres F., Schmidt T. C.,	2013	“Fully automated standard addition method for the quantification of 29 polar pesticide metabolites in different water bodies using LC-MS/MS.”; Published in: Analytical and Bioanalytical Chemistry , 2013, 405, 6337 – 6351.	Supplementary study, not to be used to derive regulatory endpoints.	Listed by RMS,	No - the Applicant has not identified the paper as a potentially relevant, probably because it was beyond the temporal limits of the literature search.
KCA 7.5.;	Mills P. C., Kolpin D. W., Scribner E. A., Thurman E. M.,	2005	“Herbicides and degradates in shallow aquifers of Illinois: spatial and temporal trends.”; Published in: JAWRA Journal of the American Water Resources Association , 2005, 41 (3), 537 – 547.	Supplementary study, not to be used to derive regulatory endpoints.	Listed by RMS,	No - the Applicant has not identified the paper as a potentially relevant.
KCA 7.5.;	Moschet C., Götz C., Longrée P., Hollender J., Singer H.,	2013	“Multi-Level Approach for the Integrated Assessment of Polar Organic Micropollutants in an International Lake Catchment: The Example of Lake Constance.”; Published in: Environmental Science and Technology , 2013, 47 (13), 7028 – 7036.	Supplementary study, not to be used to derive regulatory endpoints.	Listed by RMS,	No - the Applicant has not identified the paper as a potentially relevant, probably because it was beyond the temporal limits of the literature search.
KCA 7.5.;	Moschet C., Wittmer I., Simovic J., Junghans M., Piazzoli A., Singer H., Stamm C., Leu C. Hollender J.,	2014	“How a Complete Pesticide Screening Changes the Assessment of Surface Water Quality.”; Published in: Environmental Science and Technology , 2014, 48 (10), 5423 – 5432.	Supplementary study, not to be used to derive regulatory endpoints.	Listed by RMS,	No - the Applicant has not identified the paper as a potentially relevant, probably because it was beyond the temporal limits of the literature search.
KCA 7.5.;	Moschet C., Vermeirsser E. L. M., Singer H., Stamm C., Hollender J.,	2015	“Evaluation of in-situ calibration of Chemcatcher passive samplers for 322 micropollutants in agricultural and urban affected rivers.”; Published in: Water Research , 2015, 71, 306 – 317.	Supplementary study, not to be used to derive regulatory endpoints.	Listed by RMS,	No - the Applicant has not identified the paper as a potentially relevant, probably because it was beyond the temporal limits of the literature search.
KCA 7.5.;	Rebich R. A., Coupe R. H., Thurman E. M.,	2004	“Herbicide concentrations in the Mississippi River Basin – the importance of chloroacetanilide herbicide degradates.”; Published in: Science of the Total Environment , 2004, 321 (1-3), 189 – 199.	Supplementary study, not to be used to derive regulatory endpoints.	Listed by RMS,	No - the Applicant has not identified the paper as a potentially relevant.
KCA 7.5.;	Scott B. F., MacTavish D., Spencer C., Strachan W. M. J., Muir D. C.,	2000	“Haloacetic Acids in Canadian Lake Waters and Precipitation.”; Published in: Environmental Science and Technology , 2000, 34 (20), 1266 – 4272.	Supplementary study, not to be used to derive regulatory endpoints.	Listed by RMS,	No - the Applicant has not identified the paper as a potentially relevant.

Annex point/ reference number	Author(s)	Year	Title of publication; Reference data (source's name, publication date)	Status of the publication	Submitted by:	Submitted – Original dossier (1 st inclusion) / Supplementary dossier (renewal of the inclusion)
KCA 7.5.;	Scribner E. A., Battaglin W. A., Dieze J. E., Thurman E. M.,	2003	“Reconnaissance Data for Glyphosate, Other Selected Herbicides, Their Degradation Products, and Antibiotics in 51 Streams in Nine Mid-Western States 2002.”; US Geological Survey Open- File Report 03-217 , 2003.	Supplementary study, not to be used to derive regulatory endpoints.	Listed by RMS,	No - the Applicant has not identified the paper as a potentially relevant.
KCA 7.5.;	Wujcik C., Cahill T. M., Seiber J. N.,	1999	“Determination of Trifluoroacetic Acid in 1996 – 1997 Precipitation and Surface Waters in California and Nevada.”; Published in: Environmental Science and Technology , 1999, 33 (10), 1747 – 1751.	Supplementary study, not to be used to derive regulatory endpoints.	Listed by RMS,	No - the Applicant has not identified the paper as a potentially relevant.
KCA 7.5.;	Zimmerman L. R., Schneider R. J., Thurman E. M.,	2002	“Analysis and Detection of the Herbicides Dimethenamid and Flufenacet and Their Sulfonic and Oxalinic Acid Degradates in Natural Degradates in Natural Water.”; Published in: Journal of Agricultural and Food Chemistry , 2002, 50 (5), 1045 – 1052.	Supplementary study, not to be used to derive regulatory endpoints.	Listed by RMS,	No - the Applicant has not identified the paper as a potentially relevant.

c) other documents relevant for the evaluation

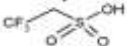

- Draft Assessment Report for Flufenacet prepared by the RMS – France in support for the inclusion of this compound into Annex I of the Council Directive 91/414/EEC and Addenda to it;
- Review Report for the active substance flufenacet – Flufenacet 7469/VI/98-final, 3 July 2003;

The specific Guidelines used in the evaluation are listed in the Volume 1, Level 3, point 3.4 – Appendices, Appendix 1 – Guidance documents used in this assessment.

B.8.8 - Appendices

B.8.8-A.1 – Appendix 1: List of evaluated compounds

Common name/ codename	Chemical (CAS or IUPAC) name	Structural formula	Molecular weight [g/mole]	Function	Occurrence
<i>Flufenacet (formerly fluthiamide)/ FOE5043</i>	N-(4-Fluorophenyl)-N-isopropyl-2-[[5-(trifluoromethyl)-1,3,4-thiadiazol-2-yl]oxy]acetamide		363.4	Active substance	Soil, water, sediment, air
<i>Flufenacet – N-Isomer</i>	N-(4-Fluorophenyl)-N-(1-methylethyl)-2-[2-oxo-5-(trifluoromethyl)-1,3,4-thiadiazol-3-yl]acetamide		363.4	Impurity of Flufenacet	Soil, water, sediment,
<i>FOE Alcohol</i>	N-(4-Fluorophenyl)-2-hydroxy-N-(1-methylethyl)acetamide		211.2	Metabolite of Flufenacet	Soil (major),
<i>FOE Oxalate</i>	[(4-Fluorophenyl) (1-methylethyl) amino] oxoacetic acid		225.2	Metabolite of Flufenacet	Soil (major),
<i>FOE Sulfoxide acid</i>	2-[(4-Fluorophenyl) (1-methylethyl) amino]-2-oxoethylsulfonic acid		275.3	Metabolite of Flufenacet	Soil (major),
<i>FOE Methylsulfoxide</i>	N-(4-Fluorophenyl)-N-(1-methylethyl)-2-(methylsulfinyl)acetamide		257.3	Metabolite of Flufenacet	Soil (major),
<i>FOE Methylsulfone</i>	N-(4-Fluorophenyl)-N-(1-methylethyl)-2-(methylsulfonyl)acetamide		273.3	Metabolite of Flufenacet	Soil (minor),
<i>FOE Methylsulfide</i>	N-(4-Fluorophenyl)-N-(1-methylethyl)-2-(methylthio)acetamide		241.0	Metabolite of Flufenacet	Water and sediment (major)
<i>FOE Thioglycolate sulfoxide</i>	4-Fluoro-N-methylethyl-aniline sulfenyldiacetic acid amide		315.4	Metabolite of Flufenacet	Soil (minor),
<i>FOE Thioglycolate</i>	4-Fluoro-N-methylethyl-aniline thiodiacetic acid amide		285.3	Metabolite of Flufenacet	Soil (minor),
<i>FOE Chloroacetanilide</i>	N-(4-Fluorophenyl)-2-chloro-N-(1-methylethyl)acetamide		229.7	Metabolite of Flufenacet	Soil (minor),
<i>FOE Thiadone</i>	5-(trifluoromethyl)-1,3,4-thiadiazol-2(3H)-one		170.1	Metabolite of Flufenacet	Soil (major),

Common name/ codename	Chemical (CAS or IUPAC) name	Structural formula	Molecular weight [g/mole]	Function	Occurrence
<i>FOE 5043- Trifluoroethane- sulfonic acid</i>	2,2,2-Trifluoroethane- Sulfonic acid		164.1	Metabolite of Flufenacet	Soil (major),
<i>Trifluoroacetic acid (TFA)</i>	Trifluoroacetic acid		114.02	Metabolite of Flufenacet	Soil (major),

B.8.8-A.2 – Appendix 2: Abbreviations and symbols used in the text:

<i>Symbol/term/ abbreviation</i>	<i>Meaning</i>
AR	Applied Radioactivity
a. s.	active substance
approx.	approximate/approximately
aver.	average
BBCH	BBCH scale or BBCH codes – a scale, and corresponding codes, used to describe phenologic growth phases for mono- and dicotyledonous plants (the abbreviation derived from the names of the organisations that developed the scale – B BA, B SA and C hemical Industry)
c	centi- ($\times 10^{-2}$), e. g. centimetre (cm, 10^{-2} metre)
°C	degree Celsius
C_{org}	Organic carbon content
CEC	Cation Exchange Capacity
Ci	Curie, the non-SI unit of the activity of radiation
CI	Confidence Interval; also Crop Interception factor
cfu	colony forming units – unit for counting microbial activity in the given matrix
d	days
DAT	Days After Treatment
DAF	Days After Flooding - a term used in soil anaerobic degradation study
DFOP	Double First Order in Parallel – one of the bi-phasic kinetic models within the 1 st order kinetics
dpm	decays per minute
DT₅₀	Period required for 50 percent degradation or dissipation
DT₉₀	Period required for 90 percent degradation or dissipation
E_h	Redox potential [mV]
EU	European Union
Eq (mEq)	Equivalent/milieuivalent – one of the alternative quantity unit
equiv.	equivalent (abbreviation commonly used in the summary of the lysimeter study)
FAO	Food and Agriculture Organisation of the UN
ff	kinetic formation fraction,
FOCUS	Forum for the Co-ordination of Pesticide Fate Models and their Use
FOMC	First Order Multi-Compartment – one of the bi-phasic kinetic models within the 1 st order kinetics
g	gram – the non-SI basic unit of weight (equal to 0.001 kg)
GAP	Good Agricultural Practice, here used to denominate the table containing the data on application of the given plant protection product/active substance (standard technical term)
Gy	Gray – the SI unit of absorbed dose
ha	hectare
HPLC	High Performance Liquid Chromatography
hr	hours
HS	Hockey Stick – one of the bi-phasic kinetic models within the 1 st order kinetics
k	degradation rate constant [days ⁻¹]
k	kilo ($\times 10^3$)
kg	kilogram – the basic SI unit of weight (1 kg = 1000 g)
L	Litre
LC	Liquid chromatography
LC/MS	Liquid chromatography with mass spectrometry detection
LC/MS/MS	Liquid chromatography with double mass spectrometry detection
LOD	Limit of Detection
LOQ	Limit of Quantitation
LSC	Liquid scintillation counting
m	metre
m	in front any unit milli- ($\times 10^{-3}$), milligram (10^{-3} gram)
mg	milligram
mL	millilitre
mm	millimetre
M	Molar
M₀	Initial concentration, expressed on the weight basis
min.	minute; also minimum or minimal
MS	Member State
MWHC	Maximum Water Holding Capacity
n	in front any unit nano- ($\times 10^{-9}$), e. g. nanogram (10^{-9} gram)
ng	nanogram
nm	nanometre
N	normal, an old way of expressing the concentration in liquids (used mainly for acids and bases), a

<i>Symbol/term/ abbreviation</i>	<i>Meaning</i>
	concentration of 1g equivalent/dm ³
NER	Non-Extractable residues
NP-	Normal Phase (for TLC analysis)
ode	oven dry equivalent
OECD	Organisation for Economic Co-operation and Development
Pa	Pascal – SI unit of pressure
PEC	Predicted Environmental Concentrations
pH	the acidity logarithmic scale
PNAP	<i>p</i> -nitroacetophenone
P_{ow}/K_{ow}	Octanol/water partition coefficient
PTFE	polytetrafluorethylene
pyr	pyridine
r	correlation coefficient
r²/R²	coefficient of determination
RMS	Rapporteur Member State
RP-	Reversed Phase (for TLC and HPLC analysis)
RP-HPLC	Reversed Phase High Performance Liquid Chromatography
RSD	relative standard deviation
s/sec.	second
S	(also) Siemens – the conductivity unit
SD/s	standard deviation
S_{aa}	Solubility in water
SFO	Single First Order kinetics – a kinetic model within the 1 st order kinetics
SPE	Solid phase extraction
T	temperature
TIC	Total Inorganic Carbon
TLC	Thin Layer Chromatography
TOC	Total Organic Carbon
TRR	Total Radioactive Residue
TWA	Time-Weighted Average (concentration)
UK	United Kingdom <i>of Great Britain and Northern Ireland</i> (specific technical term)
US	United States <i>of America</i> (specific technical term)
USDA	United States Department of Agronomy
UV	Ultraviolet radiation – the radiation within the wavelength range of 200-400 nm
UV-Vis	Ultraviolet – Visible radiation – the radiation within the wavelength range of 200-800 nm
Vis	Visible radiation – the radiation within the wavelength range of 400-800 nm
ver.	version
v/w	volume-to-weight ratio
V	Volt – the SI unit of electric potential
V_p	Vapour pressure [Pa]
WHC	Water Holding Capacity
γ–	Gamma, Greek letter, used here to denominate the gamma radiation
μ	in front of any unit - micro (x10 ⁻⁶), e.g. micrometer (μm), microgram (μg) or microlitre (μL)
λ	Lambda, Greek letter used here to denominate the wavelength

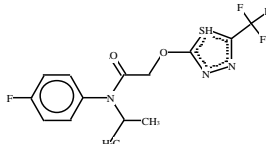
In this Appendix are presented the detailed results of QSAR calculations performed for FOE Alcohol and FOE Oxalate that had as aim to provide the data supporting the proposal to cover the exposure assessment for FOE Alcohol with that performed for FOE Oxalate. Additionally, in order to validate the results of calculations, the simulation for Flufenacet was performed. All calculations were made using EPI Suite[®] tool, developed by US EPA. Also are presented the results of the calculations performed for FOE Methylsulfide aimed on the determination of the input parameters – water solubility and adsorption coefficient, to be used in the SW model exposure assessment.

The results are presented in three separate tables, individually for each compound of concern.

Table B.8.8-A.3 CA-1: The detailed results of QSAR calculations for Flufenacet.

Compound: Flufenacet

Structural formula:



Results of calculations:

SMILES : c1cc(F)ccc1N(C(C)C)C(=O)COc2nnc(C(F)(F)F)s2

CHEM : Fluthiamide (Flufenacet)

CAS NUM: 142459-58-3

MOL FOR: C14 H13 F4 N3 O2 S1

MOL WT : 363.33

----- EPI SUMMARY (v4.10) -----

Physical Property Inputs:

Water Solubility (mg/L): -----

Vapor Pressure (mm Hg) : -----

Henry LC (atm-m3/mole) : -----

Log Kow (octanol-water): -----

Boiling Point (deg C) : -----

Melting Point (deg C) : -----

KOWWIN Program (v1.68) Results:

=====

Log Kow(version 1.68 estimate): 2.39

Experimental Database Structure Match:

Name : Fluthiamide

CAS Num : 142459-58-3

Exp Log P: 3.20

Exp Ref : WSSA (1998)

SMILES : c1cc(F)ccc1N(C(C)C)C(=O)COc2nnc(C(F)(F)F)s2

CHEM : Fluthiamide

MOL FOR: C14 H13 F4 N3 O2 S1

MOL WT : 363.33

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Frag	1	-C(=O)N [aliphatic attach]	-0.5236	-0.5236
Frag	2	Aromatic Nitrogen [5-member ring]	-0.5262	-1.0524
Factor	1	Di-N urea/acetamide aromatic correction	-0.7203	-0.7203
Factor	1	Ortho-Alkyloxy(thio) to 1 aromat nitrogen	0.4549	0.4549
Factor	1	1,3,4-Thiadiazole ring (non-fused)	-0.9800	-0.9800
Factor	1	Ring Rx: thiadiazole / alkyloxy-	0.5000**	0.5000
Const		Equation Constant		0.2290

NOTE		An estimated coefficient (**) used	
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Log Kow = 2.3949

MPBPWIN (v1.43) Program Results:

Experimental Database Structure Match:

Name : Fluthiamide
 CAS Num : 142459-58-3
 Exp MP (deg C): 76
 Exp BP (deg C): ---
 Exp VP (mm Hg): 6.75E-07
 (Pa) : 9.00E-005
 Exp VP (deg C): 20
 Exp VP ref : TOMLIN,C (1997)

SMILES : c1cc(F)ccc1N(C(C)C)C(=O)COc2nnc(C(F)(F)F)s2

CHEM : Fluthiamide

MOL FOR: C14 H13 F4 N3 O2 S1

MOL WT : 363.33

----- SUMMARY MPBPWIN v1.43 -----

Boiling Point: 433.14 deg C (Adapted Stein and Brown Method)

Melting Point: 349.84 deg C (Adapted Joback Method)

