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Renewal Assessment Report prepared according to the Commission Regulation (EU) N° 1107/2009

FENOXAPROP-P-ETHYL

Volume 3 – B.8 (AS)

Rapporteur Member State: Austria
Co-Rapporteur Member State: Finland

Version History

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B.8. ENVIRONMENTAL FATE AND BEHAVIOUR AND ENVIRONMENTAL EXPOSURE ASSESSMENT

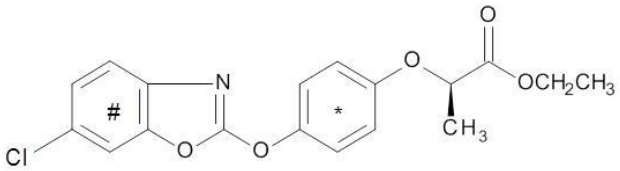
A draft version of this summary on "Fate and behaviour of fenoxaprop-P-ethyl (AE F046360) in environmental compartments" has been prepared on behalf of the Regulatory **Task Force Fenoxaprop-P-ethyl**, existing since 2013 and represented by Cheminova A/S and Bayer CropScience.

Fenoxaprop was included in Annex I to Council Directive 91/414/EEC with effect from 01 July 2009 (Commission Directive 2008/66/EC of 30 June 2008) and the associated review report is published under SANCO/3777/08 - Final dated 14 December 2007.

All data on the fate and behaviour of fenoxaprop in soil, water and air had been submitted for Annex I inclusion of fenoxaprop in the variety fenoxaprop-P-ethyl (AE F046360) by the notifier Bayer CropScience in 2003. This data were the basis for the DAR, its Addenda and were included in the Baseline Dossier.

Baseline Dossier and Supplementary Dossier have been combined by the RMS AT into one consistent document and were evaluated altogether.

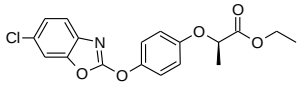
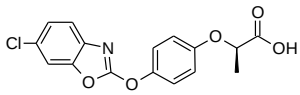
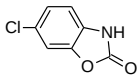
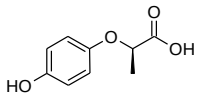
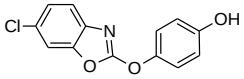
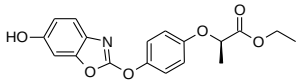
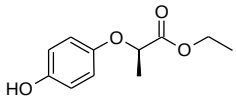
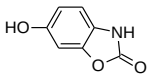
The studies investigating into the environmental fate of fenoxaprop-P-ethyl (AE F046360) were performed with the following positions of ^{14}C-radiolabel:

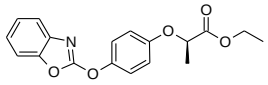
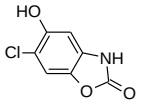
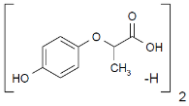


Label (#): [UL-chlorophenyl-^{14}C]-fenoxaprop-P-ethyl (AE F046360) - (ClPh label)
Label (*): [UL-phenoxy-^{14}C]-fenoxaprop-P-ethyl (AE F046360) - (Ph label)

Details of the literature search undertaken can be found in chapter B.8.6, references relied on. With the exception of Zhang et al. (2010) no relevant scientifically peer-reviewed open literature reference has been identified by the applicant for fenoxaprop-P-ethyl (AE F046360) or its metabolites with respect to fate and behaviour in the environment.

Table B.8-1 Metabolites of fenoxaprop-P-ethyl (AE F046360) considered in this summary

Code number (Synonyms)	Chemical name and molecular formula	Mol weight (g/mol)	Occurrence (% AR)	Structure
Fenoxaprop-P-ethyl[(a)] (AE F046360)	ethyl (2R)-2-{4-[(6-chloro-1,3-benzoxazol-2-yl)oxy] phenoxy}propanoate $C_{18}H_{16}ClNO_5$	361.8	Not applicable	
Fenoxaprop-P-acid[(b)] (AE F088406)	(2R)-2-{4-[(6-chloro-1,3-benzoxazol-2-yl)oxy] phenoxy}propanoic acid $C_{16}H_{12}ClNO_5$	333.7	**Aerobic soil: 85.8 %[(c)]** **Anaerobic soil: 94.8 %[(c)]** Soil photolysis: - Aquatic hydrolysis: 95.6 % (*p*H 9, 25 °C) Aerobic surface water: 101.4 % **Water/sediment: 97.2 %**	
Chlorobenz-oxazolone (AE F054014)	6-chloro-1,3-benzoxazol-2(3H)-one $C_7H_4ClNO_2$	169.6	**Aerobic soil: 19.1 %** **Anaerobic soil: 7.5 %** **Soil photolysis: 6.8 %** Aquatic hydrolysis: 102.4 % (*p*H 4, 25 °C) Aquatic photolysis: 7.1 % Aerobic surface water: 36.8 % **Water/sediment: 8.5 %**	
HOPP-acid[(d)] (AE F096918)	(2R)-2-(4-hydroxyphenoxy) propanoic acid $C_9H_{10}O_4$	182.2	Aerobic soil: - **Anaerobic soil: 74.1 %[(e)]** Soil photolysis: - Aquatic hydrolysis: 14.2 % (*p*H 9, 25 °C) Aquatic photolysis: 2.1 % Aerobic surface water: 21.0 % **Water/sediment: 26.3 %**	
Phenol metabolite (AE F040356)	4-[(6-chloro-1,3-benzoxazol-2-yl) oxy]phenol $C_{13}H_8ClNO_3$	261.7	Aerobic soil: 1.2 % Anaerobic soil: 2.2 % Soil photolysis: - Aquatic hydrolysis: - Aquatic photolysis: 5.9 % Aerobic surface water: - **Water/sediment: 13.1 %**	
Fenoxaprop-P-ethyl-dechloro-hydroxy (Fenoxaprop-dechloro-hydroxy, EHBPP, BCS-CY11271)	ethyl (2R)-2-{4-[(6-hydroxy-1,3-benzoxazol-2-yl)oxy] phenoxy}propanoate $C_{18}H_{17}NO_6$	343.3	Aerobic soil: - Anaerobic soil: - Soil photolysis: - Aquatic hydrolysis: - **Aquatic photolysis: 17.7 %** Aerobic surface water: - Water/sediment: -	
AE F029062	ethyl (2R)-2-(4-hydroxyphenoxy) propanoate $C_{11}H_{14}O_4$	210.2	Aerobic soil: - Anaerobic soil: - Soil photolysis: - Aquatic hydrolysis: 101.2 % (*p*H 4, 25 °C) Aquatic photolysis: 3.3 % Aerobic surface water: - Water/sediment: -	
Hydroxybenz-oxazolone (AE 0316854)	6-hydroxy-1,3-benzoxazol-2(3H)-one $C_7H_5NO_3$	151.1	Aerobic soil: - Anaerobic soil: - Soil photolysis: - Aquatic hydrolysis: - Aquatic photolysis: 5.5 % Aerobic surface water: - Water/sediment: -	

Code number (Synonyms)	Chemical name and molecular formula	Mol weight (g/mol)	Occurrence (% AR)	Structure
AE F031886	ethyl (2R)-2-[4-(1,3-benzoxazol-2-yloxy) phenoxy]propanoate $C_{18}H_{17}NO_5$	327.3	Aerobic soil: - Anaerobic soil: - Soil photolysis: - Aquatic hydrolysis: - Aquatic photolysis: 1.4 % Aerobic surface water: - Water/sediment: -	
AE F064124	6-chloro-5-hydroxy-1,3-benzoxazol-2(3H)-one $C_7H_4ClNO_3$	185.6	Aerobic soil: - Anaerobic soil: - Soil photolysis: - Aquatic hydrolysis: 1.0 % (*p*H 4, 40 °C) Aquatic photolysis: - Aerobic surface water: - Water/sediment: -	
HOPP-acid dimer (AE F096918 dimer)	$C_{18}H_{17}O_8$	361.1	Aerobic soil: - Anaerobic soil: - Soil photolysis: - Aquatic hydrolysis: - Aquatic hydrolysis: 10.6 % (*p*H 9, 40 °C) Aerobic surface water: - Water/sediment: -	

(a) Racemic mixture of R/S (approx. 1/1) is called AE F033171
(b) Racemic mixture of R/S (approx. 1/1) is called AE F053022
(c) Arithmetic mean of ClPh and Ph label applied to the same soil
(d) Racemic mixture of R/S (approx. 1/1) is called AF F020686
(e) Racemic mixture (AE F020686) of HOPP-acid (AE F096918) observed after application of racemic fenoxaprop-ethyl (AE F033171); HOPP acid (AE F096918) max. 49.2 % of AR in study with non-racemic fenoxaprop-P-ethyl (AE F046360) applied

B.8.1. FATE AND BEHAVIOUR IN SOIL

B.8.1.1. Route and rate of degradation in soil

B.8.1.1.1. Aerobic degradation

Studies submitted for first Annex I inclusion:

- **Stumpf & Dambach (1988)**, investigating chlorophenyl labelled fenoxaprop-P-ethyl (AE F046360) in four soils, amended by **Schwab (1993a)** and **Tarara (2004a)**
- **Buettner et al. (1992)**, investigating chlorophenyl labelled fenoxaprop-P-ethyl (AE F046360) in one soil at 21 and 11 °C
- **Buerkle et al. (1986)**, investigating phenoxy labelled racemic fenoxaprop-ethyl (AE F033171) in two soils, amended by **Schwab (1993b)** and **Tarara (2004b)**
- **Tarara (1999)**, position paper on the metabolic fate of the 4-hydroxyphenoxypropionic acid moiety

New studies submitted by the Fenoxaprop-P-ethyl Task Force:

- **Shepherd (2012)**, investigating chlorophenyl labelled fenoxaprop-P-ethyl (AE F046360) in four US soils
- **Shepherd & Ripperger (2012)**, investigating phenoxy labelled fenoxaprop-P-ethyl (AE F046360) in four US soils

Publication:

- **Zhang et al. (2010)**, investigating the enantioselective environmental behaviour of fenoxaprop-ethyl enantiomers

Reference:	**Hoe 046360 - chlorophenyl-^{14}C, aerobic soil metabolism**
Author(s), year:	Stumpf, K., Dambach, P. (1988)
Report/Doc. Number:	A39289, M-120879-01-1
Guideline(s):	US EPA OPP Guideline No. 162-1; German Guidelines of BBA part IV, 4-1
GLP:	Yes
Validity:	Yes
Status:	**Previously submitted**

including

Reference:	**Addendum to Report CB051/87 (A39289) - Study Title Hoe 046360 - chlorophenyl-^{14}C, aerobic soil metabolism**
Author(s), year:	Schwab, W. (1993a)
Report/Doc. Number:	A49512, M-138550-01-1
Guideline(s):	Not applicable
GLP:	Not applicable
Validity:	Yes
Status:	**Previously submitted**

and

Reference:	**Hoe 046360 - chlorophenyl-^{14}C, aerobic soil metabolism - Identity of volatiles as $^{14}CO_2$**
Author(s), year:	Tarara, G. (2004a)
Report/Doc. Number:	A39289
Guideline(s):	Not applicable
GLP:	Not applicable
Validity:	Yes
Status:	**Previously submitted**

[The following study report is a copy/paste of the original text in the DAR for Annex I inclusion slightly amended in order to meet editorial settings and to improve readability]

Material and methods:

The aerobic metabolism of [UL-^{14}C-chlorophenyl]-labelled fenoxaprop-P-ethyl (AE F046360, called Hoe 046360 in the report) was studied in four agricultural soils at an application rate of 0.5 mg a.i./kg corresponding to a field application rate of 0.375 kg ai/ha (5 cm soil depth, 1.5 g/cm^3 soil density). The test substance was dissolved in ethanol. Treated soils were incubated in both closed an open systems under aerobic conditions at 20 ± 2 °C and were kept at a moisture content of 40 % MWHC. The closed systems were equipped with traps to collect volatile radiocarbon products (ethanolamine/methoxyethanol for CO_2 and methoxyethanol for other volatiles). Soils were sampled in two replicates immediately after treatment and at 1, 3, 7, 15, 30, 64 and 100 days after treatment.

Soil residues were extracted firstly with acetonitrile/water (4/1) and secondly with acetonitrile/conc. HCl, 9/1 (v/v, residue method to further characterize the NER fraction). Extractable residues were identified and quantified using radio-HPLC (reversed phase) and gradient elution technique (water *p*H 3 and acetonitrile). The structures of the compounds were compared to analytical reference standards. Bound residues were measured by combustion of the dried soils. For the measurements of $^{14}CO_2$ and of volatile degradation products the absorption solutions were transferred into 50 ml graduated flasks and, after rinsing thoroughly, made up to the mark with methanol and radioactivity was measured by LSC.

Table B.8.1.1.1-1 Soil Characteristics

Soil (USDA)	% Sand	% Silt	% Clay	% OM	*p*H ($CaCl_2$)	CEC (meq/100 g)	MWHC (g/100 g)	Biomass (mg C/100 g)
Sandy loam SL V (Germany)	58.8	34.3	6.9	1.28	5.6	5.6	36.2	Begin: 15.0 End: 15.3
Loamy sand LS 2.2 (Germany)	79.7	11.2	9.1	4.53	5.8	10.6	33.0	Begin: 18.0 End: 14.3
Sandy loam SL S (US)	55.3	33.1	11.6	2.27	5.2	5.2	32.5	Begin: 20.9 End: 24.3
Silt loam SL 2 (US)	10.8	70.2	19.0	1.20	5.2	18.4	45.6	Begin: 14.0 End: 26.9

Findings:

For all soils a fast decline of extractable radioactivity was observed ranging from 92.4 % to 97.1 % AR by day 0 to values of 3.2 % to 6.9 % by the end of the study (day 100). The non-extractable residues increased up to 50 % - 70 % AR until study termination pending on the soil type. The values for CO_2 were 10 %, 25.4 %, 25.3 % and 32.5 % AR at day 100 for soils loamy sand LS 2.2, silt loam SL 2, sandy loam SL S and sandy loam SL V, respectively. No other volatiles could be measured during the study (< 0.1 % AR).

Chromatographic analysis of the soil extracts showed fenoxaprop-P-acid (AE F088406, called Hoe 088406 in the report, max. 81.1 % AR) and chlorobenzoxazolone (AE F054014, called Hoe 054014 in the report, max. 19.1 % AR) as main metabolites. The phenol metabolite (AE F040356, called Hoe 040356 in the report) was shown to be a minor metabolite (< 2 % AR). Several other metabolites were detected sporadically but due to their very low concentrations (≤ 3.4 % AR in total) identifications were not possible.

About 50 % of the non-extractable radioactivity was hydrolysed by treatment with a strong mineral acid (residue method) from soil. The radioactivity in the acidic extracts consisted to about 80 to 100 % of chlorobenzoxazolone (AE F054014).

Table B.8.1.1.1-2 Time course of degradation of fenoxaprop-P-ethyl (AE F046360) and formation of metabolites in soils (% AR, mean of duplicate samples, numbers shaded in grey indicate exceedance of 5 % AR)

DAT	Extractable (ACN/H_2O)	Fenoxaprop -P-ethyl (AE F046360)	Fenoxaprop -P-acid (AE F088406)	Chloro-benzoxa-zolone (AE F054014)	Phenol metabolite (AE F040356)	$^{14}CO_2$	NER (including ACN/conc. HCl extract)	Total
				Sandy loam SL V				
0	95.5	95.5	< 0.1	< 0.1	< 0.1	n.d.	0.4	95.9
1	84.1	11.4	67.3	5.6	< 0.1	0.4[(b)]	8.3	92.8
3	68.1	2.9	58.7	6.0	0.8	1.7[(b)]	22.8	92.6
7	33.6	2.0	27.8	2.7	1.2	5.6	51.7	90.8
15	16.5	0.7	9.4	3.4	0.5	13.7	55.9	86.1
30	9.9	3.8	3.1	2.2	0.9	21.3	58.6	89.7
64	4.6	2.2	1.0	1.1	0.4	28.1	59.2	91.9
100	3.2	2.0	0.5	0.5	0.2	32.5	55.9	91.5
CS[(a)]	3.5	1.7	1.0	0.7	0.2	32.5	55.7	91.7
				Loamy sand LS 2.2				
0	97.1	97.1	< 0.1	< 0.1	< 0.1	n.d.	0.8	97.9
1	92.0	13.1	73.1	5.9	< 0.1	0.1	2.3	94.4
3	87.2	< 0.1	81.1	6.2	< 0.1	0.3	8.1	95.5
7	80.1	2.0	63.9	12.8	< 0.1	0.7	14.1	94.9
15	66.6	< 0.1	54.2	19.1	0.4	2.2	25.6	94.3
30	18.9	4.7	6.3	4.7	0.9	4.7	59.3	82.8
64	8.0	3.8	1.8	1.7	0.2	7.7	60.3	76.0
100	6.9	3.0	1.2	2.5	< 0.1	9.7	70.1	86.6
CS[(a)]	10.0	2.5	4.9	2.8	< 0.1	9.7	67.8	87.5
				Sandy loam SL S				
0	96.9	96.9	< 0.1	< 0.1	< 0.1	n.d.	0.5	97.4
1	86.7	30.7	48.6	7.5	< 0.1	0.4	6.6	93.6
3	71.2	18.9	37.0	14.9	0.4	1.5	20.7	93.4
7	44.2	6.8	28.5	7.6	1.2	5.0	42.4	91.6
15	18.8	1.7	9.4	6.4	0.4	11.4	64.6	94.7
30	9.1	4.0	2.8	1.7	0.3	16.8	62.9	88.8
64	4.4	2.2	0.6	1.4	0.1	21.9	65.6	91.8
100	3.7	1.5	2.1	1.4	0.1	25.3	61.6	90.5
CS[(a)]	4.6	1.6	1.4	1.3	0.1	25.3	63.5	93.3
				Silt loam SL 2				
0	92.4	92.4	< 0.1	< 0.1	< 0.1	n.d.	2.1	94.4
1	77.4	22.5	41.9	13.1	< 0.1	0.4	12.7	90.5
3	50.6	7.0	29.6	13.8	0.4	2.0	34.0	86.6
7	30.4	4.1	14.8	11.2	0.3	6.2	51.0	87.5
15	15.6	3.0	3.4	9.3	< 0.1	11.6	51.1	78.3
30	9.9	3.3	1.3	4.4	0.4	16.9	55.5	82.2
64	3.7	1.8	0.4	1.1	0.1	22.3	53.8	79.7
100	3.3	1.7	0.6	1.1	< 0.1	25.4	49.4	78.1
CS[(a)]	5.3	2.5	0.6	1.9	< 0.1	25.4	50.0	80.7

(a) CS…closed system day 100
(b) Extrapolated
< 0.1 % denotes limit of detection

Conclusions:

The aerobic metabolism of fenoxaprop-P-ethyl (AE F046360) is suggested to occur via ester hydrolysis forming the free acid fenoxaprop-P-acid (AE F088406), which is still herbicidal active. The further degradation leads mainly to the benzoxazole fragment chlorobenzoxazolone (AE F054014). The phenolic metabolite (AE 040356) is of minor importance.

The results demonstrate a rather fast breakdown of the parent and its metabolites in soil connected with the formation of considerable amounts of soil bound residues and CO_2.

Comments RMS AT:

- The study broadly follows OECD guideline 307 and is still considered reliable.
- Total recovery is below 90 % of AR in several samples, particularly in LS 2.2 and SL 2 soil at later samplings. However, this is not considered to invalidate the study or parts of the study as parent residues are clearly below 10 % of AR at onset of samples with insufficient recovery in these two soils. Maximum occurrence of fenoxaprop-P-acid (AE F088406) is not affected by samples with insufficient recovery. In case of chlorobenzoxazolone (AE F054014) there is some uncertainty about the maximum occurrence in soil SL 2 as highest amounts of residues (13.8 % AR) were measured in samples with 86.6 % AR total recovery only. However, the possibly insufficient recovery of chlorobenzoxazolone (AE F054014) at this sampling point is considered to give a more conservative degradation *DegT50* for chlorobenzoxazolone in that soil. Notice that maximum occurrence of chlorobenzoxazolone (AE F054014) in aerobic soils is 19.1 % AR.
- It may be noted that the harsh extracts (ACN/conc. HCL) applied to further characterize soil residues remaining after the first extraction step (ACN/H_2O) mainly consisted of chlorobenzoxazolone (AE F054014) as well as an unknown metabolite ('m5'), exceeding 10 % AR in one sample (11.9 % AR, soil LS 2.2, closed system, 100 DAT). Notice that in two of the field studies (Belyk & Gadsby, 1991a and 1991b) a similar harsh extraction method (HRAV Analytical Method: HRAV-4B) was applied to quantitatively convert fenoxaprop-P-ethyl (AE F046360) and fenoxaprop-P-acid (AE F088406) into chlorobenzoxazolone (AE F054014).
- The study was re-assessed for degradation rates by Oberdoerster et al. (2016).

Reference:	**Hoe 046360-chlorophenyl-U-^{14}C aerobic soil metabolism study at 11 and 21 °C**
Author(s), year:	Buettner, B., Schweighoefer, U., Kuenzler, K. (1992)
Report/Doc. Number:	A47274, M-135697-01-1
Guideline(s):	Criteria for registration of pesticides, Ministry of the Environment, Denmark, 1987
GLP:	Yes
Validity:	Non-reliable (refer comment section)
Status:	**Previously submitted**

[The following study report is a copy/paste of the original text in the DAR for Annex I inclusion slightly amended in order to meet editorial settings and to improve readability]

Material and methods:

The degradation of [chlorophenyl-UL-^{14}C]-labelled fenoxaprop-P-ethyl (AE F046360, called Hoe 046360 in the report) was studied under aerobic conditions in a sandy loam soil (SL V) at 21 ± 2 °C and at 11 ± 2 °C in the dark. Samples were maintained at 40 % MWHC. The test substance was applied in an amount of 0.12 mg a.i./kg corresponding to 0.09 kg/ha (5 cm soil depth, 1.5 g/cm^3 soil density), dissolved in acetone. Flasks were fitted with a trap for absorption of volatiles (paraffin oil coated quart wool for non-polar volatiles and soda lime for CO_2 absorption). At the end of the incubation period, from each absorption tube the sodium lime was filled into an Erlenmeyer flask and analysed for $^{14}CO_2$. The absorption vessel was filled with 10 ml Carbo-Sorb. A gentle stream of air was then sucked through the apparatus and 50 ml HCl (18 %) were dropped into the flask. After stirring and heating the flask the radioactivity absorbed in Carbo-Sorb was measured.

Soil samples were continuously extracted with acetonitrile/water (8/2, v/v) using a flow through apparatus. Samples (2 replicates) were taken directly after application and on days 1, 3, 7, 14, 30, 59 and 98. Re-extraction using 100 ml solvent did not reveal additional radioactivity. 25 g of the non-extractable residues were hydrolysed by adding a mixture of 90 ml of acetonitrile and 10 ml hydrochloric acid (10 N) and heating to reflux for 6 hours. Three phases were separated: an upper acetonitrile phase which was investigated by HPLC, a water phase and a solid residue. Analyses were carried out by TLC and HPLC with gradient elution technique (water pH 2.5 and acetonitrile).