Melting Point: 139.25 deg C (Gold and Ogle Method)

Mean Melt Pt : 244.54 deg C (Joback; Gold,Ogle Methods)

Selected MP: 181.37 deg C (Weighted Value)

Vapor Pressure Estimations (25 deg C):

(Using BP: 433.14 deg C (estimated))

(Using MP: 76.00 deg C (exp database))

VP: 4.43E-008 mm Hg (Antoine Method)

: 5.91E-006 Pa (Antoine Method)

VP: 4.22E-007 mm Hg (Modified Grain Method)

: 5.62E-005 Pa (Modified Grain Method)

VP: 8.4E-007 mm Hg (Mackay Method)

: 0.000112 Pa (Mackay Method)

Selected VP: 4.22E-007 mm Hg (Modified Grain Method)

: 5.62E-005 Pa (Modified Grain Method)

Subcooled liquid VP: 2.16E-006 mm Hg (20 deg C, exp database VP)

: 0.000287 Pa (20 deg C, exp database VP)

TYPE	NUM	BOIL DESCRIPTION	COEFF	VALUE
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Group	2	-CH3	21.98	43.96
Group	1	-CH2-	24.22	24.22
Group	1	>CH-	11.86	11.86
Group	1	>C<	4.50	4.50
Group	3	-F	0.13	0.39
Group	1	-O- (nonring)	25.16	25.16
Group	1	-S- (ring)	69.00	69.00
Group	4	CH (aromatic)	28.53	114.12
Group	4	-C (aromatic)	30.76	123.04
Group	1	-C(=O)N<	142.77	142.77
Group	2	N (aromatic)	39.88	79.76
Group	1	-F (to aromat)	-7.81	-7.81
Corr	1	Other aaN-aaN	55.00	55.00
*		Equation Constant		198.18

RESULT-uncorr| BOILING POINT in deg Kelvin | 884.15

RESULT- corr | BOILING POINT in deg Kelvin | 706.30

| BOILING POINT in deg C | 433.14

TYPE	NUM	MELT DESCRIPTION	COEFF	VALUE
Group	2	-CH3	-5.10	-10.20
Group	1	-CH2-	11.27	11.27
Group	1	>CH-	12.64	12.64
Group	1	>C<	46.43	46.43
Group	3	-F	-15.78	-47.34
Group	1	-O- (nonring)	22.23	22.23
Group	1	-S- (ring)	73.93	73.93
Group	4	CH (aromatic)	8.13	32.52
Group	4	-C (aromatic)	37.02	148.08
Group	1	-C(=O)N<	142.00	142.00
Group	2	N (aromatic)	68.40	136.80
Group	1	-F (to aromat)	-15.78	-15.78
*		Equation Constant		122.50

Group	2	-CH3	-5.10	-10.20
Group	1	-CH2-	11.27	11.27
Group	1	>CH-	12.64	12.64
Group	1	>C<	46.43	46.43
Group	3	-F	-15.78	-47.34
Group	1	-O- (nonring)	22.23	22.23
Group	1	-S- (ring)	73.93	73.93
Group	4	CH (aromatic)	8.13	32.52
Group	4	-C (aromatic)	37.02	148.08
Group	1	-C(=O)N<	142.00	142.00
Group	2	N (aromatic)	68.40	136.80
Group	1	-F (to aromat)	-15.78	-15.78
*		Equation Constant		122.50

RESULT	MELTING POINT in deg Kelvin	675.08
RESULT-limit	MELTING POINT in deg Kelvin	623.00
	MELTING POINT in deg C	349.84

Water Sol from Kow (WSKOW v1.42) Results:

Water Sol: 9.516 mg/L

Experimental Water Solubility Database Match:

Name : Fluthiamide
 CAS Num : 142459-58-3
 Exp WSol : 56 mg/L (25 deg C)
 Exp Ref : TOMLIN,C (1997)

SMILES : c1cc(F)ccc1N(C(C)C)C(=O)COc2nnc(C(F)(F)F)s2

CHEM : Fluthiamide

MOL FOR: C14 H13 F4 N3 O2 S1

MOL WT : 363.33

----- WSKOW v1.42 Results -----

Log Kow (estimated) : 2.39
 Log Kow (experimental): 3.20
 Cas No: 142459-58-3
 Name : Fluthiamide
 Refer : WSSA (1998)
 Log Kow used by Water solubility estimates: 3.20

Equation Used to Make Water Sol estimate:

Log S (mol/L) = 0.796 - 0.854 log Kow - 0.00728 MW + Correction
 (used when Melting Point NOT available)

Correction(s): Value

No Applicable Correction Factors

Log Water Solubility (in moles/L) : -4.582

Water Solubility at 25 deg C (mg/L): 9.516

WATERNT Program (v1.01) Results:

Water Sol (v1.01 est): 81.616 mg/L

Experimental Water Solubility Database Match:

Name : Fluthiamide
 CAS Num : 142459-58-3
 Exp WSol : 56 mg/L (25 deg C)
 Exp Ref : TOMLIN,C (1997)

SMILES : c1cc(F)ccc1N(C(C)C)C(=O)COc2nnc(C(F)(F)F)s2

CHEM : Fluthiamide

MOL FOR: C14 H13 F4 N3 O2 S1

MOL WT : 363.33

TYPE	NUM	WATER SOLUBILITY FRAGMENT DESCRIPTION	COEFF	VALUE
Frag	2	-CH3 [aliphatic carbon]	-0.3213	-0.6425
Frag	1	-CH2- [aliphatic carbon]	-0.5370	-0.5370
Frag	1	-CH [aliphatic carbon]	-0.5285	-0.5285
Frag	1	C [aliphatic carbon - No H, not tert]	-1.0516	-1.0516
Frag	3	-F [fluorine, aliphatic attach]	-0.1580	-0.4740
Frag	4	Aromatic Carbon (C-H type)	-0.3359	-1.3435
Frag	1	-N [aliphatic N, one aromatic attach]	1.2749	1.2749
Frag	1	-O- [oxygen, one aromatic attach]	0.1980	0.1980
Frag	1	Aromatic Sulfur	-0.2743	-0.2743
Frag	1	-F [fluorine, aromatic attach]	0.1429	0.1429
Frag	1	-C(=O)N [aliphatic attach]	-0.2426	-0.2426
Frag	4	Aromatic Carbon (C-substituent type)	-0.5400	-2.1598
Frag	2	Aromatic Nitrogen [5-member ring]	0.5265	1.0530
Factor	1	Di-N urea/acetamide aromatic correction	0.6874	0.6874
Const		Equation Constant		0.2492

Log Water Sol (moles/L) at 25 dec C = -3.6485

Water Solubility (mg/L) at 25 dec C = 81.616

ECOSAR Program (v1.11) Results:

ECOSAR Version 1.11 Results Page

SMILES : c1cc(F)ccc1N(C(C)C)C(=O)COc2nnc(C(F)(F)F)s2

CHEM : Fluthiamide

CAS Num:

ChemID1:

MOL FOR: C14 H13 F4 N3 O2 S1

MOL WT : 363.33

Log Kow: 2.395 (EPI Suite Kowwin v1.68 Estimate)

Log Kow: (User Entered)

Log Kow: 3.20 (PhysProp DB exp value - for comparison only)

Melt Pt: (User Entered for Wat Sol estimate)

Melt Pt: 76.00 (deg C, PhysProp DB exp value for Wat Sol est)

Wat Sol: 37.26 (mg/L, EPI Suite WSKowwin v1.43 Estimate)

Wat Sol: (User Entered)

Wat Sol: 56 (mg/L, PhysProp DB exp value)

Values used to Generate ECOSAR Profile

Log Kow: 2.395 (EPI Suite Kowwin v1.68 Estimate)

Wat Sol: 56 (mg/L, PhysProp DB exp value)

ECOSAR v1.11 Class-specific Estimations

Amides

ECOSAR Class	Organism	Predicted Duration	End Pt	mg/L (ppm)
Amides	: Fish	96-hr	LC50	56.651 *
Amides	: Daphnid	48-hr	LC50	51.999
Amides	: Green Algae	96-hr	EC50	1.940
Amides	: Fish		ChV	0.123
Amides	: Daphnid		ChV	3.785
Amides	: Green Algae		ChV	2.153
Amides	: Fish (SW)	96-hr	LC50	50.240
Amides	: Mysid (SW)	96-hr	LC50	3.599

Neutral Organic SAR	: Fish	96-hr	LC50	131.900 *
(Baseline Toxicity)	: Daphnid	48-hr	LC50	77.675 *
	: Green Algae	96-hr	EC50	67.275 *
	: Fish		ChV	13.459
	: Daphnid		ChV	8.384
	: Green Algae		ChV	19.108

Note: * = asterisk designates: Chemical may not be soluble enough to measure this predicted effect. If the effect level exceeds the

water solubility by 10X, typically no effects at saturation (NES) are reported.

Class Specific LogKow Cut-Offs

If the log Kow of the chemical is greater than the endpoint specific cut-offs presented below, then no effects at saturation are expected for those endpoints.

Amides :

Maximum LogKow: >8.5 (LC50)

Maximum LogKow: >8.0 (EC50, ChV)

Baseline Toxicity SAR Limitations:

Maximum LogKow: 5.0 (Fish 96-hr LC50; Daphnid LC50)

Maximum LogKow: 6.4 (Green Algae EC50)

Maximum LogKow: 8.0 (ChV)

HENRY (v3.20) Program Results:
=====

Bond Est : 2.00E-011 atm-m3/mole (2.03E-006 Pa-m3/mole)

Group Est: Incomplete

SMILES : c1cc(F)ccc1N(C(C)C)C(=O)COc2nnc(C(F)(F)F)s2

CHEM : Fluthiamide

MOL FOR: C14 H13 F4 N3 O2 S1

MOL WT : 363.33

----- HENRYWIN v3.20 Results -----

Experimental Database Structure Match:

Name : Fluthiamide

CAS Num : 142459-58-3

Exp HLC : 5.76E-09 atm-m3/mole (0.000584 Pa-m3/mole)

Temper : 20 deg C

Exp Ref : VP/WSOL

CLASS	BOND CONTRIBUTION DESCRIPTION	COMMENT	VALUE
HYDROGEN	9 Hydrogen to Carbon (aliphatic) Bonds		-1.0771
HYDROGEN	4 Hydrogen to Carbon (aromatic) Bonds		-0.6172
FRAGMENT	2 C-C		0.2326
FRAGMENT	1 C-Car		0.1619
FRAGMENT	1 C-CO		1.7057
FRAGMENT	1 C-N		1.3010
FRAGMENT	1 C-O		1.0855
FRAGMENT	3 C-F		-1.2553
FRAGMENT	6 Car-Car		1.5828
FRAGMENT	2 Car-Nar		3.2564
FRAGMENT	1 Nar-Nar	ESTIMATE	3.0000
FRAGMENT	1 CO-N		2.4261
FRAGMENT	2 Car-Sar		0.7478
FRAGMENT	1 Car-N		0.7304
FRAGMENT	1 Car-F		-0.2214
FRAGMENT	1 Car-O		0.3473
FACTOR	1 Additional aromatic nitrogen(s)		-2.5000
FACTOR	1 Di-N-substituted N (to aromatic)		-0.9700
FACTOR	1 -C(=O)-C-O- group		-0.8500

RESULT | BOND ESTIMATION METHOD for LWAPC VALUE | TOTAL | 9.087

HENRYs LAW CONSTANT at 25 deg C = 2.00E-011 atm-m3/mole

= 8.19E-010 unitless

= 2.03E-006 Pa-m3/mole

	GROUP CONTRIBUTION DESCRIPTION	COMMENT	VALUE
	1 CH2 (CO)(O)	ESTIMATE	-1.40
	1 Car (N)(Car)(Car)	ESTIMATE	-0.50

	2	CH3 (X)			-1.24
	4	Car-H (Car)(Car)			0.44
	1	O (C)(Car)			1.25
	1	Car (Car)(Car)(F)		ESTIMATE	-0.34
		MISSING Value for: N (C)(CO)(Car)			
		MISSING Value for: CH (C)(C)(N)			
		MISSING Value for: CO (C)(N)			
		MISSING Value for: Car (Sar)(Nar)(O)			
		MISSING Value for: Nar (Nar)(Car)			
		MISSING Value for: Nar (Car)(Nar)			
		MISSING Value for: Car (C)(Sar)(Nar)			
		MISSING Value for: C (F)(F)(F)(Car)			
		MISSING Value for: Sar (Car)(Car)			
-----+-----+-----+-----+-----+-----					
RESULT		GROUP ESTIMATION METHOD for LOG GAMMA VALUE			INCOMPLETE -1.79
-----+-----+-----+-----+-----+-----					
For Henry LC Comparison Purposes:					
Exper Database: 5.76E-09 atm-m3/mole (5.84E-004 Pa-m3/mole)					
User-Entered Henry LC: not entered					
Henrys LC [via VP/WSol estimate using User-Entered or Estimated values]:					
HLC: 2.120E-008 atm-m3/mole (2.148E-003 Pa-m3/mole)					
VP: 4.22E-007 mm Hg (source: MPBPVP)					
WS: 9.52 mg/L (source: WSKOWWIN)					
Log Octanol-Air (KOAWIN v1.10) Results:					
=====					
		Log Koa: 9.828			
SMILES : c1cc(F)ccc1N(C(C)C)C(=O)COc2nnc(C(F)(F)F)s2					
CHEM : Fluthiamide					
MOL FOR: C14 H13 F4 N3 O2 S1					
MOL WT : 363.33					
----- KOAWIN v1.10 Results -----					
Log Koa (octanol/air) estimate: 9.828					
Koa (octanol/air) estimate: 6.73e+009					
Using:					
Log Kow: 3.20 (exp database)					
HenryLC: 5.76e-009 atm-m3/mole (exp database)					
Log Kaw: -6.628 (air/water part.coef.)					
LogKow : 3.20 (exp database)					
LogKow : 2.39 (KowWin estimate)					
Henry LC: 5.76e-009 atm-m3/mole (exp database)					
Henry LC: 2e-011 atm-m3/mole (HenryWin bond estimate)					
Log Koa (octanol/air) estimate: 11.477 (from KowWin/HenryWin)					
BIOWIN (v4.10) Program Results:					
=====					
SMILES : c1cc(F)ccc1N(C(C)C)C(=O)COc2nnc(C(F)(F)F)s2					
CHEM : Fluthiamide					
MOL FOR: C14 H13 F4 N3 O2 S1					
MOL WT : 363.33					
----- BIOWIN v4.10 Results -----					
Biowin1 (Linear Model Prediction) : Does Not Biodegrade Fast					
Biowin2 (Non-Linear Model Prediction): Does Not Biodegrade Fast					
Biowin3 (Ultimate Biodegradation Timeframe): Recalcitrant					
Biowin4 (Primary Biodegradation Timeframe): Days-Weeks					
Biowin5 (MITI Linear Model Prediction) : Does Not Biodegrade Fast					
Biowin6 (MITI Non-Linear Model Prediction): Does Not Biodegrade Fast					
Biowin7 (Anaerobic Model Prediction): Does Not Biodegrade Fast					
Ready Biodegradability Prediction: NO					
-----+-----+-----+-----+-----+-----					
TYPE	NUM	Biowin1 FRAGMENT DESCRIPTION		COEFF	VALUE
-----+-----+-----+-----+-----+-----					
Frag	1	Amide	[-C(=O)-N or -C(=S)-N]	0.2102	0.2102
Frag	1	Aromatic fluoride	[-F]	-0.8100	-0.8100

Frag	1	Aromatic ether [-O-aromatic carbon]		0.1319	0.1319
Frag	1	Trifluoromethyl group [-CF3]		-0.5204	-0.5204
MolWt	*	Molecular Weight Parameter			-0.1730
Const	*	Equation Constant		0.7475	
=====					
RESULT		Biowin1 (Linear Biodeg Probability)			-0.4138
=====					
-----+-----+-----+-----+-----					
TYPE	NUM	Biowin2 FRAGMENT DESCRIPTION		COEFF	VALUE
-----+-----+-----+-----+-----					
Frag	1	Amide [-C(=O)-N or -C(=S)-N]		2.6913	2.6913
Frag	1	Aromatic fluoride [-F]		-10.5318	-10.5318
Frag	1	Aromatic ether [-O-aromatic carbon]		2.2483	2.2483
Frag	1	Trifluoromethyl group [-CF3]		-5.6696	-5.6696
MolWt	*	Molecular Weight Parameter			-5.1593
=====					
RESULT		Biowin2 (Non-Linear Biodeg Probability)			0.0000
=====					
A Probability Greater Than or Equal to 0.5 indicates --> Biodegrades Fast					
A Probability Less Than 0.5 indicates --> Does NOT Biodegrade Fast					
-----+-----+-----+-----+-----					
TYPE	NUM	Biowin3 FRAGMENT DESCRIPTION		COEFF	VALUE
-----+-----+-----+-----+-----					
Frag	1	Amide [-C(=O)-N or -C(=S)-N]		-0.0542	-0.0542
Frag	1	Aromatic fluoride [-F]		-0.4069	-0.4069
Frag	1	Aromatic ether [-O-aromatic carbon]		-0.0581	-0.0581
Frag	1	Trifluoromethyl group [-CF3]		-0.5130	-0.5130
MolWt	*	Molecular Weight Parameter			-0.8029
Const	*	Equation Constant		3.1992	
=====					
RESULT		Biowin3 (Survey Model - Ultimate Biodeg)			1.3640
=====					
-----+-----+-----+-----+-----					
TYPE	NUM	Biowin4 FRAGMENT DESCRIPTION		COEFF	VALUE
-----+-----+-----+-----+-----					
Frag	1	Amide [-C(=O)-N or -C(=S)-N]		0.2054	0.2054
Frag	1	Aromatic fluoride [-F]		0.0135	0.0135
Frag	1	Aromatic ether [-O-aromatic carbon]		0.0771	0.0771
Frag	1	Trifluoromethyl group [-CF3]		-0.2744	-0.2744
MolWt	*	Molecular Weight Parameter			-0.5242
Const	*	Equation Constant		3.8477	
=====					
RESULT		Biowin4 (Survey Model - Primary Biodeg)			3.3451
=====					
Result Classification: 5.00 -> hours 4.00 -> days 3.00 -> weeks					
(Primary & Ultimate) 2.00 -> months 1.00 -> longer					
-----+-----+-----+-----+-----					
TYPE	NUM	Biowin5 FRAGMENT DESCRIPTION		COEFF	VALUE
-----+-----+-----+-----+-----					
Frag	1	Amide [-C(=O)-N or -C(=S)-N]		0.1266	0.1266
Frag	1	Aromatic ether [-O-aromatic carbon]		0.1952	0.1952
Frag	4	Fluorine [-F]		0.0174	0.0695
Frag	4	Aromatic-H		0.0082	0.0329
Frag	2	Methyl [-CH3]		0.0004	0.0008
Frag	1	-CH2- [linear]		0.0494	0.0494
Frag	1	-CH- [linear]		-0.0507	-0.0507
MolWt	*	Molecular Weight Parameter			-1.0809
Const	*	Equation Constant		0.7121	
=====					
RESULT		Biowin5 (MITI Linear Biodeg Probability)			0.0550
=====					
-----+-----+-----+-----+-----					
TYPE	NUM	Biowin6 FRAGMENT DESCRIPTION		COEFF	VALUE
-----+-----+-----+-----+-----					
Frag	1	Amide [-C(=O)-N or -C(=S)-N]		0.8859	0.8859
Frag	1	Aromatic ether [-O-aromatic carbon]		1.3227	1.3227
Frag	4	Fluorine [-F]		-3.9878	-15.9514
Frag	4	Aromatic-H		0.1201	0.4806

RESULT	Biowin6 (MITI Non-Linear Biodeg Probability)	0.0000
--------	--	--------

TYPE	NUM	Biowin7 FRAGMENT DESCRIPTION	COEFF	VALUE
------	-----	------------------------------	-------	-------

RESULT	Biowin7 (Anaerobic Linear Biodeg Prob)	-0.2345
--------	--	---------

Ready Biodegradability Prediction: (YES or NO)

BioHCwin (v1.01) Program Results:

----- BioHCwin v1.01 Results -----

NO Estimate Possible ... Structure NOT a Hydrocarbon
(Contains atoms other than C, H or S (-S-))

AEROWIN Program (v1.00) Results:

Sorption to aerosols (25 Dec C)[AEROWIN v1.00]:
 Vapor pressure (liquid/subcooled): 0.000288 Pa (2.16E-006 mm Hg)
 Log Koa (Koawin est): 9.828
 Kp (particle/gas partition coef. (m3/ug)):
 Mackay model : 0.0104
 Octanol/air (Koa) model: 0.00165
 Fraction sorbed to airborne particulates (phi):
 Junge-Pankow model : 0.273
 Mackay model : 0.455
 Octanol/air (Koa) model: 0.117

AOP Program (v1.92) Results:

SMILES : c1cc(F)ccc1N(C(C)C)C(=O)COc2nnc(C(F)(F)F)s2
CHEM : Fluthiamide

MOL FOR: C14 H13 F4 N3 O2 S1

MOL WT : 363.33

----- SUMMARY (AOP v1.92): HYDROXYL RADICALS (25 deg C) -----

Hydrogen Abstraction = 12.5616 E-12 cm³/molecule-secReaction with N, S and -OH = 0.0000 E-12 cm³/molecule-secAddition to Triple Bonds = 0.0000 E-12 cm³/molecule-secAddition to Olefinic Bonds = 0.0000 E-12 cm³/molecule-sec**Addition to Aromatic Rings = 4.8910 E-12 cm³/molecule-secAddition to Fused Rings = 0.0000 E-12 cm³/molecule-secOVERALL OH Rate Constant = 17.4526 E-12 cm³/molecule-secHALF-LIFE = 0.613 Days (12-hr day; 1.5E6 OH/cm³)

HALF-LIFE = 7.354 Hrs

..... ** Designates Estimation(s) Using ASSUMED Value(s)

----- SUMMARY (AOP v1.91): OZONE REACTION (25 deg C) -----

***** NO OZONE REACTION ESTIMATION *****

(ONLY Olefins and Acetylenes are Estimated)

Experimental Database: NO Structure Matches

Fraction sorbed to airborne particulates (phi):

0.364 (Junge-Pankow, Mackay avg)

0.117 (Koa method)

Note: the sorbed fraction may be resistant to atmospheric oxidation

KOCWIN Program (v2.00) Results:

=====

SMILES : c1cc(F)ccc1N(C(C)C)C(=O)COc2nnc(C(F)(F)F)s2

CHEM : Fluthiamide

MOL FOR: C14 H13 F4 N3 O2 S1

MOL WT : 363.33

----- KOCWIN v2.00 Results -----

Koc Estimate from MCI:

First Order Molecular Connectivity Index : 11.181

Non-Corrected Log Koc (0.5213 MCI + 0.60) : 6.4282

Fragment Correction(s):

1 Nitrogen to non-fused aromatic ring ... : -0.5225

1 Ether, aromatic (-C-O-C-) : -0.6791

1 N-CO-C (aliphatic carbon) : -1.0277

1 Nitrogen to Carbon (aliphatic) (-N-C).. : -0.2127

1 Aromatic ring with 2 nitrogens : -0.5964

Corrected Log Koc : 3.3898

Estimated Koc: 2453 L/kg <=====

Koc Estimate from Log Kow:

Log Kow (experimental DB) : 3.20

Non-Corrected Log Koc (0.55313 logKow + 0.9251) : 2.6951

Fragment Correction(s):

1 Nitrogen to non-fused aromatic ring ... : -0.0216

1 Ether, aromatic (-C-O-C-) : 0.0559

1 N-CO-C (aliphatic carbon) : -0.0038

1 Nitrogen to Carbon (aliphatic) (-N-C).. : -0.0218

1 Aromatic ring with 2 nitrogens : 0.3984

Corrected Log Koc : 3.1023

Estimated Koc: 1266 L/kg <=====

HYDROWIN Program (v2.00) Results:

=====

SMILES : c1cc(F)ccc1N(C(C)C)C(=O)COc2nnc(C(F)(F)F)s2

CHEM : Fluthiamide

MOL FOR: C14 H13 F4 N3 O2 S1

MOL WT : 363.33

----- HYDROWIN v2.00 Results -----

Hydrolyzable Function detected: Benzyl Halides

Neutral hydrolysis half-lives of various Benzyl Halides (25 deg C)

(Mabey and Mill, 1978; Laidler and Martin, 1969):

Benzyl chloride: 15 hrs

p-CH₃ Benzyl chloride: 0.43 hrs

p-CL Benzyl chloride: about 30 hrs
 p-NO2 Benzyl chloride: about 150-200 hrs
 Benzyl bromide: 1.32 hrs
 p-CH3 Benzyl bromide: 4.3 min
 Benzyl dichloride: 0.1 hrs
 Benzyl trichloride: 19 sec

Ring substituents that may slow the hydrolysis rate:
 include CL, Br, I, NO2, cyano

BCFBAF Program (v3.01) Results:

SMILES : c1cc(F)ccc1N(C(C)C)C(=O)COc2nnc(C(F)(F)F)s2

CHEM : Fluthiamide

MOL FOR: C14 H13 F4 N3 O2 S1

MOL WT : 363.33

----- BCFBAF v3.01 -----

Summary Results:

Log BCF (regression-based estimate): 1.78 (BCF = 60 L/kg wet-wt)
 Biotransformation Half-Life (days) : 0.533 (normalized to 10 g fish)
 Log BAF (Arnot-Gobas upper trophic): 1.98 (BAF = 95.3 L/kg wet-wt)

Log Kow (experimental): 3.20

Log Kow used by BCF estimates: 3.20

Equation Used to Make BCF estimate:

Log BCF = 0.6598 log Kow - 0.333 + Correction

Correction(s): Value
 No Applicable Correction Factors

Estimated Log BCF = 1.778 (BCF = 60.03 L/kg wet-wt)

Whole Body Primary Biotransformation Rate Estimate for Fish:

TYPE	NUM	LOG BIOTRANSFORMATION	FRAGMENT DESCRIPTION	COEFF	VALUE
Frag	1	Amide [-C(=O)-N or -C(=S)-N]		-0.5952	-0.5952
Frag	1	Aromatic fluoride [-F]		0.0000	0.0000
Frag	1	Aromatic ether [-O-aromatic carbon]		-0.0694	-0.0694
Frag	1	Trifluoromethyl group [-CF3]		-0.1881	-0.1881
Frag	4	Fluorine [-F]		0.2759	1.1035
Frag	4	Aromatic-H		0.2664	1.0655
Frag	2	Methyl [-CH3]		0.2451	0.4902
Frag	1	-CH2- [linear]		0.0242	0.0242
Frag	1	-CH- [linear]		-0.1912	-0.1912
Frag	1	Aromatic Sulfur		0.0000	0.0000
Frag	1	Benzene		-0.4277	-0.4277
L Kow	*	Log Kow = 3.20 (experimental)		0.3073	0.9835
MolWt	*	Molecular Weight Parameter			-0.9317
Const	*	Equation Constant			-1.5371
RESULT		LOG Bio Half-Life (days)			-0.2736
RESULT		Bio Half-Life (days)			0.5326
NOTE		Bio Half-Life Normalized to 10 g fish at 15 deg C			

Biotransformation Rate Constant:

kM (Rate Constant): 1.301 /day (10 gram fish)
 kM (Rate Constant): 0.7319 /day (100 gram fish)
 kM (Rate Constant): 0.4116 /day (1 kg fish)
 kM (Rate Constant): 0.2314 /day (10 kg fish)

Arnot-Gobas BCF & BAF Methods (including biotransformation rate estimates):

Estimated Log BCF (upper trophic) = 1.979 (BCF = 95.26 L/kg wet-wt)
 Estimated Log BAF (upper trophic) = 1.979 (BAF = 95.26 L/kg wet-wt)
 Estimated Log BCF (mid trophic) = 1.904 (BCF = 80.11 L/kg wet-wt)
 Estimated Log BAF (mid trophic) = 1.904 (BAF = 80.16 L/kg wet-wt)
 Estimated Log BCF (lower trophic) = 1.870 (BCF = 74.19 L/kg wet-wt)
 Estimated Log BAF (lower trophic) = 1.872 (BAF = 74.46 L/kg wet-wt)

Arnot-Gobas BCF & BAF Methods (assuming a biotransformation rate of zero):

Estimated Log BCF (upper trophic) = 2.229 (BCF = 169.5 L/kg wet-wt)
 Estimated Log BAF (upper trophic) = 2.313 (BAF = 205.6 L/kg wet-wt)

Volatilization From Water

Chemical Name: Fluthiamide

Molecular Weight : 363.33 g/mole

Water Solubility : -----

Vapor Pressure : -----

Henry's Law Constant: 5.76E-009 atm-m3/mole (Henry experimental database)

	RIVER	LAKE
	-----	-----
Water Depth (meters):	1	1
Wind Velocity (m/sec):	3	0.5
Current Velocity (m/sec):	1	0.05
HALF-LIFE (hours):	2.906E+005	2.114E+006
HALF-LIFE (days):	1.211E+004	8.808E+004
HALF-LIFE (years):	33.15	241.1

STP Fugacity Model: Predicted Fate in a Wastewater Treatment Facility

(using 10000 hr Bio P,A,S)

PROPERTIES OF: Fluthiamide

Molecular weight (g/mol)		363.33
Aqueous solubility (mg/l)		0
Vapour pressure (Pa)		0
(atm)		0
(mm Hg)		0
Henry's law constant (Atm-m3/mol)		5.76E-009
Air-water partition coefficient		2.35567E-007
Octanol-water partition coefficient (Kow)		1584.89
Log Kow		3.2
Biomass to water partition coefficient		317.779
Temperature [deg C]		25
Biodeg rate constants (h^-1), half life in biomass (h) and in 2000 mg/L MLSS (h):		
-Primary tank	0.00	3885.88 10000.00
-Aeration tank	0.00	3885.88 10000.00
-Settling tank	0.00	3885.88 10000.00

STP Overall Chemical Mass Balance:

	g/h	mol/h	percent
Influent	1.00E+001	2.8E-002	100.00
Primary sludge	3.81E-001	1.0E-003	3.81
Waste sludge	3.85E-001	1.1E-003	3.85
Primary volatilization	2.95E-006	8.1E-009	0.00
Settling volatilization	8.00E-006	2.2E-008	0.00
Aeration off gas	1.97E-005	5.4E-008	0.00
Primary biodegradation	2.70E-003	7.4E-006	0.03
Settling biodegradation	8.04E-004	2.2E-006	0.01
Aeration biodegradation	1.06E-002	2.9E-005	0.11
Final water effluent	9.22E+000	2.5E-002	92.20
Total removal	7.80E-001	2.1E-003	7.80
Total biodegradation	1.41E-002	3.9E-005	0.14

Level III Fugacity Model (Full-Output):

Chem Name : Fluthiamide
 Molecular Wt: 363.33
 Henry's LC : 5.76e-009 atm-m3/mole (Henry database)
 Vapor Press : 4.22e-007 mm Hg (Mpbwin program)
 Liquid VP : 1.49e-005 mm Hg (super-cooled)

Melting Pt : 181 deg C (Mpbwin program)
 Log Kow : 3.2 (Kowwin program)
 Soil Koc : 2.45e+003 (KOCWIN MCI method)

	Mass Amount (percent)	Half-Life (hr)	Emissions (kg/hr)
Air	0.00966	14.7	1000
Water	4.5	4.32e+003	1000
Soil	94.4	8.64e+003	1000
Sediment	1.06	3.89e+004	0

	Fugacity (atm)	Reaction (kg/hr)	Advection (kg/hr)	Reaction (percent)	Advection (percent)
Air	1.37e-012	102	21.6	3.4	0.721
Water	7.97e-014	162	1.01e+003	5.39	33.6
Soil	3.15e-013	1.7e+003	0	56.6	0
Sediment	1.57e-013	4.22	4.74	0.141	0.158

Persistence Time: 7.47e+003 hr
 Reaction Time: 1.14e+004 hr
 Advection Time: 2.16e+004 hr
 Percent Reacted: 65.5
 Percent Advected: 34.5

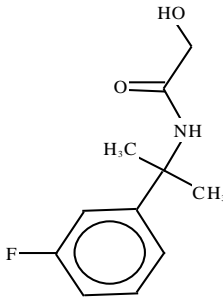
Half-Lives (hr), (based upon Biowin (Ultimate) and Aopwin):

Air: 14.71
 Water: 4320
 Soil: 8640
 Sediment: 3.888e+004
 Biowin estimate: 1.364 (recalcitrant)

Advection Times (hr):

Air: 100
 Water: 1000
 Sediment: 5e+004

Table B.8.8-A.3_CA-2: The detailed results of QSAR calculations for FOE Alcohol.