Table B.8.1.1.1-3 Soil Characteristics

Soil (BBA)	% Sand	% Silt	% Clay	% OM	*p*H ($CaCl_2$)	CEC (meq/100 g)	% MWHC	Biomass (mg C/100g)
Sandy loam, SL V (Germany)	54.4	34.4	11.3	1.55	5.8	6.9	29.9	Begin: 15.7 End: 9.2

Findings:

For the 11 °C series the total recoveries ranged from 91.1 to 101.2 % except the day 7 samples, where the mean was 60.2 %. Due to this low recovery the day 7 samples were regarded as outliers and were not used for evaluation of the kinetic data. The recoveries of the 21 °C series ranged from 84.9 to 111.3 % AR.

The CO_2 production was almost identical at the end of the study for both series accounting for 15.1 % AR (11 °C) and 14.3 % AR (21 °C). However the samples of day 1 to day 59 showed clearly that mineralization was faster at higher temperatures.

Other volatiles were evolved at a very low rate of 0.02 % AR (except day 98 at 11 °C, where it was 0.7 % AR).

Extractable residues decreased during the course of the study to 40.4 % AR (11 °C) and 19.8 % AR (21 °C) until study termination. Non-extractable residues increased to 34.9 % (11 °C) and 57.0 % AR (21 °C). Formation on non-extractable residues was clearly enhanced at higher temperature.

Up to 8 radioactive products were separated and four of these were clearly shown to be identical with the available reference substances. Major metabolites were fenoxaprop-P-acid (AE F088406, called Hoe 088406 in the report), the free acid of fenoxaprop-P-ethyl (maximum 65 % day 1, 11 °C and day 3, 21 °C) and chlorobenzoxazolone (AE F054014, called Hoe 054014 in the report, maximum 20.6 % AR day 14, 11 °C and 15 % AR day 7, 21 °C). The phenol metabolite (AE F040356, called Hoe 040356 in the report, never exceeded 5 % AR. Four unidentified metabolites ('M1' to 'M4') appeared sporadically, generally in low amounts (≤ 5.1 %, observed at one sampling point only).

Some representative samples of the non-extractable residues were hydrolysed under acidic conditions. Besides very small amounts of unknown metabolites only chlorobenzoxazolone (AE F054014) was detectable (9 - 21 % AR). The radioactivity which was not extractable even after this drastic hydrolyses step accounted for 8 to 22 %.

Table B.8.1.1.1-4 Time course of degradation of fenoxaprop-P-ethyl (AE F046360) and formation of metabolites in a sandy loam soil at two different temperatures (% AR, mean of duplicate samples, numbers shaded in grey indicate exceedance of 5 % AR)

DAT	Extractable (ACN/H_2O)	Fenoxaprop-P-ethyl (AE F046360)	Fenoxaprop-P-acid (AE F088406)[(a)]	Chlorobenz-oxazolone (AE F054014)	Phenol metabolite (AE F040356)	$^{14}CO_2$	NER	Total
				11 °C				
0	93.7	70.8	18.0	4.8	0.0	-	-	93.7
1	88.9	19.9	65.0	3.5	0.0	0.0	2.9	91.8
3	88.2	19.5	61.7	3.2	1.2	0.2	6.4	94.7
7	47.2	3.7	35.2	5.6	1.0	0.6	12.4	60.2
14	69.3	6.0	42.8	20.6	0.0	1.5	30.3	101.2
30	73.0	10.2	52.8	6.5	2.9	1.7	19.9	94.6
59	69.4	8.4	47.8	5.2	3.4	2.2	26.0	97.6
98	40.4	4.7	24.8	8.5	1.2	15.1	34.9	91.1
				21 °C				
0	95.4	78.0	16.2	1.2	0.0	-	-	95.4
1	84.7	22.7	58.4	3.6	0.0	0.3	4.8	89.8
3	79.9	13.5	64.7	1.7	0.0	1.0	14.7	95.6
7	75.1	4.9	52.6	14.9	0.0	3.2	24.4	102.8
14	66.9	1.7	56.2	5.7	3.4	4.1	40.2	111.3
30	32.8	7.0	23.1	2.7	0.0	8.9	51.3	93.0
59	19.7	1.2	2.1	9.0	1.6	12.7	52.5	84.9
98	19.8	2.9	9.2	2.8	4.9	14.3	57.0	91.1

(a) Racemic fenoxaprop-acid (AE F053022) used as chromatographic reference substance

Comments RMS AT:

- The study broadly follows OECD guideline 307 and results obtained are more or less in line with results from other lab degradation studies conducted with fenoxaprop-P-ethyl (AE F046360). However, residue data for the parent as well as for the metabolites show significant scatter in both, the 11 °C as well as in the 21 °C study (see details on individual replicates provided in the tables below). This also leads to partly inconsistent mass balances ranging from 60.2 to 111.3 % AR, particularly for the 7 and 14 DAT. In view of the RMS AT, residue data in this study are uncertain and not sufficiently robust to allow estimating maximum occurrences of metabolites as well as kinetic evaluation (parent and metabolites). On overall the RMS AT considers **this study non-reliable**.

Table B.8.1.1.1-5 Residue data (% AR, two replicates) in the 11 °C study

DAT	Fenoxaprop-P-ethyl (AE F046360)	Fenoxaprop-P-acid (AE F088406)	Phenol metabolite (AE F040356)	Chloro-benzoxa-zolone (AE F054014)	M1	M2	M3	M4
0	70.5	14.9	0.0	6.4	0.0	0.0	0.0	0.0
0	71.2	21.1	0.0	3.3	0.0	0.0	0.0	0.0
1	25.3	72.3	0.0	3.2	0.0	0.0	1.0	0.0
1	14.5	57.7	0.0	3.9	0.0	0.0	0.0	0.0
3	22.4	62.8	0.0	2.9	0.0	0.0	3.4	0.0
3	16.7	60.6	2.4	3.5	0.0	0.0	0.0	1.7
7	7.4	31.6	2.1	4.2	0.0	0.0	0.0	0.0
7	0.0	38.9	0.0	7.0	0.0	0.0	0.0	3.3
14	12.0	36.0	0.0	9.5	0.0	0.0	0.0	0.0
14	0.0	49.6	0.0	31.7	0.0	0.0	0.0	0.0
30	8.5	50.9	0.0	7.5	0.0	1.3	0.0	0.0
30	11.8	54.6	5.8	5.4	0.0	0.0	0.0	0.0
59	8.0	58.3	0.0	4.5	0.0	0.0	0.0	0.0
59	8.8	37.3	6.8	5.9	0.0	0.0	0.0	9.2
98	4.5	20.5	0.0	13.8	0.0	0.0	0.0	0.0
98	4.9	29.1	2.4	3.2	0.0	0.0	0.0	2.5

Table B.8.1.1.1-6 Residue data (% AR, two replicates) in the 21 °C study

DAT	Fenoxaprop-P-ethyl (AE F046360)	Fenoxaprop-P-acid (AE F088406)	Phenol metabolite (AE F040356)	Chloro-benzoxa-zolone (AE F054014)	M1	M2	M3	M4
0	76.0	23.9	0.0	0.0	0.0	0.0	0.0	0.0
0	79.9	8.5	0.0	2.5	0.0	0.0	0.0	0.0
1	15.2	53.7	0.0	1.8	0.0	0.0	0.0	0.0
1	30.2	63.1	0.0	5.5	0.0	0.0	0.0	0.0
3	12.0	65.8	0.0	1.6	0.0	0.0	0.0	0.0
3	15.1	63.6	0.0	1.7	0.0	0.0	0.0	0.0
7	9.8	49.5	0.0	3.7	0.0	0.0	0.0	3.3
7	0.0	55.6	0.0	26.2	0.0	0.0	2.2	0.0
14	0.0	63.1	6.8	9.2	0.0	0.0	0.0	0.0
14	3.4	49.3	0.0	2.1	0.0	0.0	0.0	0.0
30	8.7	23.6	0.0	5.5	0.0	0.0	0.0	0.0
30	5.2	22.6	0.0	0.0	0.0	0.0	0.0	0.0
59	0.0	0.0	0.0	11.8	0.0	0.0	10.2	0.0
59	3.9	4.3	3.1	6.1	0.0	0.0	0.0	0.0
98	5.9	6.9	5.3	5.6	0.0	0.0	0.0	0.0
98	0.0	11.4	4.5	0.0	0.0	0.0	0.0	0.0

Reference:	**Hoe 033171-dioxyphenyl-l-^{14}C: Aerobic Soil Metabolism Study**
Author(s), year:	Buerkle, W.L., Schuld, G., Grundschoettel, P. (1986)
Report/Doc. Number:	A32791, M-112654-01-1
Guideline(s):	EPA Pesticide Assessment Guidelines, N, 162-1
GLP:	Yes
Validity:	Supplemental information (refer to comment section)
Status:	**Previously submitted**

including

Reference:	**Addendum to Report CBQ58/85 (A32791), study Title: Hoe 033171-dioxyphenyl-l-^{14}C, aerobic soil metabolism study**
Author(s), year:	Schwab, W. (1993b)
Report/Doc. Number:	A49511, M-138549-01-1
Guideline(s):	Not applicable
GLP:	Not applicable
Validity:	Supplemental information (refer to comment section)
Status:	**Previously submitted**

and

Reference:	**Validity of study "aerobic soil metabolism study using Hoe 033171-dioxyphenyl-1-^{14}C**
Author(s), year:	Tarara, G. (2004b)
Report/Doc. Number:	C045288
Guideline(s):	Not applicable
GLP:	Not applicable
Validity:	Yes
Status:	**Previously submitted**

[The following study report is a copy/paste of the original text in the DAR for Annex I inclusion slightly amended in order to meet editorial settings and to improve readability]

Material and methods:

The degradation of [phenoxy-^{14}C]-labelled racemic fenoxaprop-ethyl (AE F033171, called Hoe 033171 in the report, 50:50 racemic mixture of both optical isomers (R/S) of fenoxaprop-ethyl) has been studied in two soils at 22 ± 2 °C under aerobic conditions. The soil samples were treated at a rate of 3.59 mg a.i./kg soil, corresponding to an application rate of 1.0 kg a.i./ha (2 cm soil depth, 1.4 g/cm^3 soil density). For the test air dried soils were passed through a 1 mm sieve. Samples were kept at 40 % MWHC in the dark. Soils were treated in two replicates with the test substance dissolved in ethanol. For the total degradation study flasks were fixed in the closed aeration system with an absorption unit containing a mixture of ethanolamine and methanol for CO_2 absorption and sulphuric acid and diethylene glycol to catch other volatiles. The formed $^{14}CO_2$ was absorbed in 8 mL of Carbo-Sorb and radioactivity was measured by LSC.

Soil samples were extracted three times with acetonitrile/water (4/1, v/v) and afterwards three times with acetonitrile/water (4/1, v/v) whereby the water had been acidified to *p*H 3 with sulphuric acid. Analyses were carried out by HPLC (^{14}C-detector) with gradient elution technique.

Table B.8.1.1.1-7 Soil Characteristics

Soil (BBA classif.)	% Sand	% Silt	% Clay	% OM	*p*H ($CaCl_2$)	CEC (meq/100 g)	% Moist. capacity	Organisms/ml
Silt loam SL 2 (Leland, US)	7.2	70.4	22.4	1.6	6.9	21.3	34.2	Aerob. Bact.: 1.8 × 10^6 Fungi: 6.5 × 10^5 Actinomyc.: 800
Silty sand SS 2 (Frankfurt, Germany)	69.5	28.4	2.1	8.11	7.0	11.5	44.4	Aerob. Bact.: 1.5 × 10^7 Fungi: 1.2 × 10^5 Actinomyc.: 200

Findings:

Total recoveries were in the range of 74 - 98 % AR in individual samples. The average total recovery of radioactivity was relatively low (85.4 % on average for the silt loam and 82.6 % for the silty sand). It must be taken into account that evolved $^{14}CO_2$ and other volatiles were determined at separate samples, which may lead to some variability in number possible in the portions of $^{14}CO_2$. In the additional statement (Tarara, 2004b) an explanation was given why this study is considered valid although the recoveries were not optimal (< 90 %). There was no sign for a loss or an inconsistency for the portion of extractable radioactivity in the course of this study. The amounts and the profiles of extractable residues are therefore adequately described. Very well degradable components can cause difficulties to obtain acceptable material balances due to errors in the collection of the volatile materials formed, mainly $^{14}CO_2$ and losses in the process of the determination of non-extractable radioactivity. In this study there is no indication that the losses were simply due to the experimental set up and the latter point was considered the most important one in this case. This is the overall time required for the work-up of a sample, namely needed to dry extracted soil in preparation of the combustion. Microbial activity can recover during this time to result in a continuation of the degradation process in the extracted soil in the phase of drying. This effect does not play a significant role when overall conversion of residues applied was low in a study. However, when degradation had already been in an advanced stage during the incubation, this effect is able to contribute to losses in material balances at a significant level. The formation of $^{14}CO_2$ continued thus lowering the portion of non-extractable radioactivity. For this study here this effect was estimated to lower the portion of non-extractable radioactivity by 10 to 20 % AR in the course of the study.