Compound: FOE Alcohol	Structural formula: 
Results of calculations: SMILES : c1ccc(F)cc1C(C)(C)NC(=O)CO CHEM : (FOE Alcohol) MOL FOR: C11 H14 F1 N1 O2 MOL WT : 211.24 ----- EPI SUMMARY (v4.10) ----- Physical Property Inputs: Water Solubility (mg/L): ----- Vapor Pressure (mm Hg) : ----- Henry LC (atm-m3/mole) : ----- Log Kow (octanol-water): ----- Boiling Point (deg C) : ----- Melting Point (deg C) : -----	

KOWWIN Program (v1.68) Results:

=====

Log Kow(version 1.68 estimate): 1.52

SMILES : c1ccc(F)cc1C(C)(C)NC(=O)CO

CHEM :

MOL FOR: C11 H14 F1 N1 O2

MOL WT : 211.24

TYPE	NUM	LOGKOW FRAGMENT DESCRIPTION	COEFF	VALUE
Frag	2	-CH3 [aliphatic carbon]	0.5473	1.0946
Frag	1	-CH2- [aliphatic carbon]	0.4911	0.4911
Frag	1	-OH [hydroxy, aliphatic attach]	-1.4086	-1.4086
Frag	1	-NH- [aliphatic attach]	-1.4962	-1.4962
Frag	6	Aromatic Carbon	0.2940	1.7640
Frag	1	-F [fluorine, aromatic attach]	0.2004	0.2004
Frag	1	-C(=O)N [aliphatic attach]	-0.5236	-0.5236
Frag	1	-tert Carbon [3 or more carbon attach]	0.2676	0.2676
Factor	1	-N-CO-CH2-OH structure correction	0.9000**	0.9000
Const		Equation Constant		0.2290

NOTE | | An estimated coefficient (**) used |

Log Kow = 1.5183

MPBPWIN (v1.43) Program Results:

=====

Experimental Database Structure Match: no data

SMILES : c1ccc(F)cc1C(C)(C)NC(=O)CO

CHEM :

MOL FOR: C11 H14 F1 N1 O2

MOL WT : 211.24

----- SUMMARY MPBPWIN v1.43 -----

Boiling Point: 369.94 deg C (Adapted Stein and Brown Method)

Melting Point: 257.07 deg C (Adapted Joback Method)

Melting Point: 102.35 deg C (Gold and Ogle Method)

Mean Melt Pt : 179.71 deg C (Joback; Gold; Ogle Methods)

Selected MP: 133.29 deg C (Weighted Value)

Vapor Pressure Estimations (25 deg C):

(Using BP: 369.94 deg C (estimated))

(Using MP: 133.29 deg C (estimated))

VP: 3.24E-008 mm Hg (Antoine Method)

: 4.32E-006 Pa (Antoine Method)

VP: 1.14E-007 mm Hg (Modified Grain Method)

: 1.52E-005 Pa (Modified Grain Method)

VP: 7.54E-006 mm Hg (Mackay Method)

: 0.00101 Pa (Mackay Method)

Selected VP: 1.14E-007 mm Hg (Modified Grain Method)

: 1.52E-005 Pa (Modified Grain Method)

Subcooled liquid VP: 1.39E-006 mm Hg (25 deg C, Mod-Grain method)

: 0.000186 Pa (25 deg C, Mod-Grain method)

TYPE	NUM	BOIL DESCRIPTION	COEFF	VALUE
Group	2	-CH3	21.98	43.96
Group	1	-CH2-	24.22	24.22
Group	1	>C<	4.50	4.50
Group	4	CH (aromatic)	28.53	114.12
Group	2	-C (aromatic)	30.76	61.52
Group	1	-OH (primary)	88.46	88.46
Group	1	-C(=O)NH-	225.09	225.09
Group	1	-F (to aromat)	-7.81	-7.81
*		Equation Constant		198.18

RESULT-uncorr| BOILING POINT in deg Kelvin | 752.24

ECOSAR Program (v1.11) Results:

=====

ECOSAR Version 1.11 Results Page

SMILES : c1ccc(F)cc1C(C)(C)NC(=O)CO

CHEM :

CAS Num:

ChemID1:

MOL FOR: C11 H14 F1 N1 O2

MOL WT : 211.24

Log Kow: 1.518 (EPISuite Kowwin v1.68 Estimate)

Log Kow: (User Entered)

Log Kow: (PhysProp DB exp value - for comparison only)

Melt Pt: (User Entered for Wat Sol estimate)

Melt Pt: (deg C, PhysProp DB exp value for Wat Sol estimate)

Wat Sol: 1933 (mg/L, EPISuite WSKowwin v1.43 Estimate)

Wat Sol: (User Entered)

Wat Sol: (PhysProp DB exp value)

Values used to Generate ECOSAR Profile

Log Kow: 1.518 (EPISuite Kowwin v1.68 Estimate)

Wat Sol: 1933 (mg/L, EPISuite WSKowwin v1.43 Estimate)

ECOSAR v1.11 Class-specific Estimations

Amides

ECOSAR Class		Organism	Predicted		Duration	End Pt	mg/L (ppm)
Amides	: Fish		96-hr	LC50			139.488
Amides	: Daphnid		48-hr	LC50			191.745
Amides	: Green Algae		96-hr	EC50			3.954
Amides	: Fish			ChV			0.180
Amides	: Daphnid			ChV			7.826
Amides	: Green Algae			ChV			3.031
Amides	: Fish (SW)		96-hr	LC50			122.607
Amides	: Mysid (SW)		96-hr	LC50			6.661

Neutral Organic SAR	: Fish	96-hr	LC50	469.880
(Baseline Toxicity)	: Daphnid	48-hr	LC50	255.194
	: Green Algae	96-hr	EC50	158.163
	: Fish		ChV	43.582
	: Daphnid		ChV	21.989
	: Green Algae		ChV	37.514

Note: * = asterisk designates: Chemical may not be soluble enough to measure this predicted effect. If the effect level exceeds the water solubility by 10X, typically no effects at saturation (NES) are reported.

Class Specific LogKow Cut-Offs

If the log Kow of the chemical is greater than the endpoint specific cut-offs presented below, then no effects at saturation are expected for those endpoints.

Amides :

Maximum LogKow: >8.5 (LC50)

Maximum LogKow: >8.0 (EC50,ChV)

Baseline Toxicity SAR Limitations:

Maximum LogKow: 5.0 (Fish 96-hr LC50; Daphnid LC50)

Maximum LogKow: 6.4 (Green Algae EC50)

Maximum LogKow: 8.0 (ChV)

HENRY (v3.20) Program Results:

Bond Est : 6.36E-010 atm-m3/mole (6.44E-005 Pa-m3/mole)
 Group Est: Incomplete

SMILES : c1ccc(F)cc1C(C)(C)NC(=O)CO

CHEM :

MOL FOR: C11 H14 F1 N1 O2

MOL WT : 211.24

----- HENRYWIN v3.20 Results -----

CLASS	BOND CONTRIBUTION DESCRIPTION	COMMENT	VALUE
HYDROGEN	8 Hydrogen to Carbon (aliphatic) Bonds		-0.9574
HYDROGEN	4 Hydrogen to Carbon (aromatic) Bonds		-0.6172
HYDROGEN	1 Hydrogen to Oxygen Bonds		3.2318
HYDROGEN	1 Hydrogen to Nitrogen Bonds		1.2835
FRAGMENT	2 C-C		0.2326
FRAGMENT	1 C-Car		0.1619
FRAGMENT	1 C-CO		1.7057
FRAGMENT	1 C-N		1.3010
FRAGMENT	1 C-O		1.0855
FRAGMENT	6 Car-Car		1.5828
FRAGMENT	1 CO-N		2.4261
FRAGMENT	1 Car-F		-0.2214
FACTOR	1 -C(=O)-C-OH group		-3.6300
RESULT	BOND ESTIMATION METHOD for LWAPC	VALUE	TOTAL 7.585

HENRYs LAW CONSTANT at 25 deg C = 6.36E-010 atm-m3/mole
 = 2.60E-008 unitless
 = 6.44E-005 Pa-m3/mole

	GROUP CONTRIBUTION DESCRIPTION	COMMENT	VALUE
	1 CH2 (CO)(O)	ESTIMATE	-1.40
	2 CH3 (X)		-1.24
	4 Car-H (Car)(Car)		0.44
	1 Car (C)(Car)(Car)		0.70
	1 O-H (C)		4.45
	1 Car (Car)(Car)(F)	ESTIMATE	-0.34
	MISSING Value for: C (C)(C)(N)(Car)		
	MISSING Value for: NH (CO)(C)		
	MISSING Value for: CO (C)(N)		
RESULT	GROUP ESTIMATION METHOD for LOG GAMMA	VALUE	INCOMPLETE 2.61

For Henry LC Comparison Purposes:

Exper Database: none available

User-Entered Henry LC: not entered

Henrys LC [via VP/WSol estimate using User-Entered or Estimated values]:

HLC: 1.639E-011 atm-m3/mole (1.661E-006 Pa-m3/mole)

VP: 1.14E-007 mm Hg (source: MPBPVP)

WS: 1.93E+003 mg/L (source: WSKOWWIN)

Log Octanol-Air (KOAWIN v1.10) Results:

Log Koa: 9.105

SMILES : c1ccc(F)cc1C(C)(C)NC(=O)CO

CHEM :

MOL FOR: C11 H14 F1 N1 O2

MOL WT : 211.24

----- KOAWIN v1.10 Results -----

Log Koa (octanol/air) estimate: 9.105

Koa (octanol/air) estimate: 1.274e+009

Using:

Log Kow: 1.52 (KowWin est)
 HenryLC: 6.36e-010 atm-m3/mole (HenryWin est)
 Log Kaw: -7.585 (air/water part.coef.)

LogKow : --- (exp database)
 LogKow : 1.52 (KowWin estimate)
 Henry LC: --- atm-m3/mole(exp database)
 Henry LC: 6.36e-010 atm-m3/mole (HenryWin bond estimate)

Log Koa (octanol/air) estimate: 9.105 (from KowWin/HenryWin)

BIOWIN (v4.10) Program Results:

=====

SMILES : c1ccc(F)cc1C(C)(C)NC(=O)CO
 CHEM :
 MOL FOR: C11 H14 F1 N1 O2
 MOL WT : 211.24

----- BIOWIN v4.10 Results -----

Biowin1 (Linear Model Prediction) : Does Not Biodegrade Fast
 Biowin2 (Non-Linear Model Prediction): Does Not Biodegrade Fast
 Biowin3 (Ultimate Biodegradation Timeframe): Months
 Biowin4 (Primary Biodegradation Timeframe): Days-Weeks
 Biowin5 (MITI Linear Model Prediction) : Biodegrades Fast
 Biowin6 (MITI Non-Linear Model Prediction): Does Not Biodegrade Fast
 Biowin7 (Anaerobic Model Prediction): Does Not Biodegrade Fast
 Ready Biodegradability Prediction: NO

TYPE	NUM	Biowin1 FRAGMENT DESCRIPTION	COEFF	VALUE
Frag	1	Aliphatic alcohol [-OH]	0.1587	0.1587
Frag	1	Amide [-C(=O)-N or -C(=S)-N]	0.2102	0.2102
Frag	1	Aromatic fluoride [-F]	-0.8100	-0.8100
Frag	1	Carbon with 4 single bonds & no hydrogens	-0.1839	-0.1839
MolWt	*	Molecular Weight Parameter		-0.1006
Const	*	Equation Constant		0.7475
=====				
RESULT		Biowin1 (Linear Biodeg Probability)		0.0219
=====				

TYPE	NUM	Biowin2 FRAGMENT DESCRIPTION	COEFF	VALUE
Frag	1	Aliphatic alcohol [-OH]	1.1178	1.1178
Frag	1	Amide [-C(=O)-N or -C(=S)-N]	2.6913	2.6913
Frag	1	Aromatic fluoride [-F]	-10.5318	-10.5318
Frag	1	Carbon with 4 single bonds & no hydrogens	-1.7232	-1.7232
MolWt	*	Molecular Weight Parameter		-2.9996
=====				
RESULT		Biowin2 (Non-Linear Biodeg Probability)		0.0002
=====				

A Probability Greater Than or Equal to 0.5 indicates --> Biodegrades Fast
 A Probability Less Than 0.5 indicates --> Does NOT Biodegrade Fast

TYPE	NUM	Biowin3 FRAGMENT DESCRIPTION	COEFF	VALUE
Frag	1	Aliphatic alcohol [-OH]	0.1600	0.1600
Frag	1	Amide [-C(=O)-N or -C(=S)-N]	-0.0542	-0.0542
Frag	1	Aromatic fluoride [-F]	-0.4069	-0.4069
Frag	1	Carbon with 4 single bonds & no hydrogens	-0.2121	-0.2121
MolWt	*	Molecular Weight Parameter		-0.4668
Const	*	Equation Constant		3.1992
=====				
RESULT		Biowin3 (Survey Model - Ultimate Biodeg)		2.2191
=====				

TYPE	NUM	Biowin4 FRAGMENT DESCRIPTION	COEFF	VALUE
Frag	1	Aliphatic alcohol [-OH]	0.1294	0.1294
Frag	1	Amide [-C(=O)-N or -C(=S)-N]	0.2054	0.2054

```

Frag | 1 | Aromatic fluoride [-F] | 0.0135 | 0.0135
Frag | 1 | Carbon with 4 single bonds & no hydrogens | -0.1534 | -0.1534
MolWt | * | Molecular Weight Parameter | | -0.3048
Const | * | Equation Constant | | 3.8477

```

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=====
RESULT | Biowin4 (Survey Model - Primary Biodeg) | | 3.7379
=====

```

Result Classification: 5.00 -> hours 4.00 -> days 3.00 -> weeks
(Primary & Ultimate) 2.00 -> months 1.00 -> longer

```

-----+-----+-----+-----+-----+
TYPE | NUM | Biowin5 FRAGMENT DESCRIPTION | COEFF | VALUE
-----+-----+-----+-----+-----+

```

```

Frag | 1 | Aliphatic alcohol [-OH] | 0.1611 | 0.1611
Frag | 1 | Amide [-C(=O)-N or -C(=S)-N] | 0.1266 | 0.1266
Frag | 1 | Carbon with 4 single bonds & no hydrogens | 0.0676 | 0.0676
Frag | 1 | Fluorine [-F] | 0.0174 | 0.0174
Frag | 4 | Aromatic-H | 0.0082 | 0.0329
Frag | 2 | Methyl [-CH3] | 0.0004 | 0.0008
Frag | 1 | -CH2- [linear] | 0.0494 | 0.0494
MolWt | * | Molecular Weight Parameter | | -0.6284
Const | * | Equation Constant | | 0.7121

```

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=====
RESULT | Biowin5 (MITI Linear Biodeg Probability) | | 0.5396
=====

```

```

-----+-----+-----+-----+-----+
TYPE | NUM | Biowin6 FRAGMENT DESCRIPTION | COEFF | VALUE
-----+-----+-----+-----+-----+

```

```

Frag | 1 | Aliphatic alcohol [-OH] | 1.0041 | 1.0041
Frag | 1 | Amide [-C(=O)-N or -C(=S)-N] | 0.8859 | 0.8859
Frag | 1 | Carbon with 4 single bonds & no hydrogens | 0.3990 | 0.3990
Frag | 1 | Fluorine [-F] | -3.9878 | -3.9878
Frag | 4 | Aromatic-H | 0.1201 | 0.4806
Frag | 2 | Methyl [-CH3] | 0.0194 | 0.0389
Frag | 1 | -CH2- [linear] | 0.4295 | 0.4295
MolWt | * | Molecular Weight Parameter | | -6.0982

```

```

=====
RESULT | Biowin6 (MITI Non-Linear Biodeg Probability) | | 0.0131
=====

```

A Probability Greater Than or Equal to 0.5 indicates --> Readily Degradable
A Probability Less Than 0.5 indicates --> NOT Readily Degradable

```

-----+-----+-----+-----+-----+
TYPE | NUM | Biowin7 FRAGMENT DESCRIPTION | COEFF | VALUE
-----+-----+-----+-----+-----+

```

```

Frag | 1 | Aliphatic alcohol [-OH] | 0.1328 | 0.1328
Frag | 1 | Amide [-C(=O)-N or -C(=S)-N] | -0.5679 | -0.5679
Frag | 1 | Aromatic fluoride [-F] | 0.0000 | 0.0000
Frag | 1 | Carbon with 4 single bonds & no hydrogens | -0.3342 | -0.3342
Frag | 1 | Fluorine [-F] | 0.0000 | 0.0000
Frag | 4 | Aromatic-H | -0.0954 | -0.3817
Frag | 2 | Methyl [-CH3] | -0.0796 | -0.1591
Frag | 1 | -CH2- [linear] | 0.0260 | 0.0260
Const | * | Equation Constant | | 0.8361

```

```

=====
RESULT | Biowin7 (Anaerobic Linear Biodeg Prob) | | -0.4481
=====

```

A Probability Greater Than or Equal to 0.5 indicates --> Biodegrades Fast
A Probability Less Than 0.5 indicates --> Does NOT Biodegrade Fast

Ready Biodegradability Prediction: (YES or NO)

Criteria for the YES or NO prediction: If the Biowin3 (ultimate survey model) result is "weeks" or faster (i.e. "days", "days to weeks", or "weeks" AND the Biowin5 (MITI linear model) probability is ≥ 0.5 , then the prediction is YES (readily biodegradable). If this condition is not satisfied, the prediction is NO (not readily biodegradable). This method is based on application of Bayesian analysis to ready biodegradation data (see Help). Biowin5 and 6 also predict ready biodegradability, but for degradation in the OECD301C test only; using data from the Chemicals

Evaluation and Research Institute Japan (CERIJ) database.

BioHCwin (v1.01) Program Results:

SMILES : c1ccc(F)cc1C(C)(C)NC(=O)CO

CHEM :

MOL FOR: C11 H14 F1 N1 O2

MOL WT : 211.24

----- BioHCwin v1.01 Results -----

NO Estimate Possible ... Structure NOT a Hydrocarbon
(Contains atoms other than C, H or S (-S-))

AEROWIN Program (v1.00) Results:

=====

Sorption to aerosols (25 Dec C)[AEROWIN v1.00]:

Vapor pressure (liquid/subcooled): 0.000185 Pa (1.39E-006 mm Hg)

Log Koa (Koawin est) : 9.105

Kp (particle/gas partition coef. (m3/ug)):

Mackay model : 0.0162

Octanol/air (Koa) model: 0.000313

Fraction sorbed to airborne particulates (phi):

Junge-Pankow model : 0.369

Mackay model : 0.564

Octanol/air (Koa) model: 0.0244

AOP Program (v1.92) Results:

=====

SMILES : c1ccc(F)cc1C(C)(C)NC(=O)CO

CHEM :

MOL FOR: C11 H14 F1 N1 O2

MOL WT : 211.24

----- SUMMARY (AOP v1.92): HYDROXYL RADICALS (25 deg C) -----

Hydrogen Abstraction = 2.7863 E-12 cm3/molecule-sec

Reaction with N, S and -OH = 5.6400 E-12 cm3/molecule-sec

Addition to Triple Bonds = 0.0000 E-12 cm3/molecule-sec

Addition to Olefinic Bonds = 0.0000 E-12 cm3/molecule-sec

**Addition to Aromatic Rings = 5.3810 E-12 cm3/molecule-sec

Addition to Fused Rings = 0.0000 E-12 cm3/molecule-sec

OVERALL OH Rate Constant = 13.8073 E-12 cm3/molecule-sec

HALF-LIFE = 0.775 Days (12-hr day; 1.5E6 OH/cm3)

HALF-LIFE = 9.296 Hrs

***** ** Designates Estimation(s) Using ASSUMED Value(s)

----- SUMMARY (AOP v1.91): OZONE REACTION (25 deg C) -----

***** NO OZONE REACTION ESTIMATION *****
(ONLY Olefins and Acetylenes are Estimated)

Experimental Database: NO Structure Matches

Fraction sorbed to airborne particulates (phi):

0.467 (Junge-Pankow, Mackay avg)

0.0244 (Koa method)

Note: the sorbed fraction may be resistant to atmospheric oxidation

KOCWIN Program (v2.00) Results:

=====

SMILES : c1ccc(F)cc1C(C)(C)NC(=O)CO

CHEM :

MOL FOR: C11 H14 F1 N1 O2

MOL WT : 211.24

----- KOCWIN v2.00 Results -----

Koc Estimate from MCI:

First Order Molecular Connectivity Index : 6.954

Non-Corrected Log Koc (0.5213 MCI + 0.60) : 4.2247

Fragment Correction(s):

1 N-CO-C (aliphatic carbon) : -1.0277

1 Nitrogen to Carbon (aliphatic) (-N-C).. : -0.2127

1 Aliphatic Alcohol (-C-OH) : -1.3179
 Corrected Log Koc : 1.6663

Estimated Koc: 46.38 L/kg <=====

Koc Estimate from Log Kow:

 Log Kow (Kowwin estimate) : 1.52
 Non-Corrected Log Koc (0.55313 logKow + 0.9251) : 1.7659
 Fragment Correction(s):
 1 N-CO-C (aliphatic carbon) : -0.0038
 1 Nitrogen to Carbon (aliphatic) (-N-C).. : -0.0218
 1 Aliphatic Alcohol (-C-OH) : -0.4114
 Corrected Log Koc : 1.3288

Estimated Koc: 21.32 L/kg <=====

HYDROWIN Program (v2.00) Results:

=====

SMILES : c1ccc(F)cc1C(C)(C)NC(=O)CO

CHEM :

MOL FOR: C11 H14 F1 N1 O2

MOL WT : 211.24

----- HYDROWIN v2.00 Results -----

Hydrolyzable Function detected: Amides

-C-C(=O)-N-C-

With the exception of a few halogenated acetamides, most amides hydrolyze to acids extremely slowly at 25 degC and pH7 with half-lives measured in centuries. Electronegative groups on carbon or nitrogen greatly accelerate base catalyzed hydrolysis, but alkyl groups on nitrogen retard both acid and base catalyzed processes. No neutral hydrolysis is evident (Mabey and Mill, 1978). Selected amides half-lives include:

Half-Live (in years at 25C, pH7)

Acetamide	3950
Chloroacetamide	1.46
Dichloroacetamide	0.73
Trichloroacetamide	0.23
N-Methylacetamide	38000

Additional experimental amide data are available in the HYDRO on-line User Guide (help file).

BCFBAF Program (v3.01) Results:

=====

SMILES : c1ccc(F)cc1C(C)(C)NC(=O)CO

CHEM :

MOL FOR: C11 H14 F1 N1 O2

MOL WT : 211.24

----- BCFBAF v3.01 -----

Summary Results:

Log BCF (regression-based estimate): 0.41 (BCF = 2.59 L/kg wet-wt)
 Biotransformation Half-Life (days) : 0.0726 (normalized to 10 g fish)
 Log BAF (Arnot-Gobas upper trophic): 0.52 (BAF = 3.31 L/kg wet-wt)

Log Kow (experimental): not available from database

Log Kow used by BCF estimates: 1.52

Equation Used to Make BCF estimate:

Log BCF = 0.6598 log Kow - 0.333 + Correction

Correction(s):	Value
Aromatic ring-CH-OH	-0.256

Estimated Log BCF = 0.413 (BCF = 2.589 L/kg wet-wt)

=====

Whole Body Primary Biotransformation Rate Estimate for Fish:

=====

TYPE	NUM	LOG BIOTRANSFORMATION FRAGMENT DESCRIPTION	COEFF	VALUE
------	-----	--	-------	-------

Frag	1	Aliphatic alcohol [-OH]		-0.0616	-0.0616
Frag	1	Amide [-C(=O)-N or -C(=S)-N]		-0.5952	-0.5952
Frag	1	Aromatic fluoride [-F]		0.0000	0.0000
Frag	1	Carbon with 4 single bonds & no hydrogens		-0.2984	-0.2984
Frag	1	Fluorine [-F]		0.2759	0.2759
Frag	4	Aromatic-H		0.2664	1.0655
Frag	2	Methyl [-CH3]		0.2451	0.4902
Frag	1	-CH2- [linear]		0.0242	0.0242
Frag	1	Benzene		-0.4277	-0.4277
L Kow	*	Log Kow = 1.52 (KowWin estimate)		0.3073	0.4666
MolWt	*	Molecular Weight Parameter			-0.5417
Const	*	Equation Constant			-1.5371
=====					
RESULT		LOG Bio Half-Life (days)			-1.1393
RESULT		Bio Half-Life (days)			0.07257
NOTE		Bio Half-Life Normalized to 10 g fish at 15 deg C			
=====					

Biotransformation Rate Constant:

kM (Rate Constant): 9.552 /day (10 gram fish)
 kM (Rate Constant): 5.371 /day (100 gram fish)
 kM (Rate Constant): 3.021 /day (1 kg fish)
 kM (Rate Constant): 1.699 /day (10 kg fish)

Arnot-Gobas BCF & BAF Methods (including biotransformation rate estimates):

Estimated Log BCF (upper trophic) = 0.520 (BCF = 3.313 L/kg wet-wt)
 Estimated Log BAF (upper trophic) = 0.520 (BAF = 3.313 L/kg wet-wt)
 Estimated Log BCF (mid trophic) = 0.446 (BCF = 2.793 L/kg wet-wt)
 Estimated Log BAF (mid trophic) = 0.446 (BAF = 2.793 L/kg wet-wt)
 Estimated Log BCF (lower trophic) = 0.420 (BCF = 2.627 L/kg wet-wt)
 Estimated Log BAF (lower trophic) = 0.420 (BAF = 2.627 L/kg wet-wt)

Arnot-Gobas BCF & BAF Methods (assuming a biotransformation rate of zero):

Estimated Log BCF (upper trophic) = 0.645 (BCF = 4.421 L/kg wet-wt)
 Estimated Log BAF (upper trophic) = 0.651 (BAF = 4.48 L/kg wet-wt)

Volatilization From Water

Chemical Name:

Molecular Weight : 211.24 g/mole

Water Solubility : ----

Vapor Pressure : ----

Henry's Law Constant: 6.36E-010 atm-m³/mole (estimated by Bond SAR Method)

	RIVER	LAKE
	-----	-----
Water Depth (meters):	1	1
Wind Velocity (m/sec):	3	0.5
Current Velocity (m/sec):	1	0.05
HALF-LIFE (hours) :	2.007E+006	1.46E+007
HALF-LIFE (days) :	8.362E+004	6.082E+005
HALF-LIFE (years) :	228.9	1665

STP Fugacity Model: Predicted Fate in a Wastewater Treatment Facility

(using 10000 hr Bio P,A,S)

PROPERTIES OF:

Molecular weight (g/mol)	211.24
Aqueous solubility (mg/l)	0
Vapour pressure (Pa)	0
(atm)	0
(mm Hg)	0
Henry's law constant (Atm-m ³ /mol)	6.36E-010
Air-water partition coefficient	2.60105E-008
Octanol-water partition coefficient (Kow)	33.1131
Log Kow	1.52
Biomass to water partition coefficient	7.42262
Temperature [deg C]	25

Biodeg rate constants (h^{-1}), half life in biomass (h) and in 2000 mg/L MLSS (h):

-Primary tank	0.00	146.28	10000.00
-Aeration tank	0.00	146.28	10000.00
-Settling tank	0.00	146.28	10000.00

STP Overall Chemical Mass Balance:

	g/h	mol/h	percent
Influent	1.00E+001	4.7E-002	100.00
Primary sludge	3.29E-002	1.6E-004	0.33
Waste sludge	1.56E-001	7.4E-004	1.56
Primary volatilization	3.46E-007	1.6E-009	0.00
Settling volatilization	9.43E-007	4.5E-009	0.00
Aeration off gas	2.32E-006	1.1E-008	0.00
Primary biodegradation	1.78E-003	8.4E-006	0.02
Settling biodegradation	5.33E-004	2.5E-006	0.01
Aeration biodegradation	7.02E-003	3.3E-005	0.07
Final water effluent	9.80E+000	4.6E-002	98.02
Total removal	1.98E-001	9.4E-004	1.98
Total biodegradation	9.33E-003	4.4E-005	0.09

Level III Fugacity Model (Full-Output):

Chem Name :
Molecular Wt: 211.24
Henry's LC : 6.36e-010 atm-m³/mole (Henrywin program)
Vapor Press : 1.14e-007 mm Hg (Mpbpwin program)
Liquid VP : 1.34e-006 mm Hg (super-cooled)
Melting Pt : 133 deg C (Mpbpwin program)
Log Kow : 1.52 (Kowwin program)
Soil Koc : 46.4 (KOCWIN MCI method)

	Mass Amount (percent)	Half-Life (hr)	Emissions (kg/hr)
Air	0.00733	18.6	1000
Water	22.1	1.44e+003	1000
Soil	77.8	2.88e+003	1000
Sediment	0.0932	1.3e+004	0

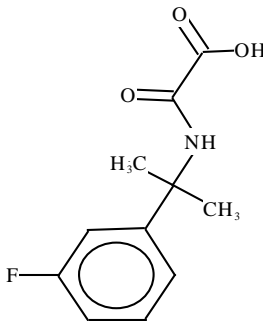
	Fugacity (atm)	Reaction (kg/hr)	Advection (kg/hr)	Reaction (percent)	Advection (percent)
Air	2.94e-013	15.8	4.24	0.527	0.141
Water	1.93e-014	616	1.28e+003	20.5	42.7
Soil	5.33e-013	1.08e+003	0	36.1	0
Sediment	1.92e-014	0.289	0.108	0.00962	0.0036

Persistence Time: 1.93e+003 hr
Reaction Time: 3.37e+003 hr
Advection Time: 4.51e+003 hr
Percent Reacted: 57.2
Percent Advected: 42.8

Half-Lives (hr), (based upon Biowin (Ultimate) and Aopwin):
Air: 18.59
Water: 1440
Soil: 2880
Sediment: 1.296e+004
Biowin estimate: 2.219 (months)

Advection Times (hr):
Air: 100
Water: 1000
Sediment: 5e+004

Table B.8.8-A.3_CA-3: The detailed results of QSAR calculations for FOE Oxalate.

Compound: FOE Oxalate	Structural formula: <div></div>
Results of calculations: <div>SMILES : c1ccc(F)cc1C(C)(C)NC(=O)C(=O)O CHEM : (FOE Oxalate) MOL FOR: C11 H12 F1 N1 O3 MOL WT : 225.22 ----- EPI SUMMARY (v4.10) ----- Physical Property Inputs: Water Solubility (mg/L): ----- Vapor Pressure (mm Hg) : ----- Henry LC (atm-m3/mole) : ----- Log Kow (octanol-water): ----- Boiling Point (deg C) : ----- Melting Point (deg C) : ----- KOWWIN Program (v1.68) Results: =====</div> <div>Log Kow(version 1.68 estimate): 0.85</div> <div>SMILES : c1ccc(F)cc1C(C)(C)NC(=O)C(=O)O CHEM : MOL FOR: C11 H12 F1 N1 O3 MOL WT : 225.22 -----+-----</div>	

Melting Point: 118.33 deg C (Gold and Ogle Method)
 Mean Melt Pt : 234.09 deg C (Joback; Gold,Ogle Methods)
 Selected MP: 164.63 deg C (Weighted Value)

Vapor Pressure Estimations (25 deg C):
 (Using BP: 397.32 deg C (estimated))
 (Using MP: 164.63 deg C (estimated))
 VP: 7.88E-008 mm Hg (Antoine Method)
 : 1.05E-005 Pa (Antoine Method)
 VP: 3.53E-007 mm Hg (Modified Grain Method)
 : 4.71E-005 Pa (Modified Grain Method)
 VP: 8.22E-007 mm Hg (Mackay Method)
 : 0.00011 Pa (Mackay Method)
 Selected VP: 3.53E-007 mm Hg (Modified Grain Method)
 : 4.71E-005 Pa (Modified Grain Method)
 Subcooled liquid VP: 9.66E-006 mm Hg (25 deg C, Mod-Grain method)
 : 0.00129 Pa (25 deg C, Mod-Grain method)

```
-----+-----+-----+-----+
TYPE | NUM | BOIL DESCRIPTION | COEFF | VALUE
```

```
-----+-----+-----+-----+
Group | 2 | -CH3          | 21.98 | 43.96
Group | 1 | >C<           | 4.50 | 4.50
Group | 1 | -COOH (acid)  | 169.83 | 169.83
Group | 4 | CH (aromatic) | 28.53 | 114.12
Group | 2 | -C (aromatic) | 30.76 | 61.52
Group | 1 | -C(=O)NH-     | 225.09 | 225.09
Group | 1 | -F (to aromat) | -7.81 | -7.81
* | | Equation Constant | | 198.18
```

```
=====+=====+=====+=====+
RESULT-uncorr| BOILING POINT in deg Kelvin | 809.39
RESULT- corr | BOILING POINT in deg Kelvin | 670.48
              | BOILING POINT in deg C      | 397.32
```

```
-----+-----+-----+-----+
TYPE | NUM | MELT DESCRIPTION | COEFF | VALUE
```

```
-----+-----+-----+-----+
Group | 2 | -CH3          | -5.10 | -10.20
Group | 1 | >C<           | 46.43 | 46.43
Group | 1 | -COOH (acid)  | 155.50 | 155.50
Group | 4 | CH (aromatic) | 8.13 | 32.52
Group | 2 | -C (aromatic) | 37.02 | 74.04
Group | 1 | -C(=O)NH-     | 225.00 | 225.00
Group | 1 | -F (to aromat) | -15.78 | -15.78
* | | Equation Constant | | 122.50
```

```
=====+=====+=====+=====+
RESULT | MELTING POINT in deg Kelvin | 630.01
RESULT-limit| MELTING POINT in deg Kelvin | 623.00
          | MELTING POINT in deg C      | 349.84
```

Water Sol from Kow (WSKOW v1.42) Results:

Water Sol: 6113 mg/L

SMILES : c1ccc(F)cc1C(C)(C)NC(=O)C(=O)O
 CHEM :
 MOL FOR: C11 H12 F1 N1 O3
 MOL WT : 225.22

----- WSKOW v1.42 Results -----
 Log Kow (estimated) : 0.85
 Log Kow (experimental): not available from database
 Log Kow used by Water solubility estimates: 0.85

Equation Used to Make Water Sol estimate:
 $\text{Log S (mol/L)} = 0.796 - 0.854 \log \text{Kow} - 0.00728 \text{ MW} + \text{Correction}$
 (used when Melting Point NOT available)

Correction(s): Value

 No Applicable Correction Factors

Log Water Solubility (in moles/L) : -1.566
 Water Solubility at 25 deg C (mg/L): 6113

WATERNT Program (v1.01) Results:

=====

Water Sol (v1.01 est): 1.4972e+005 mg/L

SMILES : c1ccc(F)cc1C(C)(C)NC(=O)C(=O)O

CHEM :

MOL FOR: C11 H12 F1 N1 O3

MOL WT : 225.22

TYPE	NUM	WATER SOLUBILITY FRAGMENT DESCRIPTION	COEFF	VALUE
Frag	2	-CH3 [aliphatic carbon]	-0.3213	-0.6425
Frag	1	-NH- [aliphatic attach]	2.1357	2.1357
Frag	4	Aromatic Carbon (C-H type)	-0.3359	-1.3435
Frag	1	-COOH [acid, aliphatic attach]	1.1808	1.1808
Frag	1	-F [fluorine, aromatic attach]	0.1429	0.1429
Frag	1	-C(=O)N [aliphatic attach]	-0.2426	-0.2426
Frag	2	Aromatic Carbon (C-substituent type)	-0.5400	-1.0799
Frag	1	-tert Carbon [3 or more carbon attach]	-0.5774	-0.5774
Const		Equation Constant		0.2492

Log Water Sol (moles/L) at 25 dec C = -0.1773
 Water Solubility (mg/L) at 25 dec C =1.4972e+005

ECOSAR Program (v1.11) Results:

=====

ECOSAR Version 1.11 Results Page

SMILES : c1ccc(F)cc1C(C)(C)NC(=O)C(=O)O

CHEM :

CAS Num:

ChemID1:

MOL FOR: C11 H12 F1 N1 O3

MOL WT : 225.22

Log Kow: 0.846 (EPIsuite Kowwin v1.68 Estimate)

Log Kow: (User Entered)

Log Kow: (PhysProp DB exp value - for comparison only)

Melt Pt: (User Entered for Wat Sol estimate)

Melt Pt: (deg C, PhysProp DB exp value for Wat Sol estimate)

Wat Sol: 6113 (mg/L, EPIsuite WSKowwin v1.43 Estimate)

Wat Sol: (User Entered)

Wat Sol: (PhysProp DB exp value)

Values used to Generate ECOSAR Profile

Log Kow: 0.846 (EPIsuite Kowwin v1.68 Estimate)
 Wat Sol: 6113 (mg/L, EPIsuite WSKowwin v1.43 Estimate)

ECOSAR v1.11 Class-specific Estimations

 | Not Related to an Existing ECOSAR Class Definition |
 |
 | Estimates provided below use the Neutral Organics QSAR equations which |
 | represent baseline toxicity potential (minimum toxicity) assuming a simple |
 | non-polar narcosis model. Without empirical data on structurally similar |
 | chemicals, it is uncertain if this substance will present significantly |
 | higher toxicity above baseline estimates. |

ECOSAR Class	Organism	Predicted Duration	End Pt	mg/L (ppm)
Neutral Organics	: Fish	96-hr	LC50	2010.702

Neutral Organics	: Daphnid	48-hr	LC50	1026.323
Neutral Organics	: Green Algae	96-hr	EC50	492.154
Neutral Organics	: Fish		ChV	173.332
Neutral Organics	: Daphnid		ChV	74.410
Neutral Organics	: Green Algae		ChV	101.666
Neutral Organics	: Fish (SW)	96-hr	LC50	2513.900
Neutral Organics	: Mysid	96-hr	LC50	4081.939
Neutral Organics	: Fish (SW)		ChV	134.892
Neutral Organics	: Mysid (SW)		ChV	496.647
Neutral Organics	: Earthworm	14-day	LC50	515.761

Note: * = asterisk designates: Chemical may not be soluble enough to measure this predicted effect. If the effect level exceeds the water solubility by 10X, typically no effects at saturation (NES) are reported.