Whereas extractable radioactivity decreased continually during the course of the study the proportion of the non-extractable residues reached constant levels at approximately 28 % (soil SL 2) and 32 % AR (soil SS 2) until study termination. Mineralization to CO_2 was high accounting for 54.7 % AR and 44.8 % AR at the end of the incubation time. Other volatile compounds were found only sporadically, in negligible amounts.

The parent substance, racemic fenoxaprop-ethyl (AE F033171) disappeared very quickly to form racemic fenoxaprop-acid (AE F055022, called Hoe 053022 in the report,) as the predominant metabolite. Other metabolites, including AE F020686 (the racemic mixture of HOPP-acid, AE F096918), were detected as minor components. Due to their occurrence at a very low level (individual up to 3.6 % AR), these components were not further identified.

The results from work on chlorophenyl-label in other studies implicate the cleavage at the heterocyclic ether bond in the parent molecule (AE F033171) or fenoxaprop-acid (AE F053022) to form a phenol-type component, hydroxyphenyloxypropionic acid. As the parent compound was applied in its racemic form, this study is also able to show the formation and degradation of the P-isomer of the propionic acid (HOPP-acid) with the code AE F096918. However, there were no indications for an occurrence of this propionic acid as major metabolite in the course of the study.

The fractions of the 1st and the 2nd extract which were eluted in the same retention interval were assumed to be generated by the same component. Therefore their proportions were added numerically.

Table B.8.1.1.1-8 Distribution of radioactivity in two soils (% AR)

DAT	1st extract (acetonitrile/ water)	2nd extract (acetonitrile/ acidified water)	Sum of the extracts	NER	$^{14}CO_2$	Total
			Silt loam SL 2			
0	85.5	8.7	94.2	3.6	-	97.8
1	54.5	14.3	68.8	13.3	1.3	83.4
2	47.1	16.2	63.3	15.6	3.5	82.2
4	40.8	13.1	53.9	22.0	7.3	83.3
8	24.9	10.3	35.2	26.3	17.9	79.4
16	9.8	6.9	16.7	31.9	34.2	82.8
32	4.8	4.8	9.7	28.0	46.6	84.2
64	2.3	2.7	5.0	28.2	54.6	87.8
			Silty sand SS 2			
0	82.3	8.7	91.0	4.5	-	93.4
1	61.3	9.5	70.8	13.3	1.3	85.0
2	51.7	10.9	62.6	18.3	3.1	83.9

4	44.7	8.0	52.7	22.9	6.6	82.3
8	37.1	7.6	44.8	24.3	13.8	82.9
16	10.3	4.3	14.6	33.4	26.0	73.9
32	6.5	3.1	9.6	29.7	37.2	76.6
64	3.8	1.5	5.3	32.1	44.8	82.2

Table B.8.1.1.1-9 Time course of degradation of racemic fenoxaprop-ethyl (AE F033171) and formation of metabolites in two soils (% AR, mean of duplicate samples, numbers shaded in grey indicate exceedance of 5 % AR)

Day	Racemic fenoxaprop-ethyl (AE F033171)	Racemic fenoxaprop-acid (AE F053022)	Sum of unknown metabolites
		Silt loam SL 2	
0	84.3	7.3	5.2
1	26.3	39.5	3.1
2	18.4	38.2	6.5
4	5.6	43.6	4.9
8	2.4	26.9	5.9
16	1.5	12.5	2.7
32	1.4	4.9	3.4
64	1.5	1.6	1.8
		Silty sand SS 2	
0	80.5	8.1	2.4
1	7.1	63.0	0.5
2	9.9	56.9	1.5
4	7.6	45.2	0.0
8	4.7	40.2	0.0
16	3.8	10.8	0.0
32	1.5	7.6	0.5
64	4.0	1.4	0.0

Conclusions:

The rate of CO_2-formation was high, 55 % AR and 45 % AR after 64 days in soils SL 2 and SS 2, respectively. Bound residues amounted for approx. 30 % AR at the end of the study.

Comments RMS AT:

- Due to the fact, that this study did not investigate fenoxaprop-P-ethyl (AE F046360) but its 1:1 racemic mixture fenoxaprop-ethyl (AE F033171), **this study is considered as supplemental information**, only. As no chiral analysis was applied, no information is available on individual isomers. The RMS AT notes that the overall degradation pattern obtained in this study is indeed similar to results obtained in studies investigating non-racemic fenoxaprop-P-ethyl (AE F046360). However, results from Zhang et al. (2010), who investigated individual enantiomers of fenoxaprop-ethyl and fenoxaprop-acid in Chinese soils indicate that the R-enantiomers ('P') are usually more slowly degrading than the S-enantiomers ('M'). For that reason degradation rates obtained from the racemic mixtures of fenoxaprop-ethyl (AE F033171) or of fenoxaprop-acid (AE F053022) should in general not be used as a surrogate for the pure R-enantiomers fenoxaprop-P-ethyl (AE F0463609 and fenoxaprop-P-acid (AE F088406).

Reference:	**Fenoxaprop-P-Ethyl -Metabolic fate of the 4-hydroxyphenoxypropionic acid moiety and discussion of the radiolabel position**
Author(s), year:	Tarara, G. (1999)
Report/Doc. Number:	C005529, M-192232-01-1
Guideline(s):	Not applicable
GLP:	Not applicable
Validity:	Not relevant (refer to comment section)

Status:	**Previously submitted**

Comments RMS AT:

- This position paper provides argumentations why metabolism studies were preferably conducted using the label in the chlorophenyl position and why studies with phenoxy labelled parent would not result in a significantly different understanding of the metabolism of fenoxaprop-P-ethyl (AE F046360) in plant, soil or animals. For renewal, sufficient environmental studies are available with fenoxaprop-P-ethyl (AE F046360) labelled in both positions, the chlorophenyl as well as phenoxy moiety, thus **this position paper is considered irrelevant**.

Reference:	**[Chlorophenyl-UL-^{14}C]fenoxaprop-P-ethyl: Aerobic soil metabolism in four US soils**
Author(s), year:	Shepherd, J. J. (2012)
Report/Doc. Number:	MEFPL006-1, M-424708-02-1
Guideline(s):	OECD Guideline 307 (2002), OPPTS 835.4100 (2008)
GLP:	Yes
Validity:	Yes
Status:	**New submission**

Executive Summary:

The biotransformation of [UL-chlorophenyl-^{14}C]-fenoxaprop-P-ethyl was investigated under aerobic conditions of the laboratory in four US soils Pikeville (sandy loam), Sanger (sandy loam), Porterville (loamy sand) and Springfield (silt loam) following incubation in the dark at 20 °C and soil moisture between *p*F 2 and *p*F 2.5 for 37 days in maximum. A nominal test concentration of 0.96 mg active substance/kg soil was applied based on four times the single maximum rate of 90 g a.s./ha in the field. For the two soils Pikeville and Sanger sterile samples were investigated in addition to the non-sterile, microbial active test systems.

Total recovery of applied radioactivity (AR) ranged from 94.5 to 103.7 % (soil Pikeville), 91.2 to 105.4 % (Sanger), 97.9 to 102.3 % (Porterville) and from 96.6 to 101.2 % for soil Springfield. For sterile test systems the overall mean total recovery was 97.7 ± 1.3 % AR for soil Pikeville and 97.7 ± 0.4 % for soil Sanger.

Total extractable radioactivity decreased from 99.9 % (soil Pikeville), 99.8 % (Sanger), 99.8 % (Porterville) and 99.6 % (Springfield) by day zero to 15.0 %, 9.8 %, 26.0 % and 12.5 %, respectively, by day 37. For sterilised soil samples total extractable radioactivity decreased from 80.5 % to 47.6 % in soil Pikeville and from 87.6 % to 53.8 % in soil Sanger following the same incubation period.

The decrease of extractable radioactivity was paralleled by formation of non-extractable residues (NER) to account for 65.7 % of AR (Pikeville), 66.6 % (Sanger), 63.5 % (Porterville) and 68.7 % (Springfield) after 37 days. In sterilised test systems, NER were 48.1 % AR (Pikeville) and 42.4 % (Sanger) in maximum after 37 days.

Micro-biological degradation finally resulted in ^{14}C-carbon dioxide formation at 16.3 % AR (Pikeville), 16.6 % (Sanger), 8.4 % (Porterville) and 15.4 % (Springfield) in maximum, each by day 37. Formation of other organic volatiles was negligible (< 0.1 % AR). Formation of $^{14}CO_2$ in sterilised soils was minimal (≤ 1.1 % AR). The results confirmed microbial processes to be the predominant factor of influence for the biotransformation of fenoxaprop residues in soil.

In non-sterile samples, values of fenoxaprop-P-ethyl decreased from 99.9 % AR (Pikeville), 98.7 % (Sanger), 99.4 % (Porterville) and 95.8 % (Springfield) by day 0 to 3.3 % (Pikeville) and below the limit of detection (LOD) of 0.7 % AR for the other soils after 37 days of incubation.

Degradation of fenoxaprop-P-ethyl (AE F046360) proceeded rapidly via biologically induced ester hydrolysis to fenoxaprop-P-acid (AE F088406) observed at maximum values of 49.9 % AR (DAT 0.5, Pikeville), 77.6 % (DAT 3, Sanger), 87.2 % (DAT 1, Porterville) and 81.5 % (DAT 0.25, Springfield). Values for fenoxaprop-P

acid decreased to 4.0 % (Pikeville), 7.5 % (Sanger), 21.7 % (Porterville) and 6.4 % AR (Springfield) at the end of the study.

In addition, the minor metabolite chlorobenzoxazolone (AE F054014) was observed at maximum values of 7.8 % AR (DAT 1, Pikeville), 1.5 % (DAT 1 and DAT 37, Sanger), 4.6 % (DAT 37, Porterville) and 2.4 % (DAT 37, Springfield).

Fenoxaprop-P-ethyl (AE F046360) was rapidly degraded in soil forming fenoxaprop-P-acid (AE F088406) as the predominant degradation product. Degradation was paralleled by the formation of chlorobenzoxazolone (AE F054014) and biologically mediated non-extractable residues.

Material and methods:

Test Material**:** [UL-chlorophenyl- ^{14}C]-fenoxaprop-P-ethyl (AE F046360)
Specific radioactivity: 3.97 MBq/mg (107.3 µCi/mg, 38.82 mCi/mmole)
Radiochemical purity: > 98 %
Chemical purity: > 98 %
Ratio of enantiomers: R : S = 99.3 : 0.7
Sample/Batch ID: KML 9054 / C-1143

Soils
The soils had been fresh collected from the field followed by sieving to 2 mm.

Table B.8.1.1.1-10 Characteristics of test soils

Soil	Pikeville	Sanger	Porterville	Springfield
Geographic Location (City / State / Country)	Pikeville / North Carolina / US	Sanger / California / US	Porterville / California / US	Springfield / Nebraska / US
GPS coordinates	N 35° 48.8533‘ W 78° 04.0717‘	N 36° 42.0868’ W 119° 27.4929’	N 36° 00.492’ W 119° 04.525’	N 41° 03.725’ W 96° 15.085’
Pesticide use history	None used last five years	Paraquat, glyphosate and oxyfluorfen within previous 5 years, i.e. not same chemical class or mode of action	Several [B] applied within previous 5 years, i.e. not same chemical class or mode of action	None used last five years
Sampling depth (cm)	0-20	0-15	0-15	0-20
Storage prior to test / length	Storage at 4.0 °C (3 d)	Storage at 4.0 °C (3 d)	Storage at 4.0 °C (28 d)	Storage at 4.0 °C (9 d)
Storage at test facility	Sieved to 2 mm and acclimated to study conditions			
Textural Class (USDA)	Sandy loam	Sandy loam	Loamy sand	Silt loam
Sand [50 µm - 2 mm] (%)	62.2	64.4	79.8	14.8
Silt [2 µm - 50 µm] (%)	30.1	28.1	10.5	59.6
Clay [< 2 µm] (%)	7.7	7.5	9.7	25.6
*p*H in Water	5.7	6.8	7.0	7.0
*p*H in $CaCl_2$ (0.01 M)	5.2	6.2	6.9	6.6
*p*H, saturated paste	5.6	6.6	6.9	6.8
Organic matter (%)	2.3	0.82	0.80	3.3
Organic carbon [A] (%)	1.4	0.48	0.46	1.9
CEC (meq/100 g)	6.3	6.5	10.3	17.4
Bulk density (g/mL)	1.25	1.30	1.34	1.01
MWHC (g/100 g) at *p*F 0	37.1	31.6	25.1	44.3
MWHC (g/100 g) at 0.1 bar (*p*F 2.0)	22.5	20.7	15.8	36.4
MWHC (g/100 g) at 0.33 bar (*p*F 2.5)	12.8	9.1	8.5	25.8
Test moisture (g/100 g)	9.5	13.1	14.2	32.8
Microbial biomass (mg microbial C/100 g dry weight of soil)				
Initial (Day 0/2)	15.4	14.3	5.5	34.1
Middle (Day 15)	9.9 [B] / 7.0 [C]	10.1 [B] / 8.5 [C]	6.1	35.9
Final (Day 37)	7.4 [B] / 5.5 [C]	8.1 [B] / 6.6 [C]	5.5 [B] / 5.7 [C]	22.4 [B] / 30.8 [C]

[A)] % organic carbon = % organic matter / 1.724
[B)] Untreated control sample
[C)] Solvent-treated controls

[D)] glufosinate-ammonium, saflufenacil, glyphosate, propyzamide, picoxystrobin, spinetoram
CEC: Cation exchange capacity; MWHC: Maximum Water Holding Capacity

Experimental conditions
Samples of 50 g dry weight of soil each were filled into glass incubation flasks and pre-equilibrated prior to treatment at approximate study conditions (darkness, 20 ± 2 °C, soil moisture between *p*F 2 (0.1 bar) and *p*F 2.5 (0.33 bar)). In addition, samples of soil Pikeville and soil Sanger were sterilised via gamma irradiation. Sterilised soil samples were pre-incubated in sterilised incubation flasks; sterility was tested at each sampling interval.

At start, each sample received 0.96 mg test substance/kg soil: This rate was equivalent to four times single maximum field-use rate of 90 g a.s./ha (assuming 2.5 cm soil depth, 1.5 g/cm^3 soil density). Following application, the samples were attached to flow-through incubation systems with traps to collect ^{14}C-carbon dioxide and other volatile components. Samples were incubated and maintained at 20 ± 2 °C and at 0.1 to 0.33 bar moisture in the dark for 37 days in maximum. Untreated soil samples were incubated under the same conditions for determination of soil microbial activity.

Sampling
Duplicate samples were removed for analysis after 0, 6 and 12 hours and 1, 3, 7, 15 and 37 days of incubation while duplicates of sterilised samples were processed by 7, 15 and 37 days after treatment.

Analytical procedures
The entire soil sample of each test vessel was extracted three times successively with aqueous acetonitrile (8:2, by vol.) containing 1 % acetic acid at ambient temperature (10 min). Ambient temperature extraction was followed by two successive microwave extractions using acetonitrile (70 °C, 10 min). Each extraction step was followed by centrifugation and filtration of soil extracts. Ambient and microwave soil extracts were pooled separately.

A full ^{14}C-material balance was established for each sampling interval by determination of radioactivity in soil extracts, volatiles in traps and of non-extractable residues (NER) in soil by combustion. The determination of NER was performed by combustion/LSC of aliquots of the air-dried extracted soil. Following quantitation by LSC, analysis of concentrated aliquots of extracts was performed by reversed phase HPLC and ^{14}C-flow-through detection techniques as primary analytical methods. The limit of detection (LOD) was 0.7 % AR and the limit of quantitation (LOQ) was 0.9 % AR.

The identity of fenoxaprop-P-ethyl (AE F046360), fenoxaprop-P acid (AE F088406) and chlorobenzoxazolone (AE F054014) was confirmed by isolation of HPLC peaks from soil extracts followed initially by comparison of HPLC retention-times to reference standards. Identity of isolated HPLC peaks and corresponding standards was finally confirmed in addition by LC-MS/MS analyses.

Characterisation of NER was performed by fractionation of soil organic matter of extracted soils for a DAT 15 sampling interval to separate into humic acids, fulvic acids and humins. Identity of $^{14}CO_2$ was confirmed by co-precipitation of residues in traps for volatiles of DAT-15 via precipitation as barium carbonate.

Results and discussion:

Table B.8.1.1.1-11 Degradation of [UL-chlorophenyl-^{14}C]-fenoxaprop-P-ethyl (AE F046360) in sandy loam soil Pikeville under aerobic conditions (% AR, mean ± SD, numbers shaded in grey indicate exceedance of 5 % AR)

Component		Sampling interval (days)							
		0	0.25	0.5	1	3	7	15	37
Fenoxaprop-P-ethyl	Mean	**99.9**	**61.2**	**41.5**	**28.6**	**15.4**	**9.4**	**6.3**	**3.3**
(AE F046360)	SD	± 0.2	± 16.1	± 0.3	± 6.3	± 1.2	± 0.6	± 0.9	± 0.0
Fenoxaprop-P-acid	Mean	**0.0**	**37.2**	**49.9**	**42.7**	**43.2**	**26.6**	**10.7**	**4.0**
(AE F088406)	SD	± 0.0	± 11.7	± 1.4	± 2.0	± 0.6	± 0.6	± 0.2	± 0.1
Chlorobenzoxazolone	Mean	**0.0**	**0.8**	**2.8**	**7.8**	**6.6**	**6.4**	**6.2**	**4.7**
(AE F054014)	SD	± 0.0	± 1.2	± 0.0	± 1.7	± 0.4	± 1.6	± 0.4	± 0.3
Unidentified	Mean	**0.0**	**0.8**	**1.8**	**4.5**	**4.7**	**5.0**	**3.9**	**3.2**
Radioactivity[(a)]	SD	± 0.0	± 1.2	± 0.7	± 0.8	± 0.3	± 2.8	± 1.2	± 0.5
Total extractable	Mean	**99.9**	**100.0**	**96.0**	**83.6**	**69.9**	**47.5**	**27.1**	**15.0**
radioactivity	SD	± 0.2	± 2.1	± 0.9	± 1.8	± 1.1	± 0.1	± 0.5	± 0.0

Non-extractable radioactivity	Mean	**0.1**	**3.2**	**7.5**	**10.7**	**27.7**	**45.2**	**66.5**	**65.7**
	SD	± 0.0	± 1.3	± 0.8	± 2.1	± 0.6	± 0.2	± 2.0	± 4.0
$^{14}C-CO_2$	Mean	**0.0**	**0.1**	**0.1**	**0.2**	**1.6**	**4.5**	**8.0**	**16.3**
	SD	± 0.0	± 0.0	± 0.0	± 0.1	± 0.1	± 0.2	± 0.3	± 0.7
Other volatiles	Mean	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**
	SD	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0
Total radioactivity (%)	Mean	**100.0**	**103.3**	**103.7**	**94.5**	**99.1**	**97.1**	**101.5**	**96.9**
	SD	± 0.2	± 0.8	± 1.7	± 0.3	± 0.4	± 0.3	± 1.8	± 3.2

(a) No individual peak amount to more than 3.6 % of AR

Table B.8.1.1.1-12 Degradation of [UL-chlorophenyl-^{14}C]-fenoxaprop-P-ethyl (AE F046360) in <u>sandy loam soil Sanger</u> under aerobic conditions (% AR, mean ± SD, numbers shaded in grey indicate exceedance of 5 % AR)

Component		Sampling interval (days)							
		0	**0.25**	**0.5**	**1**	**3**	**7**	**15**	**37**
Fenoxaprop-P-ethyl (AE F046360)	Mean	**98.7**	**34.4**	**20.2**	**13.1**	**3.4**	**1.5**	**0.5**	**0.0**
	SD	± 1.9	± 1.8	± 2.3	± 0.4	± 0.2	± 0.5	± 0.7	± 0.0
Fenoxaprop-P-acid (AE F088406)	Mean	**0.0**	**63.2**	**77.0**	**69.3**	**77.6**	**56.9**	**34.5**	**7.5**
	SD	± 0.0	± 1.7	± 5.7	± 0.9	± 1.1	± 1.0	± 4.0	± 0.4
Chlorobenzoxazolone (AE F054014)	Mean	**1.1**	**0.0**	**1.3**	**1.5**	**1.3**	**0.8**	**0.0**	**1.5**
	SD	± 1.6	± 0.0	± 0.5	± 0.2	± 0.3	± 1.2	± 0.0	± 0.4
Unidentified Radioactivity[(a)]	Mean	**0.0**	**0.0**	**1.2**	**1.0**	**1.7**	**2.2**	**1.7**	**0.8**
	SD	± 0.0	± 0.0	± 0.4	± 0.3	± 0.1	± 0.0	± 0.9	± 1.1
Total extractable radioactivity	Mean	**99.8**	**97.6**	**99.8**	**84.9**	**84.0**	**61.5**	**36.7**	**9.8**
	SD	± 0.3	± 0.1	± 4.3	± 0.1	± 0.6	± 1.6	± 3.8	± 0.2
Non-extractable radioactivity	Mean	**0.2**	**3.0**	**5.3**	**6.1**	**14.6**	**30.5**	**53.8**	**66.6**
	SD	± 0.0	± 0.1	± 0.4	± 0.0	± 0.7	± 0.5	± 3.2	± 0.4
$^{14}C-CO_2$	Mean	**0.0**	**0.1**	**0.3**	**0.2**	**1.3**	**4.1**	**8.8**	**16.6**
	SD	0.0	± 0.0	± 0.2	± 0.2	± 0.1	± 0.0	± 1.3	± 0.5
Other volatiles	Mean	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**
	SD	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0
Total radioactivity (%)	Mean	**100.0**	**100.7**	**105.4**	**91.2**	**99.8**	**96.2**	**99.3**	**93.0**
	SD	± 0.3	± 0.0	± 4.4	± 0.1	± 1.3	± 1.1	± 0.6	± 0.1

(a) No individual peak amount to more than 2.3 % of AR

Table B.8.1.1.1-13 Degradation of [UL-chlorophenyl-^{14}C]-fenoxaprop-P-ethyl (AE F046360) in <u>loamy sand soil Porterville</u> under aerobic conditions (% AR, mean ± SD, numbers shaded in grey indicate exceedance of 5 % AR)