Class Specific LogKow Cut-Offs

If the log Kow of the chemical is greater than the endpoint specific cut-offs presented below, then no effects at saturation are expected for those endpoints.

Neutral Organics:

Maximum LogKow: 5.0 (Fish 96-hr LC50; Daphnid LC50, Mysid LC50)
 Maximum LogKow: 6.0 (Earthworm LC50)
 Maximum LogKow: 6.4 (Green Algae EC50)
 Maximum LogKow: 8.0 (ChV)

HENRY (v3.20) Program Results:

Bond Est : 1.79E-013 atm-m3/mole (1.82E-008 Pa-m3/mole)
 Group Est: Incomplete

SMILES : c1ccc(F)cc1C(C)(C)NC(=O)C(=O)O

CHEM :

MOL FOR: C11 H12 F1 N1 O3

MOL WT : 225.22

HENRYWIN v3.20 Results

CLASS	BOND CONTRIBUTION DESCRIPTION	COMMENT	VALUE
HYDROGEN	6 Hydrogen to Carbon (aliphatic) Bonds		-0.7181
HYDROGEN	4 Hydrogen to Carbon (aromatic) Bonds		-0.6172
HYDROGEN	1 Hydrogen to Oxygen Bonds		3.2318
HYDROGEN	1 Hydrogen to Nitrogen Bonds		1.2835
FRAGMENT	2 C-C		0.2326
FRAGMENT	1 C-Car		0.1619
FRAGMENT	1 C-N		1.3010
FRAGMENT	6 Car-Car		1.5828
FRAGMENT	1 CO-O		0.0714
FRAGMENT	1 CO-N		2.4261
FRAGMENT	1 CO-CO		2.4000
FRAGMENT	1 Car-F		-0.2214

RESULT | BOND ESTIMATION METHOD for LWAPC VALUE | TOTAL | 11.135

HENRY's LAW CONSTANT at 25 deg C = 1.79E-013 atm-m3/mole
 = 7.33E-012 unitless
 = 1.82E-008 Pa-m3/mole

GROUP CONTRIBUTION DESCRIPTION	COMMENT	VALUE
2 CH3 (X)		-1.24
4 Car-H (Car)(Car)		0.44
1 Car (C)(Car)(Car)		0.70
1 O-H (CO)		1.45
1 Car (Car)(Car)(F)	ESTIMATE	-0.34
MISSING Value for: C (C)(C)(N)(Car)		
MISSING Value for: NH (CO)(C)		
MISSING Value for: CO (CO)(N)		

MISSING Value for: CO (O)(CO)			
RESULT	GROUP ESTIMATION METHOD for LOG GAMMA VALUE	INCOMPLETE	1.01
For Henry LC Comparison Purposes:			
Exper Database: none available			
User-Entered Henry LC: not entered			
Henrys LC [via VP/WSol estimate using User-Entered or Estimated values]:			
HLC: 1.711E-011 atm-m3/mole (1.734E-006 Pa-m3/mole)			
VP: 3.53E-007 mm Hg (source: MPBPVP)			
WS: 6.11E+003 mg/L (source: WSKOWWIN)			
Log Octanol-Air (KOAWIN v1.10) Results:			
=====			
Log Koa: 11.986			
SMILES : c1ccc(F)cc1C(C)(C)NC(=O)C(=O)O			
CHEM :			
MOL FOR: C11 H12 F1 N1 O3			
MOL WT : 225.22			
----- KOAWIN v1.10 Results -----			
Log Koa (octanol/air) estimate: 11.986			
Koa (octanol/air) estimate: 9.674e+011			
Using:			
Log Kow: 0.85 (KowWin est)			
HenryLC: 1.79e-013 atm-m3/mole (HenryWin est)			
Log Kaw: -11.136 (air/water part.coef.)			
LogKow : ---- (exp database)			
LogKow : 0.85 (KowWin estimate)			
Henry LC: --- atm-m3/mole(exp database)			
Henry LC: 1.79e-013 atm-m3/mole (HenryWin bond estimate)			
Log Koa (octanol/air) estimate: 11.986 (from KowWin/HenryWin)			
BIOWIN (v4.10) Program Results:			
=====			
SMILES : c1ccc(F)cc1C(C)(C)NC(=O)C(=O)O			
CHEM :			
MOL FOR: C11 H12 F1 N1 O3			
MOL WT : 225.22			
----- BIOWIN v4.10 Results -----			
Biowin1 (Linear Model Prediction) : Does Not Biodegrade Fast			
Biowin2 (Non-Linear Model Prediction): Does Not Biodegrade Fast			
Biowin3 (Ultimate Biodegradation Timeframe): Weeks-Months			
Biowin4 (Primary Biodegradation Timeframe): Days			
Biowin5 (MITI Linear Model Prediction) : Does Not Biodegrade Fast			
Biowin6 (MITI Non-Linear Model Prediction): Does Not Biodegrade Fast			
Biowin7 (Anaerobic Model Prediction): Does Not Biodegrade Fast			
Ready Biodegradability Prediction: NO			
-----+-----+-----+-----			
TYPE NUM	Biowin1 FRAGMENT DESCRIPTION	COEFF	VALUE
-----+-----+-----+-----			
Frag 1	Aliphatic acid [-C(=O)-OH]	0.0727	0.0727
Frag 1	Amide [-C(=O)-N or -C(=S)-N]	0.2102	0.2102
Frag 1	Aromatic fluoride [-F]	-0.8100	-0.8100
Frag 1	Carbon with 4 single bonds & no hydrogens	-0.1839	-0.1839
MolWt *	Molecular Weight Parameter		-0.1072
Const *	Equation Constant		0.7475
=====+=====+=====+=====			
RESULT	Biowin1 (Linear Biodeg Probability)		-0.0708
=====+=====+=====+=====			
-----+-----+-----+-----			
TYPE NUM	Biowin2 FRAGMENT DESCRIPTION	COEFF	VALUE
-----+-----+-----+-----			
Frag 1	Aliphatic acid [-C(=O)-OH]	0.6431	0.6431

```

Frag | 1 | Amide [-C(=O)-N or -C(=S)-N] | 2.6913 | 2.6913
Frag | 1 | Aromatic fluoride [-F] | -10.5318 | -10.5318
Frag | 1 | Carbon with 4 single bonds & no hydrogens | -1.7232 | -1.7232
MolWt | * | Molecular Weight Parameter | | -3.1981

```

```

=====
RESULT | Biowin2 (Non-Linear Biodeg Probability) | | 0.0001
=====

```

A Probability Greater Than or Equal to 0.5 indicates --> Biodegrades Fast
A Probability Less Than 0.5 indicates --> Does NOT Biodegrade Fast

```

-----+-----+-----+-----+-----+
TYPE | NUM | Biowin3 FRAGMENT DESCRIPTION | COEFF | VALUE
-----+-----+-----+-----+-----+

```

```

Frag | 1 | Aliphatic acid [-C(=O)-OH] | 0.3646 | 0.3646
Frag | 1 | Amide [-C(=O)-N or -C(=S)-N] | -0.0542 | -0.0542
Frag | 1 | Aromatic fluoride [-F] | -0.4069 | -0.4069
Frag | 1 | Carbon with 4 single bonds & no hydrogens | -0.2121 | -0.2121
MolWt | * | Molecular Weight Parameter | | -0.4977
Const | * | Equation Constant | | 3.1992

```

```

=====
RESULT | Biowin3 (Survey Model - Ultimate Biodeg) | | 2.3928
=====

```

```

-----+-----+-----+-----+-----+
TYPE | NUM | Biowin4 FRAGMENT DESCRIPTION | COEFF | VALUE
-----+-----+-----+-----+-----+

```

```

Frag | 1 | Aliphatic acid [-C(=O)-OH] | 0.3856 | 0.3856
Frag | 1 | Amide [-C(=O)-N or -C(=S)-N] | 0.2054 | 0.2054
Frag | 1 | Aromatic fluoride [-F] | 0.0135 | 0.0135
Frag | 1 | Carbon with 4 single bonds & no hydrogens | -0.1534 | -0.1534
MolWt | * | Molecular Weight Parameter | | -0.3249
Const | * | Equation Constant | | 3.8477

```

```

=====
RESULT | Biowin4 (Survey Model - Primary Biodeg) | | 3.9738
=====

```

Result Classification: 5.00 -> hours 4.00 -> days 3.00 -> weeks
(PPrimary & Ultimate) 2.00 -> months 1.00 -> longer

```

-----+-----+-----+-----+-----+
TYPE | NUM | Biowin5 FRAGMENT DESCRIPTION | COEFF | VALUE
-----+-----+-----+-----+-----+

```

```

Frag | 1 | Aliphatic acid [-C(=O)-OH] | 0.1812 | 0.1812
Frag | 1 | Amide [-C(=O)-N or -C(=S)-N] | 0.1266 | 0.1266
Frag | 1 | Carbon with 4 single bonds & no hydrogens | 0.0676 | 0.0676
Frag | 1 | Fluorine [-F] | 0.0174 | 0.0174
Frag | 4 | Aromatic-H | 0.0082 | 0.0329
Frag | 2 | Methyl [-CH3] | 0.0004 | 0.0008
MolWt | * | Molecular Weight Parameter | | -0.6700
Const | * | Equation Constant | | 0.7121

```

```

=====
RESULT | Biowin5 (MITI Linear Biodeg Probability) | | 0.4686
=====

```

```

-----+-----+-----+-----+-----+
TYPE | NUM | Biowin6 FRAGMENT DESCRIPTION | COEFF | VALUE
-----+-----+-----+-----+-----+

```

```

Frag | 1 | Aliphatic acid [-C(=O)-OH] | 1.1346 | 1.1346
Frag | 1 | Amide [-C(=O)-N or -C(=S)-N] | 0.8859 | 0.8859
Frag | 1 | Carbon with 4 single bonds & no hydrogens | 0.3990 | 0.3990
Frag | 1 | Fluorine [-F] | -3.9878 | -3.9878
Frag | 4 | Aromatic-H | 0.1201 | 0.4806
Frag | 2 | Methyl [-CH3] | 0.0194 | 0.0389
MolWt | * | Molecular Weight Parameter | | -6.5019

```

```

=====
RESULT | Biowin6 (MITI Non-Linear Biodeg Probability) | | 0.0065
=====

```

A Probability Greater Than or Equal to 0.5 indicates --> Readily Degradable
A Probability Less Than 0.5 indicates --> NOT Readily Degradable

```

-----+-----+-----+-----+-----+
TYPE | NUM | Biowin7 FRAGMENT DESCRIPTION | COEFF | VALUE
-----+-----+-----+-----+-----+

```

A Probability Greater Than or Equal to 0.5 indicates --> Biodegrades Fast
A Probability Less Than 0.5 indicates --> Does NOT Biodegrade Fast

Criteria for the YES or NO prediction: If the Biowin3 (ultimate survey model) result is "weeks" or faster (i.e. "days", "days to weeks", or "weeks" AND the Biowin5 (MITI linear model) probability is ≥ 0.5 , then the prediction is YES (readily biodegradable). If this condition is not satisfied, the prediction is NO (not readily biodegradable). This method is based on application of Bayesian analysis to ready biodegradation data (see Help). Biowin5 and 6 also predict ready biodegradability, but for degradation in the OECD301C test only; using data from the Chemicals Evaluation and Research Institute Japan (CERIJ) database.

NO Estimate Possible ... Structure NOT a Hydrocarbon
(Contains atoms other than C, H or S (-S-))

Sorption to aerosols (25 Dec C)[AEROWIN v1.00]:
 Vapor pressure (liquid/subcooled): 0.00129 Pa (9.66E-006 mm Hg)
 Log Koa (Koawin est): 11.986
 Kp (particle/gas partition coef. (m3/ug)):
 Mackay model : 0.00233
 Octanol/air (Koa) model: 0.238
 Fraction sorbed to airborne particulates (phi):
 Junge-Pankow model : 0.0776
 Mackay model : 0.157
 Octanol/air (Koa) model: 0.95

----- SUMMARY (AOP v1.91): OZONE REACTION (25 deg C) -----

***** NO OZONE REACTION ESTIMATION *****
(ONLY Olefins and Acetylenes are Estimated)

Experimental Database: NO Structure Matches

Fraction sorbed to airborne particulates (phi):

0.117 (Junge-Pankow, Mackay avg)

0.95 (Koa method)

Note: the sorbed fraction may be resistant to atmospheric oxidation

KOCWIN Program (v2.00) Results:

SMILES : c1ccc(F)cc1C(C)(C)NC(=O)C(=O)O

CHEM :

MOL FOR: C11 H12 F1 N1 O3

Koc may be sensitive to pH!

----- KOCWIN v2.00 Results -----

Koc Estimate from MCI:

First Order Molecular Connectivity Index : 7.326

Non-Corrected Log Koc (0.5213 MCI + 0.60) : 4.4190

Fragment Correction(s):

1 Nitrogen to Carbon (aliphatic) (-N-C).. : -0.2127

* Organic Acid (-CO-OH) : -1.6249

1 Misc (C=O) Group (aliphatic attach).... : -1.6047

Corrected Log Koc : 0.9767

Over Correction Adjustment to Lower Limit Log Koc ... : 1.0000

Estimated Koc: 10 L/kg <=====

Koc Estimate from Log Kow:

Log Kow (Kowwin estimate) : 0.85

Non-Corrected Log Koc (0.55313 logKow + 0.9251) : 1.3953

Fragment Correction(s):

1 Nitrogen to Carbon (aliphatic) (-N-C).. : -0.0218

* Organic Acid (-CO-OH) : -0.7694

1 Misc (C=O) Group (aliphatic attach).... : -0.2293

Corrected Log Koc : 0.3748

Estimated Koc: 2.37 L/kg <=====

* NOTE: *
* The Koc of this structure may be sensitive to pH! The estimated *
* Koc represents a best-fit to the majority of experimental values *
* however, the Koc may vary significantly with pH. *

HYDROWIN Program (v2.00) Results:

SMILES : c1ccc(F)cc1C(C)(C)NC(=O)C(=O)O

CHEM :

MOL FOR: C11 H12 F1 N1 O3

MOL WT : 225.22

----- HYDROWIN v2.00 Results -----

Currently, this program can NOT estimate a hydrolysis rate constant for
the type of chemical structure entered!!

ONLY Esters, Carbamates, Epoxides, Halomethanes (containing 1-3 halogens),
Specific Alkyl Halides & Phosphorus Esters can be estimated!!