Component		Sampling interval (days)							
		0	**0.25**	**0.5**	**1**	**3**	**7**	**15**	**37**
Fenoxaprop-P-ethyl (AE F046360)	Mean	**99.4**	**50.2**	**16.1**	**8.5**	**2.3**	**0.9**	**0.7**	**0.0**
	SD	± 0.7	± 0.2	± 6.8	± 1.5	± 0.4	± 0.0	± 0.2	± 0.0
Fenoxaprop-P-acid (AE F088406)	Mean	**0.5**	**49.5**	**79.3**	**87.2**	**83.0**	**71.5**	**50.7**	**21.7**
	SD	± 0.7	± 0.8	± 2.7	± 0.8	± 0.4	± 1.1	± 1.8	± 1.0
Chlorobenzoxazolone (AE F054014)	Mean	**0.0**	**0.0**	**1.8**	**0.7**	**0.0**	**1.0**	**3.2**	**4.6**
	SD	± 0.0	± 0.0	± 1.8	± 0.9	± 0.0	± 0.0	± 0.6	± 0.8
Unidentified Radioactivity[(a)]	Mean	**0.0**	**0.0**	**0.8**	**0.0**	**1.3**	**2.7**	**4.6**	**2.6**
	SD	± 0.0	± 0.0	± 0.5	± 0.0	± 0.1	± 0.6	± 0.8	± 0.3
Total extractable radioactivity	Mean	**99.8**	**99.7**	**98.0**	**96.3**	**86.6**	**76.2**	**59.1**	**26.0**
	SD	± 0.0	± 1.0	± 1.8	± 1.4	± 0.7	± 0.5	± 1.4	± 0.5
Non-extractable radioactivity	Mean	**0.2**	**1.5**	**4.2**	**5.2**	**14.9**	**23.9**	**38.8**	**63.5**
	SD	± 0.0	± 0.1	± 0.4	± 0.0	± 0.2	± 0.9	± 2.5	± 0.5
$^{14}C-CO_2$	Mean	**0.0**	**0.1**	**0.1**	**0.1**	**0.5**	**1.2**	**2.7**	**8.4**
	SD	0.0	± 0.1	± 0.1	± 0.0	± 0.0	± 0.1	± 0.3	± 0.2
Other volatiles	Mean	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**
	SD	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0
Total radioactivity (%)	Mean	**100.0**	**101.3**	**102.3**	**101.6**	**102.1**	**101.3**	**100.7**	**97.9**
	SD	± 0.0	± 1.1	± 1.5	± 1.5	± 0.9	± 0.2	± 1.5	± 1.1

(a) No individual peak amount to more than 3.2 % of AR

Table B.8.1.1.1-14 Degradation of [UL-chlorophenyl-^{14}C]-fenoxaprop-P-ethyl (AE F046360) in <u>silt loam</u>

soil Springfield under aerobic conditions (% AR, mean ± SD, numbers shaded in grey indicate exceedance of 5 % AR)

Component		Sampling interval (days)							
		0	0.25	0.5	1	3	7	15	37
Fenoxaprop-P-ethyl	Mean	**95.8**	**9.0**	**3.8**	**2.6**	**1.2**	**0.6**	**0.4**	**0.0**
(AE F046360)	SD	± 0.5	± 1.1	± 1.2	± 0.2	± 0.3	± 0.8	± 0.6	± 0.0
Fenoxaprop-P-acid	Mean	**3.8**	**81.5**	**80.7**	**78.3**	**58.9**	**43.7**	**28.9**	**6.4**
(AE F088406)	SD	± 0.6	± 0.2	± 1.1	± 0.3	± 0.4	± 2.8	± 1.0	± 0.2
Chlorobenzoxazolone	Mean	**0.0**	**1.1**	**1.3**	**1.0**	**1.0**	**0.0**	**1.6**	**2.4**
(AE F054014)	SD	± 0.0	± 0.5	± 0.3	± 0.2	± 0.1	± 0.0	± 0.2	± 0.0
Unidentified	Mean	**0.0**	**1.2**	**2.8**	**2.3**	**2.4**	**2.2**	**2.9**	**3.7**
Radioactivity[(a)]	SD	± 0.0	± 0.6	± 0.2	± 0.3	± 0.4	± 0.1	± 0.1	± 0.2
Total extractable	Mean	**99.6**	**92.8**	**88.6**	**84.2**	**63.5**	**46.4**	**33.9**	**12.5**
radioactivity	SD	± 0.1	± 0.2	± 0.1	± 0.6	± 0.2	± 3.5	± 0.7	± 0.0
Non-extractable	Mean	**0.4**	**7.5**	**12.3**	**15.4**	**34.6**	**47.3**	**58.3**	**68.7**
radioactivity	SD	± 0.1	± 0.3	± 0.5	± 0.0	± 0.6	± 3.2	± 0.5	± 0.1
$^{14}C\text{-}CO_2$	Mean	**0.0**	**0.1**	**0.3**	**0.5**	**1.8**	**3.8**	**7.3**	**15.4**
	SD	± 0.0	± 0.0	± 0.0	± 0.1	± 0.1	± 0.8	± 0.1	± 1.0
Other volatiles	Mean	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**
	SD	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0
Total radioactivity	Mean	**100.0**	**100.4**	**101.2**	**100.2**	**99.9**	**97.4**	**99.6**	**96.6**
(%)	SD	± 0.2	± 0.1	± 0.5	± 0.5	± 0.4	± 0.5	± 1.3	± 0.9

(a) No individual peak amount to more than 3.0 % of AR

Table B.8.1.1.1-15 Mass balance after application of [chlorophenyl-UL-^{14}C]-fenoxaprop-P-ethyl (AE F046360) to sterilised soils Pikeville and Sanger, incubated under aerobic conditions (mean ± SD)

Component	Sampling interval (days)					
	-------- Pikeville (sterile) --------			-------- Sanger (sterile) --------		
	7	15	37	7	15	37
Total extractable radioactivity	80.5	63.1	47.6	87.6	76.1	53.8
Non-extractable radioactivity	17.7	35.2	48.1	9.7	21.5	42.4
$^{14}C\text{-}CO_2$	0.0	0.2	0.5	0.1	0.4	1.1
Other volatiles	0.0	0.0	0.0	0.1	0.5	1.6
Total radioactivity (%)	98.3	98.6	96.2	97.4	98.1	97.5

Mass balance

The values for total material balances of radioactivity ranged from 94.5 to 103.7 % AR for soil Pikeville, from 91.2 to 105.4 % AR for soil Sanger, from 97.9 to 102.3 % AR for Porterville and from 96.6 to 101.2 % AR for soil Springfield. In sterile test systems, the total recovery ranged from 96.2 to 98.6 % AR for soil Pikeville and from 97.4 to 98.1 % AR for Sanger soil. In conclusion, there were no signs for losses of radioactivity during work-up and processing.

Table B.8.1.1.1-16 Total material balances of radioactivity of ^{14}C-fenoxaprop-P-ethyl (AE F046360) in four US soils

Soil	Pikeville	Sanger	Porterville	Springfield	Pikeville (sterile)	Sanger (sterile)
Total Recovery (% AR)	94.5 – 103.7	91.2 – 105.4	97.9 – 102.3	96.6 – 101.2	96.2 – 98.6	97.4 – 98.1
Mean (% AR)	99.5	98.2	100.9	99.4	97.7	97.7
Rel. standard deviation	3.2	4.6	1.4	1.6	1.3	0.4

Values given as percentages of initially applied radioactivity

Bound and extractable residues

Values of extractable radioactivity decreased strongly with time accompanied by formation of NER. Starting from a complete extractability (99.6 to 99.9 % AR) by day zero, values decreased to 9.8 to 26.0 % after 37 days of incubation. In turn, formation of NER was fast starting from 0.1 to 0.4 % AR by day zero to 63.5 to 68.7 % after 37 days of incubation.

Table B.8.1.1.1-17 Extractable and non-extractable residues of ^{14}C-fenoxaprop-P-ethyl (AE F046360) in

four US soils (mean ± SD)

Soil	Extractable residues (%)		Non-extractable residues (%)	
	(day 0)	(day 37)	(day 0)	(day 37)
Pikeville	99.9 ± 0.2	15.0 ± 0.0	0.1 ± 0.0	65.7 ± 4.0
Sanger	99.8 ± 0.3	9.8 ± 0.2	0.2 ± 0.0	66.6 ± 0.4
Porterville	99.8 ± 0.0	26.0 ± 0.5	0.2 ± 0.0	63.5 ± 0.5
Springfield	99.6 ± 0.1	12.5 ± 0.0	0.4 ± 0.1	68.7± 0.1

Values given as percentages of initially applied radioactivity

Volatile radioactivity

Mineralisation of ^{14}C-fenoxaprop-P-ethyl (AE F046360) to ^{14}C-carbon dioxide was significant to account for 16.3 % (soil Pikeville), 16.6 % (soil Sanger), 8.4 % (soil Porterville) and 15.4 % AR (soil Springfield) after 37 days of incubation. Formation of other volatile radioactivity was insignificant (< 0.1 % AR) at any sampling interval.

Transformation of test substance

Under aerobic conditions, the active substance was extensively transformed to form fenoxaprop-P-acid (AE F088406), NER and ^{14}C-carbon dioxide as predominant transformation products. The degradation of fenoxaprop-P-acid (AE F088406) was paralleled by the formation of chlorobenzoxazolone (AE F054014) to account in maximum for 7.8 % AR (DAT 1, soil Pikeville), 1.5 % (DAT 1 and 37, soil Sanger), 4.6 % (DAT 37, Porterville) and 2.4 % (DAT 37, Springfield) in the course of the study. No significant formation of other metabolites was observed in the course of the study. The biotic character of degradation of fenoxaprop-P-ethyl (AE F046360) residues in soil is underlined by the formation carbon dioxide including non-extractable (bound) residues that could not be converted fully during the runtime of the study.

Soil sterilisation showed some impact on the rate of NER formation with time. In both soils (Pikeville and Sanger), NER formed were approximately 20 % higher for non-sterile soils when being compared to sterilised samples. This serves as an additional indication that formation of NER is caused by soil biological activity.

Characterisation of non-extractable residues (NER)

The majority of NER was associated with the humin fraction. Following extraction with strong base, an average of 31.0 % AR (Pikeville), 46.6 % (Sanger), 43.5 % (Porterville) and 40.9 % remained un-extracted supporting the observations of NER by biologically-mediated processes.

Table B.8.1.1.1-18 Non-extractable residue (NER) fractionation

Soil	Sampling date (days after application)	Humin (%)	Fulvic acid (%)	Humic acid (%)
Pikeville	15	31.0	22.1	46.9
Sanger	15	46.6	16.7	36.7
Porterville	15	43.5	28.2	28.3
Springfield	15	40.9	22.4	36.7

Values given as percentages of initially applied radioactivity

Conclusion:

Fenoxaprop-P-ethyl (AE F046360) degraded rapidly in aerobic soil to form fenoxaprop-P acid (AE F088406, maximum: 87.2 % AR, DAT-1, Porterville), non-extractable residues (maximum: 68.7 %, DAT-37, Springfield) and ^{14}C-carbon dioxide (maximum: 16.6 %, DAT-37, soil Sanger) as predominant transformation products of microbial induced degradation. In addition, metabolite chlorobenzoxazolone (AE F054014) was observed as a minor metabolite (maximum: 7.8 %, DAT-1, soil Pikeville).

Degradation in aerobic soil therefore contributes significantly to the overall elimination of residues of fenoxaprop-P-ethyl (AE F046360) from the environment.

Comments RMS AT:

- The study follows OECD guideline 307 and is considered reliable.

- The study was re-assessed for degradation rates by Oberdoerster et al. (2016).