When present, various hydrolyzable compound-types will be identified.
For more information, (Click OVERVIEW in Help or see the User's Guide)

***** CALCULATION NOT PERFORMED *****

BCFBAF Program (v3.01) Results:

SMILES : c1ccc(F)cc1C(C)(C)NC(=O)C(=O)O

CHEM :

MOL FOR: C11 H12 F1 N1 O3

MOL WT : 225.22

----- BCFBAF v3.01 -----

Summary Results:

Log BCF (regression-based estimate): 0.50 (BCF = 3.16 L/kg wet-wt)

Biotransformation Half-Life (days) : 0.109 (normalized to 10 g fish)

Log BAF (Arnot-Gobas upper trophic): 0.17 (BAF = 1.5 L/kg wet-wt)

Log Kow (experimental): not available from database

Log Kow used by BCF estimates: 0.85

Equation Used to Make BCF estimate:

Log BCF = 0.50 (Ionic; Log Kow dependent)

Estimated Log BCF = 0.500 (BCF = 3.162 L/kg wet-wt)

Whole Body Primary Biotransformation Rate Estimate for Fish:

TYPE	NUM	LOG BIOTRANSFORMATION FRAGMENT DESCRIPTION	COEFF	VALUE
Frag	1	Aliphatic acid [-C(=O)-OH]	0.3803	0.3803
Frag	1	Amide [-C(=O)-N or -C(=S)-N]	-0.5952	-0.5952
Frag	1	Aromatic fluoride [-F]	0.0000	0.0000
Frag	1	Carbon with 4 single bonds & no hydrogens	-0.2984	-0.2984
Frag	1	Fluorine [-F]	0.2759	0.2759
Frag	4	Aromatic-H	0.2664	1.0655
Frag	2	Methyl [-CH3]	0.2451	0.4902
Frag	1	Benzene	-0.4277	-0.4277
L Kow	*	Log Kow = 0.85 (KowWin estimate)	0.3073	0.2601
MolWt	*	Molecular Weight Parameter	-0.5775	
Const	*	Equation Constant	-1.5371	
RESULT		LOG Bio Half-Life (days)	-0.9640	
RESULT		Bio Half-Life (days)	0.1086	
NOTE		Bio Half-Life Normalized to 10 g fish at 15 deg C		

Frag	1	Aliphatic acid [-C(=O)-OH]	0.3803	0.3803
Frag	1	Amide [-C(=O)-N or -C(=S)-N]	-0.5952	-0.5952
Frag	1	Aromatic fluoride [-F]	0.0000	0.0000
Frag	1	Carbon with 4 single bonds & no hydrogens	-0.2984	-0.2984
Frag	1	Fluorine [-F]	0.2759	0.2759
Frag	4	Aromatic-H	0.2664	1.0655
Frag	2	Methyl [-CH3]	0.2451	0.4902
Frag	1	Benzene	-0.4277	-0.4277
L Kow	*	Log Kow = 0.85 (KowWin estimate)	0.3073	0.2601
MolWt	*	Molecular Weight Parameter	-0.5775	
Const	*	Equation Constant	-1.5371	

RESULT | LOG Bio Half-Life (days) | -0.9640

RESULT | Bio Half-Life (days) | 0.1086

NOTE | Bio Half-Life Normalized to 10 g fish at 15 deg C |

Biotransformation Rate Constant:

kM (Rate Constant): 6.38 /day (10 gram fish)

kM (Rate Constant): 3.588 /day (100 gram fish)

kM (Rate Constant): 2.017 /day (1 kg fish)

kM (Rate Constant): 1.135 /day (10 kg fish)

Arnot-Gobas BCF & BAF Methods (including biotransformation rate estimates):

Estimated Log BCF (upper trophic) = 0.175 (BCF = 1.496 L/kg wet-wt)

Estimated Log BAF (upper trophic) = 0.175 (BAF = 1.496 L/kg wet-wt)

Estimated Log BCF (mid trophic) = 0.134 (BCF = 1.363 L/kg wet-wt)

Estimated Log BAF (mid trophic) = 0.134 (BAF = 1.363 L/kg wet-wt)

Estimated Log BCF (lower trophic) = 0.122 (BCF = 1.325 L/kg wet-wt)

Estimated Log BAF (lower trophic) = 0.122 (BAF = 1.325 L/kg wet-wt)

Arnot-Gobas BCF & BAF Methods (assuming a biotransformation rate of zero):

Estimated Log BCF (upper trophic) = 0.216 (BCF = 1.644 L/kg wet-wt)

Estimated Log BAF (upper trophic) = 0.219 (BAF = 1.654 L/kg wet-wt)

Volatilization From Water

Chemical Name:

Molecular Weight : 225.22 g/mole

Water Solubility : -----

Vapor Pressure : -----

Henry's Law Constant: 1.79E-013 atm-m³/mole (estimated by Bond SAR Method)

RIVER LAKE

Water Depth (meters):	1	1
Wind Velocity (m/sec):	3	0.5
Current Velocity (m/sec):	1	0.05

HALF-LIFE (hours) : 7.363E+009 5.355E+010
 HALF-LIFE (days) : 3.068E+008 2.231E+009
 HALF-LIFE (years) : 8.4E+005 6.109E+006

STP Fugacity Model: Predicted Fate in a Wastewater Treatment Facility

(using 10000 hr Bio P,A,S)

PROPERTIES OF:

 Molecular weight (g/mol) 225.22
 Aqueous solubility (mg/l) 0
 Vapour pressure (Pa) 0
 (atm) 0
 (mm Hg) 0
 Henry's law constant (Atm-m³/mol) 1.79E-013
 Air-water partition coefficient 7.32057E-012
 Octanol-water partition coefficient (Kow) 7.07946
 Log Kow 0.85
 Biomass to water partition coefficient 2.21589
 Temperature [deg C] 25
 Biodeg rate constants (h⁻¹), half life in biomass (h) and in 2000 mg/L MLSS (h):
 -Primary tank 0.02 44.12 10000.00
 -Aeration tank 0.02 44.12 10000.00
 -Settling tank 0.02 44.12 10000.00

STP Overall Chemical Mass Balance:

	g/h	mol/h	percent
Influent	1.00E+001	4.4E-002	100.00
Primary sludge	2.66E-002	1.2E-004	0.27
Waste sludge	1.52E-001	6.7E-004	1.52
Primary volatilization	9.75E-011	4.3E-013	0.00
Settling volatilization	2.66E-010	1.2E-012	0.00
Aeration off gas	6.55E-010	2.9E-012	0.00
Primary biodegradation	1.76E-003	7.8E-006	0.02
Settling biodegradation	5.28E-004	2.3E-006	0.01
Aeration biodegradation	6.95E-003	3.1E-005	0.07
Final water effluent	9.81E+000	4.4E-002	98.13
Total removal	1.87E-001	8.3E-004	1.87
Total biodegradation	9.24E-003	4.1E-005	0.09

Level III Fugacity Model (Full-Output):

 Chem Name :
 Molecular Wt: 225.22
 Henry's LC : 1.79e-013 atm-m³/mole (Henrywin program)
 Vapor Press : 3.53e-007 mm Hg (Mpbpwin program)
 Liquid VP : 8.49e-006 mm Hg (super-cooled)
 Melting Pt : 165 deg C (Mpbpwin program)
 Log Kow : 0.85 (Kowwin program)
 Soil Koc : 10 (KOCWIN MCI method)

	Mass Amount (percent)	Half-Life (hr)	Emissions (kg/hr)
Air	2.35e-006	21.9	1000
Water	35	900	1000
Soil	64.9	1.8e+003	1000
Sediment	0.0835	8.1e+003	0

	Fugacity (atm)	Reaction (kg/hr)	Advection (kg/hr)	Reaction (percent)	Advection (percent)
Air	7.95e-017	0.00257	0.00081	8.56e-005	2.7e-005
Water	4.8e-018	930	1.21e+003	31	40.2
Soil	1.83e-016	863	0	28.8	0
Sediment	4.62e-018	0.247	0.0577	0.00822	0.00192

Persistence Time: 1.15e+003 hr

Reaction Time: 1.93e+003 hr
 Advection Time: 2.86e+003 hr
 Percent Reacted: 59.8
 Percent Advected: 40.2

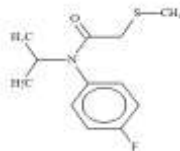
Half-Lives (hr), (based upon Biowin (Ultimate) and Aopwin):

Air: 21.87
 Water: 900
 Soil: 1800
 Sediment: 8100
 Biowin estimate: 2.393 (weeks-months)

Advection Times (hr):

Air: 100
 Water: 1000
 Sediment: 5e+004

Table B.8.8-A.3_CA-4: The detailed results of QSAR calculations for FOE Methylsulfide.

Compound: FOE Methylsulfide	Structural formula: <div></div>
Results of calculations:	
SMILES : c1c(F)ccc(N(C(C)(C))C(=O)CSC)c1	
CHEM :	
MOL FOR: C12 H16 F1 N1 O1 S1	
MOL WT : 241.33	
----- EPI SUMMARY (v4.10) -----	
Physical Property Inputs:	
Water Solubility (mg/L): -----	
Vapor Pressure (mm Hg) : -----	
Henry LC (atm-m3/mole) : -----	
Log Kow (octanol-water): -----	
Boiling Point (deg C) : -----	
Melting Point (deg C) : -----	
KOWWIN Program (v1.68) Results:	
=====	
Log Kow(version 1.68 estimate): 2.77	
SMILES : c1c(F)ccc(N(C(C)(C))C(=O)CSC)c1	
CHEM :	
MOL FOR: C12 H16 F1 N1 O1 S1	
MOL WT : 241.33	
-----+	

SMILES : c1c(F)ccc(N(C(C)(C))C(=O)CSC)c1

CHEM :

MOL FOR: C12 H16 F1 N1 O1 S1

MOL WT : 241.33

----- WSKOW v1.42 Results -----

Log Kow (estimated) : 2.77

Log Kow (experimental): not available from database

Log Kow used by Water solubility estimates: 2.77

Equation Used to Make Water Sol estimate:

Log S (mol/L) = 0.796 - 0.854 log Kow - 0.00728 MW + Correction
 (used when Melting Point NOT available)

Correction(s): Value

No Applicable Correction Factors

Log Water Solubility (in moles/L) : -3.328

Water Solubility at 25 deg C (mg/L): 113.3

WATERNT Program (v1.01) Results:

=====

Water Sol (v1.01 est): 875.82 mg/L

SMILES : c1c(F)ccc(N(C(C)(C))C(=O)CSC)c1

CHEM :

MOL FOR: C12 H16 F1 N1 O1 S1

MOL WT : 241.33

-----+-----+-----+-----+-----				
TYPE	NUM	WATER SOLUBILITY FRAGMENT DESCRIPTION	COEFF	VALUE
-----+-----+-----+-----+-----				
Frag	3	-CH3 [aliphatic carbon]	-0.3213	-0.9638
Frag	1	-CH2- [aliphatic carbon]	-0.5370	-0.5370
Frag	1	-CH [aliphatic carbon]	-0.5285	-0.5285
Frag	4	Aromatic Carbon (C-H type)	-0.3359	-1.3435
Frag	1	-N [aliphatic N, one aromatic attach]	1.2749	1.2749
Frag	1	-F [fluorine, aromatic attach]	0.1429	0.1429
Frag	1	-C(=O)N [aliphatic attach]	-0.2426	-0.2426
Frag	2	Aromatic Carbon (C-substituent type)	-0.5400	-1.0799
Frag	1	-S- [aliphatic attach]	-0.0993	-0.0993
Factor	1	Di-N urea/acetamide aromatic correction	0.6874	0.6874
Const		Equation Constant		0.2492
-----+-----+-----+-----+-----				

Log Water Sol (moles/L) at 25 dec C = -2.4402

Water Solubility (mg/L) at 25 dec C = 875.82

ECOSAR Program (v1.11) Results:

=====

ECOSAR Version 1.11 Results Page

SMILES : c1c(F)ccc(N(C(C)(C))C(=O)CSC)c1

CHEM :

CAS Num:

ChemID1:

MOL FOR: C12 H16 F1 N1 O1 S1

MOL WT : 241.33

Log Kow: 2.772 (EPISuite Kowwin v1.68 Estimate)

Log Kow: (User Entered)

Log Kow: (PhysProp DB exp value - for comparison only)

Melt Pt: (User Entered for Wat Sol estimate)

Melt Pt: (deg C, PhysProp DB exp value for Wat Sol estimate)

Wat Sol: 113.3 (mg/L, EPISuite WSKowwin v1.43 Estimate)

Wat Sol: (User Entered)

Wat Sol: (PhysProp DB exp value)

Values used to Generate ECOSAR Profile-----
Log Kow: 2.772 (EPISuite Kowwin v1.68 Estimate)

Wat Sol: 113.3 (mg/L, EPISuite WSKowwin v1.43 Estimate)

ECOSAR v1.11 Class-specific Estimations

Amides

ECOSAR Class	Organism	Predicted Duration	End Pt	mg/L (ppm)
Amides	: Fish	96-hr	LC50	20.210
Amides	: Daphnid	48-hr	LC50	15.588
Amides	: Green Algae	96-hr	EC50	0.751
Amides	: Fish	ChV		0.055
Amides	: Daphnid	ChV		1.456
Amides	: Green Algae	ChV		0.977
Amides	: Fish (SW)	96-hr	LC50	17.991
Amides	: Mysid (SW)	96-hr	LC50	1.452

Neutral Organic SAR	: Fish	96-hr	LC50	40.134
(Baseline Toxicity)	: Daphnid	48-hr	LC50	24.473
	: Green Algae	96-hr	EC50	24.482
	: Fish	ChV		4.267
	: Daphnid	ChV		2.911
	: Green Algae	ChV		7.515

Note: * = asterisk designates: Chemical may not be soluble enough to measure this predicted effect. If the effect level exceeds the water solubility by 10X, typically no effects at saturation (NES) are reported.

Class Specific LogKow Cut-Offs

If the log Kow of the chemical is greater than the endpoint specific cut-offs presented below, then no effects at saturation are expected for those endpoints.

Amides :

Maximum LogKow: >8.5 (LC50)
Maximum LogKow: >8.0 (EC50,ChV)

Baseline Toxicity SAR Limitations:

Maximum LogKow: 5.0 (Fish 96-hr LC50; Daphnid LC50)
Maximum LogKow: 6.4 (Green Algae EC50)
Maximum LogKow: 8.0 (ChV)

HENRY (v3.20) Program Results:

Bond Est : 2.77E-009 atm-m3/mole (2.81E-004 Pa-m3/mole)
Group Est: Incomplete

SMILES : c1c(F)ccc(N(C(C)(C))C(=O)CSC)c1

CHEM :

MOL FOR: C12 H16 F1 N1 O1 S1

MOL WT : 241.33

----- HENRYWIN v3.20 Results -----

CLASS	BOND CONTRIBUTION DESCRIPTION	COMMENT	VALUE
HYDROGEN	12 Hydrogen to Carbon (aliphatic) Bonds		-1.4361
HYDROGEN	4 Hydrogen to Carbon (aromatic) Bonds		-0.6172
FRAGMENT	2 C-C		0.2326
FRAGMENT	1 C-CO		1.7057
FRAGMENT	1 C-N		1.3010
FRAGMENT	2 C-S		2.2112
FRAGMENT	6 Car-Car		1.5828
FRAGMENT	1 CO-N		2.4261
FRAGMENT	1 Car-N		0.7304
FRAGMENT	1 Car-F		-0.2214

FACTOR	1 Di-N-substituted N (to aromatic)		-0.9700
RESULT	BOND ESTIMATION METHOD for LWAPC VALUE	TOTAL	6.945
HENRYs LAW CONSTANT at 25 deg C = 2.77E-009 atm-m3/mole			
= 1.13E-007 unitless			
= 2.81E-004 Pa-m3/mole			

	GROUP CONTRIBUTION DESCRIPTION	COMMENT	VALUE
	1 Car (N)(Car)(Car)	ESTIMATE	-0.50
	3 CH3 (X)		-1.86
	4 Car-H (Car)(Car)		0.44
	1 S (C)(C)		2.35
	1 Car (Car)(Car)(F)	ESTIMATE	-0.34
	MISSING Value for: N (C)(CO)(Car)		
	MISSING Value for: CH (C)(C)(N)		
	MISSING Value for: CO (C)(N)		
	MISSING Value for: CH2 (S)(CO)		
RESULT	GROUP ESTIMATION METHOD for LOG GAMMA VALUE	INCOMPLETE	0.09

For Henry LC Comparison Purposes:

Exper Database: none available

User-Entered Henry LC: not entered

Henrys LC [via VP/WSol estimate using User-Entered or Estimated values]:

HLC: 1.693E-007 atm-m3/mole (1.715E-002 Pa-m3/mole)

VP: 6.04E-005 mm Hg (source: MPBPVP)

WS: 113 mg/L (source: WSKOWWIN)

Log Octanol-Air (KOWWIN v1.10) Results:

=====

Log Koa: 9.716

SMILES : c1c(F)ccc(N(C(C)(C))C(=O)CSC)c1

CHEM :

MOL FOR: C12 H16 F1 N1 O1 S1

MOL WT : 241.33

----- KOAWIN v1.10 Results -----

Log Koa (octanol/air) estimate: 9.716

Koa (octanol/air) estimate: 5.2e+009

Using:

Log Kow: 2.77 (KowWin est)

HenryLC: 2.77e-009 atm-m3/mole (HenryWin est)

Log Kaw: -6.946 (air/water part.coef.)