Reference:	**[Phenoxy-UL-^{14}C]fenoxaprop-P-ethyl: Aerobic soil metabolism in four US soils**
Author(s), year:	Shepherd, J. J., Ripperger, R. J. (2012)
Report/Doc. Number:	M-424988-02-1
Guideline(s):	OECD Guideline 307 (2002), OPPTS 835.4100 (2008)
GLP:	Yes
Validity:	Yes
Status:	**New submission**

Executive Summary:

The biotransformation of [UL-phenoxy-^{14}C]-fenoxaprop-P-ethyl (AE F046360) was investigated under aerobic conditions of the laboratory in four US soils Pikeville (sandy loam), Sanger (sandy loam), Porterville (loamy sand) and Springfield (silt loam) following incubation in the dark at 20 °C and soil moisture between pF 2 and pF 2.5 for 37 days in maximum.

A nominal test concentration of 0.96 mg active substance/kg soil was applied based on four times the single maximum rate of 90 g a.s./ha in the field. For the two soils Pikeville and Sanger sterilised samples were investigated in addition to microbial active test systems.

Total recoveries of applied radioactivity (AR) ranged from 96.7 to 104.7 % (soil Pikeville), 97.3 to 102.4 % (Sanger), 96.9 to 101.1 % (Porterville) and 93.5 to 100.3 % (Springfield). For sterilised test systems the overall mean material balance was 99.7 ± 2.3 % AR for soil Pikeville and 96.7 ± 3.45 % for soil Sanger.

Total extractable radioactivity decreased from 99.9 % (soil Pikeville), 99.8 % (Sanger), 99.7 % (Porterville) and 99.4 % (Springfield) by day zero to 11.4 %, 6.7 %, 25.8 % and 8.3 %, respectively, by day 37. For sterilised soil samples the total extractable radioactivity decreased from 69.6 to 26.6 % AR in soil Pikeville and from 80.0 to 53.6 % AR in soil Sanger following the same incubation period.

The decrease of extractable radioactivity was accompanied by the formation of non-extractable residues (NER) to account for 51.3 % of AR (Pikeville), 41.0 % (Sanger), 37.6 % (Porterville) and 38.1 % (Springfield) in maximum after 37 days. In sterilised soils, NER were 75.6 % AR (Pikeville) and 39.8 % (Sanger) after 37 days.

Micro-biological degradation finally resulted in ^{14}C-carbon dioxide formation at 42.0 % AR (Pikeville), 49.6 % (Sanger), 33.5 % (Porterville) and 49.5 % AR (Springfield) each by day 37. Organic volatiles were detected at < 0.1 % AR in this study. Formation of $^{14}CO_2$ in sterilised test systems was minimal (≤ 4.7 % AR). The results confirmed that degradation of fenoxaprop residues in soil is driven by microbial processes.

In non-sterile samples, values of fenoxaprop-P-ethyl (AE F046360) decreased from 98.9 % AR (Pikeville), 98.6 % (Sanger), 92.7 % (Porterville) and 91.0 % (Springfield) by day 0 to 2.9 % (Pikeville), 0.8 % (Sanger) and below the limit of detection (LOD) of 0.7 % for the two soils Porterville and Springfield at study end.

Degradation of fenoxaprop-P-ethyl (AE F046360) proceeded rapidly via biologically induced ester hydrolysis to fenoxaprop-P-acid (AE F088406) observed at maximum of 55.9 % AR (soil Pikeville, DAT 0.5), 78.0 % (Sanger soil, DAT 0.5), 84.3 % (Porterville, DAT 1) and 82.2 % Springfield (DAT 0.5). Fenoxaprop-P-acid (AE F088406) decreased to 3.4 % AR (Pikeville), 3.0 % (Sanger), 21.4 % (Porterville) and 3.4 % (Springfield) at the end of the study.

For fenoxaprop-P-ethyl (AE F046360) chiral HPLC analyses of soil extracts resulted in enantiomer ratios to range from 98:2 (R to S-form) to 100:0 for all samples investigated. No significant change of the enantiomer ratio was therefore observed.

For metabolite fenoxaprop-P-acid (AE F088406), enantiomer ratios were from 94:6 (R to S-form) to 100:0 in all samples of the three soils Pikeville, Sanger and Porterville, while ratios showed some variability for extracts of soil Springfield, i.e. ranging from 94:6 to 79:21. Considering errors in enantiomer-specific analysis there was

interconversion between enantiomers of fenoxaprop-P-acid (AE F088406) to a minor extent and for the minority of soils in this study.

It should be noted in this context that the R-enantiomer is the biologically active form. Its conversion, completely or in part, can therefore be regarded as process contributing to the degradation of the active substance and its relevant metabolite in soil. Test were performed with the R-enantiomer and by taking the values for the active substance and fenoxaprop-P-acid (AE F088406) 'as they are', i.e. without considering any conversion to the non-biologically active enantiomer, this approach is regarded as worst case and thus conservative for the risk assessment.

Following application of UL-phenoxy-^{14}C-labelled fenoxaprop-P-ethyl (AE F046360) to soil residues are degraded rapidly to form fenoxaprop-P-acid (AE F088406) as predominant degradate followed by NER formation and significant mineralisation to ^{14}C-carbon dioxide.

Material and methods:

Test Material: [UL-phenoxy- ^{4}C]-fenoxaprop-P-ethyl (AE F046360)
Specific radioactivity: 4.14 MBq/mg (111.9 µCi/mg; 40.48 mCi/mmol)
Radiochemical purity: 100 %
R Isomer purity: 98.2 %
Sample/Batch ID: C-1142A

Soils
The soils had been freshly collected from the field followed by sieving to 2 mm.

Table B.8.1.1.1-19 Characteristics of test soils

Soil	Pikeville	Sanger	Porterville	Springfield
Geographic Location (City / State / Country)	Pikeville / North Carolina / US	Sanger / California / US	Porterville / California / US	Springfield / Nebraska / US
GPS coordinates	N 35° 48.8533' W 78° 04.0717'	N 36° 42.0868' W 119° 27.4929'	N 36° 00.492' W 119° 04.525'	N 41° 03.725' W 96° 15.085'
Pesticide use history	None used last five years	Paraquat, glyphosate and oxyfluorfen within previous 5 years, i.e. not same chemical class or mode of action	Several [D] applied within previous 5 years, i.e. not same chemical class or mode of action	None used last five years
Sampling depth (inches/cm)	0-8 / 0-20	0-6 / 0-15	0-6 / 0-15	0-8 / 0-20
Storage prior to test / length	Storage at 4.0 °C (3 d)	Storage at 4.0 °C (3 d)	Storage at 4.0 ± °C (28 d)	Storage at 4.0 ± °C (9 d)
Textural Class (USDA)	sandy loam	sandy loam	loamy sand	silt loam
Sand [50 µm - 2 mm] (%)	62.2	64.4	79.8	14.8
Silt [2 µm - 50 µm] (%)	30.1	28.1	10.5	59.6
Clay [< 2 µm] (%)	7.7	7.5	9.7	25.6
*p*H in Water	5.7	6.8	7.0	7.0
*p*H in $CaCl_2$ (0.01 M)	5.2	6.2	6.9	6.6
*p*H, saturated paste	5.6	6.6	6.9	6.8
Organic Matter (%)	2.3	0.82	0.80	3.3
Organic Carbon [A] (%)	1.4	0.48	0.46	1.9
CEC (meq/100 g)	9.66.3	6.5	10.3	17.4
Bulk density (g/mL)	1.25	1.30	1.34	1.01
MWHC (g/100 g) at pF 0	37.1	31.6	25.1	44.3
MWHC (g/100 g) at 0.1 bar (*p*F 2.0)	22.5	20.7	15.8	36.4
MWHC (g/100 g) at 0.33 bar (*p*F 2.5)	12.8	9.1	8.5	25.8
Test moisture (g/100 g)	9.5	13.1	14.2	32.8
Microbial biomass (mg microbial C/100 g dry weight of soil)				
Initial (Day 0/2)	15.4	14.3	5.5	34.1
Middle (Day 15)	9.9 [B] / 7.0 [C]	10.1 [B] / 8.5 [C]	6.1	35.9
Final (Day 37)	7.4 [B] / 5.5 [C]	8.1 [B] / 6.6 [C]	5.5 [B] / 5.7 [C]	22.4 [B] / 30.8 [C]

[A)] % organic carbon = % organic matter / 1.724;
[B)] Untreated control sample

[C)] Solvent-treated control samples (acetonitrile : water 6 : 4)
[D)] glufosinate-ammonium, saflufenacil, glyphosate, propyzamide, picoxystrobin, spinetoram
CEC: Cation exchange capacity; MWHC: Maximum Water Holding Capacity

Experimental conditions
Samples of 50 g dry weight of soil each were filled into glass incubation flasks and pre-equilibrated prior to treatment at approximate study conditions (darkness, 20 ± 2 °C, soil moisture between *p*F 2 [0.1 bar] and *p*H 2.5 [0.33 bar]). For the sterile incubation, samples of soil Pikeville and soil Sanger were sterilised via gamma irradiation. Sterilised soil samples were pre-incubated in sterilised incubation flasks; sterility was tested at each sampling interval.

At start, each sample received 0.96 mg test substance/kg soil. This rate was equivalent to four times single maximum field-use rate of 90 g a.s./ha (assuming 2.5 cm soil depth, 1.5 g/cm^3 soil density). Following application, the samples were attached to flow-through incubation systems with traps to collect ^{14}C-carbon dioxide and other volatile components. Samples were incubated at 20 ± 2 °C in the dark for 37 days in maximum. Untreated soil samples were incubated under the same conditions for determination of soil microbial activity.

Sampling
Duplicate samples were removed for work-up after 0, 6 and 12 hours and 1, 3, 7, 15 and 37 days of incubation. Duplicate sterile test systems were processed 7, 15 and 37 days after treatment. Samples for determination of soil microbial biomass were investigated after 0/2, 15 and 37 days of incubation.

Analytical procedures
The entire soil sample of each test vessel was extracted for 10 minutes with acetonitrile/1-%-acetic acid in water (8:2, by vol.) on a horizontal table top shaker at room temperature. After centrifugation and decantation through a glass fibre filter, the remaining soil was extracted similarly two additional times. The soil was then extracted two times using acetonitrile in the microwave extractor at 70 °C for 10 minutes, with centrifugation and filtration between extractions. The ambient and microwave supernatants were pooled separately.

Soils were extracted and analysed by liquid scintillation counting (LSC) on the day of sampling. The soil extracts were analysed by high performance liquid chromatography (HPLC) within nine days of sample extraction. Concentrated extracts were stored in a laboratory freezer (-20.0 ± 1.7 °C).

The ^{14}C-material balance was established for each sample by extraction, analysis of volatiles and combustion of non-extractable residues (NER). The determination of NER was performed by combustion/LSC of aliquots of the air-dried extracted soil. Following quantitation of radioactivity in extracts by LSC, analysis of concentrated aliquots was performed by reversed phase HPLC and ^{14}C-flow-through detection as primary analytical method. The limit of detection (LOD) was 0.7 % AR and the limit of quantitation (LOQ) was 0.95 % AR.

The identity of fenoxaprop-P-ethyl (AE F046360) and fenoxaprop-P-acid (AE F088406) was confirmed by HPLC retention-time comparison to reference standards, followed by HPLC/fraction collection of sample extracts and investigation of selected isolated fractions by LC-MS/MS.

A second analytical method was used for enantio-selective analyses of the active substance and for fenoxaprop-P-acid (AE F088406) after derivatisation (methylation) in isolated fractions of combined soil extracts. Following fractionation via a modified primary HPLC method, the enantiomer ratio was determined for fenoxaprop-P-ethyl (AE F046360) in selected soil extracts, i.e. DAT-0.25, DAT-0.5 and DAT-3 (soil Pikeville), DAT-0.25 and DAT-1 (Sanger), DAT-0.25, DAT-0.5 and DAT-15 (Porterville), DAT-0, DAT-1 and DAT-3 (Springfield). For fenoxaprop-P-acid (AE F088406), the analysis was performed for soil extracts of DAT-0.25 to DAT-7 (Pikeville), DAT-0.25 to 15 (Sanger, Porterville and Springfield).