LogKow : ---- (exp database)

LogKow : 2.77 (KowWin estimate)

Henry LC: --- atm-m3/mole(exp database)

Henry LC: 2.77e-009 atm-m3/mole (HenryWin bond estimate)

Log Koa (octanol/air) estimate: 9.716 (from KowWin/HenryWin)

BIOWIN (v4.10) Program Results:

=====

SMILES : c1c(F)ccc(N(C(C)(C))C(=O)CSC)c1

CHEM :

MOL FOR: C12 H16 F1 N1 O1 S1

MOL WT : 241.33

----- BIOWIN v4.10 Results -----

Biowin1 (Linear Model Prediction) : Does Not Biodegrade Fast

Biowin2 (Non-Linear Model Prediction): Does Not Biodegrade Fast

Biowin3 (Ultimate Biodegradation Timeframe): Months

Biowin4 (Primary Biodegradation Timeframe): Days-Weeks

Biowin5 (MITI Linear Model Prediction) : Does Not Biodegrade Fast

Biowin6 (MITI Non-Linear Model Prediction): Does Not Biodegrade Fast

Biowin7 (Anaerobic Model Prediction): Does Not Biodegrade Fast

Ready Biodegradability Prediction: NO

TYPE	NUM	Biowin1 FRAGMENT DESCRIPTION	COEFF	VALUE
Frag	1	Amide [-C(=O)-N or -C(=S)-N]	0.2102	0.2102
Frag	1	Aromatic fluoride [-F]	-0.8100	-0.8100
MolWt	*	Molecular Weight Parameter		-0.1149
Const	*	Equation Constant		0.7475
=====				
RESULT		Biowin1 (Linear Biodeg Probability)		0.0328
=====				

TYPE	NUM	Biowin2 FRAGMENT DESCRIPTION	COEFF	VALUE
Frag	1	Amide [-C(=O)-N or -C(=S)-N]	2.6913	2.6913
Frag	1	Aromatic fluoride [-F]	-10.5318	-10.5318
MolWt	*	Molecular Weight Parameter		-3.4268
=====				
RESULT		Biowin2 (Non-Linear Biodeg Probability)		0.0003
=====				

A Probability Greater Than or Equal to 0.5 indicates --> Biodegrades Fast

A Probability Less Than 0.5 indicates --> Does NOT Biodegrade Fast

TYPE	NUM	Biowin3 FRAGMENT DESCRIPTION	COEFF	VALUE
Frag	1	Amide [-C(=O)-N or -C(=S)-N]	-0.0542	-0.0542
Frag	1	Aromatic fluoride [-F]	-0.4069	-0.4069
MolWt	*	Molecular Weight Parameter		-0.5333
Const	*	Equation Constant		3.1992
=====				
RESULT		Biowin3 (Survey Model - Ultimate Biodeg)		2.2047
=====				

TYPE	NUM	Biowin4 FRAGMENT DESCRIPTION	COEFF	VALUE
Frag	1	Amide [-C(=O)-N or -C(=S)-N]	0.2054	0.2054
Frag	1	Aromatic fluoride [-F]	0.0135	0.0135
MolWt	*	Molecular Weight Parameter		-0.3482
Const	*	Equation Constant		3.8477
=====				
RESULT		Biowin4 (Survey Model - Primary Biodeg)		3.7185
=====				

Result Classification: 5.00 -> hours 4.00 -> days 3.00 -> weeks
(Primary & Ultimate) 2.00 -> months 1.00 -> longer

TYPE	NUM	Biowin5 FRAGMENT DESCRIPTION	COEFF	VALUE
Frag	1	Amide [-C(=O)-N or -C(=S)-N]	0.1266	0.1266
Frag	1	Fluorine [-F]	0.0174	0.0174
Frag	4	Aromatic-H	0.0082	0.0329
Frag	3	Methyl [-CH3]	0.0004	0.0012
Frag	1	-CH2- [linear]	0.0494	0.0494
Frag	1	-CH- [linear]	-0.0507	-0.0507
MolWt	*	Molecular Weight Parameter		-0.7179
Const	*	Equation Constant		0.7121
=====				
RESULT		Biowin5 (MITI Linear Biodeg Probability)		0.1711
=====				

TYPE	NUM	Biowin6 FRAGMENT DESCRIPTION	COEFF	VALUE
Frag	1	Amide [-C(=O)-N or -C(=S)-N]	0.8859	0.8859
Frag	1	Fluorine [-F]	-3.9878	-3.9878
Frag	4	Aromatic-H	0.1201	0.4806
Frag	3	Methyl [-CH3]	0.0194	0.0583
Frag	1	-CH2- [linear]	0.4295	0.4295
Frag	1	-CH- [linear]	-0.0998	-0.0998

MolWt| * | Molecular Weight Parameter | | -6.9668

RESULT | Biowin6 (MITI Non-Linear Biodeg Probability)| | 0.0013

A Probability Greater Than or Equal to 0.5 indicates --> Readily Degradable

A Probability Less Than 0.5 indicates --> NOT Readily Degradable

TYPE | NUM | Biowin7 FRAGMENT DESCRIPTION | COEFF | VALUE

Frag | 1 | Amide [-C(=O)-N or -C(=S)-N] | -0.5679 | -0.5679

Frag | 1 | Aromatic fluoride [-F] | 0.0000 | 0.0000

Frag | 1 | Fluorine [-F] | 0.0000 | 0.0000

Frag | 4 | Aromatic-H | -0.0954 | -0.3817

Frag | 3 | Methyl [-CH3] | -0.0796 | -0.2387

Frag | 1 | -CH2- [linear] | 0.0260 | 0.0260

Frag | 1 | -CH- [linear] | -0.1659 | -0.1659

Const| * | Equation Constant | | 0.8361

RESULT | Biowin7 (Anaerobic Linear Biodeg Prob) | | -0.4921

A Probability Greater Than or Equal to 0.5 indicates --> Biodegrades Fast

A Probability Less Than 0.5 indicates --> Does NOT Biodegrade Fast

Ready Biodegradability Prediction: (YES or NO)

Criteria for the YES or NO prediction: If the Biowin3 (ultimate survey model) result is "weeks" or faster (i.e. "days", "days to weeks", or "weeks" AND the Biowin5 (MITI linear model) probability is ≥ 0.5 , then the prediction is YES (readily biodegradable). If this condition is not satisfied, the prediction is NO (not readily biodegradable). This method is based on application of Bayesian analysis to ready biodegradation data (see Help). Biowin5 and 6 also predict ready biodegradability, but for degradation in the OECD301C test only; using data from the Chemicals Evaluation and Research Institute Japan (CERIJ) database.

BioHCwin (v1.01) Program Results:

SMILES : c1c(F)ccc(N(C(C)(C))C(=O)CSC)c1

CHEM :

MOL FOR: C12 H16 F1 N1 O1 S1

MOL WT : 241.33

----- BioHCwin v1.01 Results -----

NO Estimate Possible ... Structure NOT a Hydrocarbon
(Contains atoms other than C, H or S (-S-))

AEROWIN Program (v1.00) Results:

Sorption to aerosols (25 Dec C)[AEROWIN v1.00]:

Vapor pressure (liquid/subcooled): 0.0396 Pa (0.000297 mm Hg)

Log Koa (Koawin est): 9.716

Kp (particle/gas partition coef. (m3/ug)):

Mackay model : 7.58E-005

Octanol/air (Koa) model: 0.00128

Fraction sorbed to airborne particulates (phi):

Junge-Pankow model : 0.00273

Mackay model : 0.00602

Octanol/air (Koa) model: 0.0927

AOP Program (v1.92) Results:

SMILES : c1c(F)ccc(N(C(C)(C))C(=O)CSC)c1

CHEM :

MOL FOR: C12 H16 F1 N1 O1 S1

MOL WT : 241.33

----- SUMMARY (AOP v1.92): HYDROXYL RADICALS (25 deg C) -----

Hydrogen Abstraction = 14.8133 E-12 cm3/molecule-sec

```

Reaction with N, S and -OH = 1.7000 E-12 cm3/molecule-sec
Addition to Triple Bonds = 0.0000 E-12 cm3/molecule-sec
Addition to Olefinic Bonds = 0.0000 E-12 cm3/molecule-sec
**Addition to Aromatic Rings = 4.1910 E-12 cm3/molecule-sec
Addition to Fused Rings = 0.0000 E-12 cm3/molecule-sec

OVERALL OH Rate Constant = 20.7043 E-12 cm3/molecule-sec
HALF-LIFE = 0.517 Days (12-hr day; 1.5E6 OH/cm3)
HALF-LIFE = 6.199 Hrs
..... ** Designates Estimation(s) Using ASSUMED Value(s)
----- SUMMARY (AOP v1.91): OZONE REACTION (25 deg C) -----

***** NO OZONE REACTION ESTIMATION *****
(ONLY Olefins and Acetylenes are Estimated)

NOTE: Reaction with Nitrate Radicals May Be Important!

Experimental Database: NO Structure Matches
Fraction sorbed to airborne particulates (phi):
0.00438 (Junge-Pankow, Mackay avg)
0.0927 (Koa method)
Note: the sorbed fraction may be resistant to atmospheric oxidation

KOCWIN Program (v2.00) Results:
=====
SMILES : c1c(F)ccc(N(C(C)(C))C(=O)CSC)c1
CHEM :
MOL FOR: C12 H16 F1 N1 O1 S1
MOL WT : 241.33
----- KOCWIN v2.00 Results -----

Koc Estimate from MCI:
-----
First Order Molecular Connectivity Index ..... : 7.558
Non-Corrected Log Koc (0.5213 MCI + 0.60) ..... : 4.5397
Fragment Correction(s):
  1 Nitrogen to non-fused aromatic ring ... : -0.5225
  1 N-CO-C (aliphatic carbon) ..... : -1.0277
  1 Nitrogen to Carbon (aliphatic) (-N-C).. : -0.2127
Corrected Log Koc ..... : 2.7767

Estimated Koc: 598 L/kg <=====

Koc Estimate from Log Kow:
-----
Log Kow (Kowwin estimate) ..... : 2.77
Non-Corrected Log Koc (0.55313 logKow + 0.9251) .... : 2.4573
Fragment Correction(s):
  1 Nitrogen to non-fused aromatic ring ... : -0.0216
  1 N-CO-C (aliphatic carbon) ..... : -0.0038
  1 Nitrogen to Carbon (aliphatic) (-N-C).. : -0.0218
Corrected Log Koc ..... : 2.4101

Estimated Koc: 257.1 L/kg <=====

HYDROWIN Program (v2.00) Results:
=====
SMILES : c1c(F)ccc(N(C(C)(C))C(=O)CSC)c1
CHEM :
MOL FOR: C12 H16 F1 N1 O1 S1
MOL WT : 241.33
----- HYDROWIN v2.00 Results -----

Currently, this program can NOT estimate a hydrolysis rate constant for
the type of chemical structure entered!!

ONLY Esters, Carbamates, Epoxides, Halomethanes (containing 1-3 halogens),
Specific Alkyl Halides & Phosphorus Esters can be estimated!!

When present, various hydrolyzable compound-types will be identified.

```

For more information, (Click OVERVIEW in Help or see the User's Guide)

***** CALCULATION NOT PERFORMED *****

BCFBAF Program (v3.01) Results:

=====

SMILES : c1c(F)ccc(N(C(C)(C))C(=O)CSC)c1

CHEM :

MOL FOR: C12 H16 F1 N1 O1 S1

MOL WT : 241.33

----- BCFBAF v3.01 -----

Summary Results:

Log BCF (regression-based estimate): 1.50 (BCF = 31.3 L/kg wet-wt)

Biotransformation Half-Life (days) : 0.383 (normalized to 10 g fish)

Log BAF (Arnot-Gobas upper trophic): 1.65 (BAF = 44.5 L/kg wet-wt)

Log Kow (experimental): not available from database

Log Kow used by BCF estimates: 2.77

Equation Used to Make BCF estimate:

Log BCF = 0.6598 log Kow - 0.333 + Correction

Correction(s): Value

No Applicable Correction Factors

Estimated Log BCF = 1.496 (BCF = 31.35 L/kg wet-wt)

=====

Whole Body Primary Biotransformation Rate Estimate for Fish:

=====

TYPE	NUM	LOG BIOTRANSFORMATION FRAGMENT DESCRIPTION	COEFF	VALUE
Frag	1	Amide [-C(=O)-N or -C(=S)-N]	-0.5952	-0.5952
Frag	1	Aromatic fluoride [-F]	0.0000	0.0000
Frag	1	Fluorine [-F]	0.2759	0.2759
Frag	4	Aromatic-H	0.2664	1.0655
Frag	3	Methyl [-CH3]	0.2451	0.7353
Frag	1	-CH2- [linear]	0.0242	0.0242
Frag	1	-CH- [linear]	-0.1912	-0.1912
Frag	1	Benzene	-0.4277	-0.4277
L Kow	*	Log Kow = 2.77 (KowWin estimate)	0.3073	0.8521
MolWt	*	Molecular Weight Parameter		-0.6188
Const	*	Equation Constant		-1.5371

=====

RESULT	LOG Bio Half-Life (days)	-0.4171
RESULT	Bio Half-Life (days)	0.3827
NOTE	Bio Half-Life Normalized to 10 g fish at 15 deg C	

=====

Biotransformation Rate Constant:

kM (Rate Constant): 1.811 /day (10 gram fish)

kM (Rate Constant): 1.018 /day (100 gram fish)

kM (Rate Constant): 0.5727 /day (1 kg fish)

kM (Rate Constant): 0.3221 /day (10 kg fish)

Arnot-Gobas BCF & BAF Methods (including biotransformation rate estimates):

Estimated Log BCF (upper trophic) = 1.648 (BCF = 44.45 L/kg wet-wt)

Estimated Log BAF (upper trophic) = 1.648 (BAF = 44.45 L/kg wet-wt)

Estimated Log BCF (mid trophic) = 1.537 (BCF = 34.41 L/kg wet-wt)

Estimated Log BAF (mid trophic) = 1.537 (BAF = 34.41 L/kg wet-wt)

Estimated Log BCF (lower trophic) = 1.495 (BCF = 31.27 L/kg wet-wt)

Estimated Log BAF (lower trophic) = 1.496 (BAF = 31.3 L/kg wet-wt)

Arnot-Gobas BCF & BAF Methods (assuming a biotransformation rate of zero):

Estimated Log BCF (upper trophic) = 1.807 (BCF = 64.1 L/kg wet-wt)

Estimated Log BAF (upper trophic) = 1.843 (BAF = 69.65 L/kg wet-wt)

Volatilization From Water

=====

Chemical Name:

Molecular Weight : 241.33 g/mole
 Water Solubility : -----
 Vapor Pressure : -----
 Henry's Law Constant: 2.77E-009 atm-m³/mole (estimated by Bond SAR Method)

	RIVER	LAKE
	-----	-----
Water Depth (meters):	1	1
Wind Velocity (m/sec):	5	0.5
Current Velocity (m/sec):	1	0.05
HALF-LIFE (hours) :	3.284E+005	3.582E+006
HALF-LIFE (days) :	1.368E+004	1.493E+005
HALF-LIFE (years) :	37.46	408.6

STP Fugacity Model: Predicted Fate in a Wastewater Treatment Facility

=====

(using 10000 hr Bio P,A,S)

PROPERTIES OF:

Molecular weight (g/mol)	241.33
Aqueous solubility (mg/l)	0
Vapour pressure (Pa)	0
(atm)	0
(mm Hg)	0
Henry's law constant (Atm-m ³ /mol)	2.77E-009
Air-water partition coefficient	1.13285E-007
Octanol-water partition coefficient (Kow)	588.844
Log Kow	2.77
Biomass to water partition coefficient	118.569
Temperature [deg C]	25
Biodeg rate constants (h ⁻¹), half life in biomass (h) and in 2000 mg/L MLSS (h):	
-Primary tank	0.00 1916.82 10000.00
-Aeration tank	0.00 1916.82 10000.00
-Settling tank	0.00 1916.82 10000.00

STP Overall Chemical Mass Balance:

	g/h	mol/h	percent
Influent	1.00E+001	4.1E-002	100.00
Primary sludge	1.62E-001	6.7E-004	1.62
Waste sludge	2.41E-001	1.0E-003	2.41
Primary volatilization	1.48E-006	6.1E-009	0.00
Settling volatilization	4.01E-006	1.7E-008	0.00
Aeration off gas	9.88E-006	4.1E-008	0.00
Primary biodegradation	2.12E-003	8.8E-006	0.02
Settling biodegradation	6.34E-004	2.6E-006	0.01
Aeration biodegradation	8.35E-003	3.5E-005	0.08
Final water effluent	9.59E+000	4.0E-002	95.85
Total removal	4.15E-001	1.7E-003	4.15
Total biodegradation	1.11E-002	4.6E-005	0.11

Level III Fugacity Model (Full-Output):

=====

Chem Name :
 Molecular Wt: 241.33
 Henry's LC : 2.77e-009 atm-m³/mole (Henrywin program)
 Vapor Press : 6.04e-005 mm Hg (Mppbpwin program)
 Liquid VP : 0.000307 mm Hg (super-cooled)
 Melting Pt : 96.4 deg C (Mppbpwin program)
 Log Kow : 2.77 (Kowwin program)
 Soil Koc : 598 (KOCWIN MCI method)

	Mass Amount (percent)	Half-Life (hr)	Emissions (kg/hr)
Air	0.0132	12.4	1000
Water	10.3	1.44e+003	1000

Soil 89.3 2.88e+003 1000
Sediment 0.382 1.3e+004 0

	Fugacity (atm)	Reaction (kg/hr)	Advection (kg/hr)	Reaction (percent)	Advection (percent)
Air	1.06e-012	58.9	10.5	1.96	0.351
Water	4.7e-014	394	819	13.1	27.3
Soil	3.1e-013	1.72e+003	0	57.2	0
Sediment	5.69e-014	1.63	0.609	0.0543	0.0203

Persistence Time: 2.66e+003 hr

Reaction Time: 3.68e+003 hr

Advection Time: 9.61e+003 hr

Percent Reacted: 72.3

Percent Advected: 27.7

Half-Lives (hr), (based upon Biowin (Ultimate) and Aopwin):

Air: 12.4

Water: 1440

Soil: 2880

Sediment: 1.296e+004

Biowin estimate: 2.205 (months)

Advection Times (hr):

Air: 100

Water: 1000

Sediment: 5e+004