NER were characterised by fractionation of soil organic matter of extracted soil samples of day 15 into humic acid, fulvic acid, and humins. Confirmation of $^{14}CO_2$ was performed for volatile radioactivity of day 15 samples using barium carbonate co-precipitation.

Results and discussion:

Table B.8.1.1.1-20 Degradation of [UL-phenoxy-^{14}C]-fenoxaprop-P-ethyl (AE F046360) in sandy loam

soil Pikeville under aerobic conditions (% AR, mean ± SD, numbers shaded in grey indicate exceedance of 5 % AR)

Component		Sampling interval (days)							
		0	0.25	0.5	1	3	7	15	37
Fenoxaprop-P-ethyl	Mean	**98.9**	**68.2**	**33.0**	**30.2**	**16.4**	**9.6**	**6.1**	**2.9**
(AE F046360)	SD	± 2.2	± 2.5	± 0.4	± 1.9	± 0.5	± 0.9	± 0.4	± 0.2
Fenoxaprop-P-acid	Mean	**0.5**	**30.6**	**55.9**	**53.1**	**46.8**	**29.8**	**13.5**	**3.4**
(AE F088406)	SD	± 0.7	± 0.2	± 0.7	± 0.7	± 0.0	± 0.9	± 0.3	± 0.2
Unidentified components[(a)]	Mean	**0.5**	**0.0**	**0.0**	**1.9**	**2.5**	**2.7**	**3.0**	**4.4**
	SD	± 0.7	± 0.0	± 0.0	± 0.1	± 0.6	± 1.2	± 1.2	± 1.1
Total extractable radioactivity	Mean	**99.9**	**98.8**	**88.9**	**85.3**	**65.7**	**42.7**	**23.2**	**11.4**
	SD	± 0.8	± 2.8	± 0.2	± 1.4	± 0.0	± 0.2	± 0.3	± 0.0
Non-extractable radioactivity	Mean	**0.1**	**2.7**	**9.1**	**13.7**	**24.6**	**37.1**	**48.5**	**51.3**
	SD	± 0.0	± 0.1	± 0.0	± 0.8	± 2.0	± 4.7	± 2.2	± 0.1
$^{14}C\text{-}CO_2$	Mean	**0.0**	**0.1**	**1.0**	**1.7**	**7.0**	**16.9**	**28.7**	**42.0**
	SD	± 0.0	± 0.0	± 0.0	± 0.2	± 0.3	± 0.4	± 0.4	± 0.6
Other volatiles	Mean	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**
	SD	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0
Total radioactivity (%)	Mean	**100.0**	**101.5**	**99.1**	**100.7**	**97.2**	**96.7**	**100.4**	**104.7**
	SD	± 0.8	± 2.9	± 0.2	± 0.3	± 2.3	± 5.3	± 2.9	± 0.7

(a) No individual peak amount to more than 3.6 % AR

Table B.8.1.1.1-21 Degradation of [UL-phenoxy-^{14}C]-fenoxaprop-P-ethyl (AE F046360) in sandy loam soil Sanger under aerobic conditions (% AR, mean ± SD, numbers shaded in grey indicate exceedance of 5 % AR)

Component		Sampling interval (days)							
		0	0.25	0.5	1	3	7	15	37
Fenoxaprop-P-ethyl	Mean	**98.6**	**53.7**	**19.0**	**10.4**	**2.7**	**1.2**	**0.9**	**0.8**
(AE F046360)	SD	± 0.7	± 0.9	± 3.8	± 0.5	± 0.3	± 0.6	± 0.0	± 0.1
Fenoxaprop-P-acid	Mean	**1.2**	**46.5**	**78.0**	**76.7**	**69.4**	**50.1**	**26.9**	**3.0**
(AE F088406)	SD	± 0.7	± 0.3	± 3.5	± 1.2	± 1.1	± 2.7	± 2.0	± 0.3
Unidentified components[(a)]	Mean	**0.0**	**0.0**	**0.0**	**3.0**	**2.6**	**2.2**	**1.9**	**5.9**
	SD	± 0.0	± 0.0	± 0.4	± 0.3	± 0.4	± 0.1	± 0.2	± 0.2
Total extractable radioactivity	Mean	**99.8**	**100.2**	**97.0**	**90.2**	**74.7**	**53.5**	**29.8**	**6.7**
	SD	± 0.1	± 0.7	± 0.2	± 1.0	± 1.0	± 1.9	± 2.2	± 0.2
Non-extractable radioactivity	Mean	**0.2**	**1.4**	**4.6**	**7.3**	**15.5**	**26.8**	**37.2**	**41.0**
	SD	± 0.1	± 0.0	± 0.3	± 0.5	± 0.4	± 0.5	± 1.6	± 0.6
$^{14}C\text{-}CO_2$	Mean	**0.0**	**0.1**	**0.8**	**2.5**	**9.1**	**18.9**	**33.9**	**49.6**
	SD	± 0.0	± 0.0	± 0.0	± 0.1	± 0.7	± 2.2	± 2.8	± 1.6
Other volatiles	Mean	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**
	SD	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0
Total radioactivity (%)	Mean	**100.0**	**101.7**	**102.4**	**100.0**	**99.3**	**99.3**	**100.9**	**97.3**
	SD	± 0.1	± 0.7	± 0.1	± 1.7	± 0.2	± 0.2	± 1.1	± 1.9

(a) No individual peak amount to more than 2.9 % AR

Table B.8.1.1.1-22 Degradation of [UL-phenoxy-^{14}C]-fenoxaprop-P-ethyl (AE F046360) in loamy sand soil Porterville under aerobic conditions (% AR, mean ± SD, numbers shaded in grey indicate exceedance of 5 % AR)

Component		Sampling interval (days)							
		0	0.25	0.5	1	3	7	15	37
Fenoxaprop-P-ethyl	Mean	**92.7**	**35.1**	**22.9**	**7.0**	**2.3**	**1.4**	**0.9**	**0.0**
(AE F046360)	SD	± 0.9	± 1.7	± 1.3	± 0.4	± 0.1	± 0.1	± 0.0	± 0.0
Fenoxaprop-P-acid	Mean	**7.0**	**63.3**	**74.3**	**84.3**	**81.7**	**71.7**	**49.8**	**21.4**
(AE F088406)	SD	± 0.8	± 3.1	± 1.0	± 0.4	± 1.9	± 0.5	± 0.2	± 3.7
Unidentified components[(a)]	Mean	**0.0**	**0.0**	**0.0**	**1.9**	**1.6**	**2.0**	**4.1**	**4.4**
	SD	± 0.0	± 0.0	± 0.0	± 1.5	± 0.1	± 0.3	± 0.0	± 0.4
Total extractable radioactivity	Mean	**99.7**	**98.4**	**97.1**	**93.2**	**85.6**	**75.1**	**54.8**	**25.8**
	SD	± 0.2	± 1.4	± 0.3	± 0.7	± 2.0	± 0.2	± 0.2	± 4.2
Non-extractable radioactivity	Mean	**0.3**	**1.8**	**3.2**	**5.5**	**13.0**	**18.6**	**27.9**	**37.6**
	SD	± 0.1	± 0.1	± 0.1	± 0.4	± 1.0	± 1.3	± 0.7	± 1.0
$^{14}C\text{-}CO_2$	Mean	**0.0**	**0.1**	**0.1**	**0.5**	**2.4**	**6.1**	**14.4**	**33.5**

	SD	± 0.0	± 0.0	± 0.1	± 0.1	± 0.5	± 0.6	± 1.1	± 5.9
Other volatiles	Mean	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.1**	**0.1**	**0.0**
	SD	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0
Total radioactivity (%)	Mean	**100.0**	**100.3**	**100.4**	**99.2**	**101.1**	**99.9**	**97.2**	**96.9**
	SD	± 0.2	± 1.5	± 0.3	± 0.3	± 0.5	± 1.7	± 0.3	± 2.7

(a) No individual peak amount to more than 3.7 % AR

Table B.8.1.1.1-23 Degradation of [UL-phenoxy-^{14}C]-fenoxaprop-P-ethyl (AE F046360) in silt loam soil Springfield under aerobic conditions (% AR, mean ± SD, numbers shaded in grey indicate exceedance of 5 % AR)

		Sampling interval (days)							
Component		**0**	**0.25**	**0.5**	**1**	**3**	**7**	**15**	**37**
Fenoxaprop-P-ethyl	Mean	**91.0**	**9.7**	**4.4**	**2.4**	**1.4**	**0.9**	**0.8**	**0.0**
(AE F046360)	SD	± 2.6	± 3.3	± 0.2	± 0.3	± 0.4	± 0.1	± 0.0	± 0.0
Fenoxaprop-P-acid	Mean	**8.4**	**81.9**	**82.2**	**69.8**	**46.2**	**29.3**	**20.4**	**3.4**
(AE F088406)	SD	± 3.8	± 3.1	± 1.3	± 2.1	± 4.1	± 1.7	± 0.2	± 0.2
Unidentified components[(a)]	Mean	**0.0**	**0.0**	**2.2**	**3.9**	**4.0**	**2.8**	**2.4**	**4.9**
	SD	± 0.0	± 0.0	± 0.4	± 0.6	± 0.1	± 0.0	± 0.1	± 0.2
Total extractable radioactivity	Mean	**99.4**	**91.6**	**88.8**	**76.1**	**51.7**	**33.1**	**23.6**	**8.3**
	SD	± 1.2	± 0.2	± 1.1	± 1.3	± 3.6	± 1.5	± 0.3	± 0.4
Non-extractable radioactivity	Mean	**0.6**	**8.1**	**10.7**	**19.1**	**33.9**	**38.7**	**39.3**	**38.1**
	SD	± 0.0	± 0.4	± 0.5	± 0.6	± 1.1	± 1.0	± 0.1	± 0.6
$^{14}C\text{-}CO_2$	Mean	**0.0**	**0.4**	**0.9**	**4.3**	**11.2**	**21.6**	**36.0**	**49.5**
	SD	± 0.0	± 0.1	± 0.1	± 0.3	± 1.4	± 0.7	± 0.4	± 0.4
Other volatiles	Mean	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.1**	**0.1**	**0.0**
	SD	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0
Total radioactivity (%)	Mean	**100.0**	**100.0**	**100.3**	**99.6**	**96.7**	**93.5**	**99.0**	**96.0**
	SD	± 1.2	± 0.2	± 0.5	± 0.4	± 1.2	± 0.2	± 0.6	± 0.6

(a) No individual peak amount to more than 4.3 % AR

Table B.8.1.1.1-24 Material balance following application of fenoxaprop-P-ethyl to sterile sandy loam soils Pikeville and Sanger, incubated under aerobic conditions (mean ± SD)

	Sampling interval (days)					
Component	----- **Pikeville soil** (sterile) -----			----- **Sanger soil** (sterile) -----		
	7	**15**	**37**	**7**	**15**	**37**
Total extractable radioactivity	69.6	45.3	26.6	80.0	74.3	53.6
Non-extractable radioactivity	28.6	52.2	75.6	11.6	21.4	39.8
$^{14}C\text{-}CO_2$	0.1	0.2	0.7	0.3	1.0	4.7
Other volatiles	0.0	0.0	0.0	0.0	0.0	0.0
Total radioactivity (%)	98.3	97.7	102.8	91.8	96.7	98.2

Material balance

In non-sterile test systems, total material balances of radioactivity ranged from 96.7 to 104.7 % AR for soil Pikeville, from 97.3 to 102.4 % AR for soil Sanger, from 96.9 to 101.1 % AR for Porterville and from 93.5 to 100.3 % AR for soil Springfield. In sterile test systems, the total recovery ranged from 97.7 to102.8 % AR for soil Pikeville and from 91.8 to 98.2 % AR for Sanger soil. In conclusion, there were no signs for losses of radioactivity during work-up and processing.

Table B.8.1.1.1-25 Total material balances of radioactivity (% AR) of ^{14}C-fenoxaprop-P-ethyl in four US soils

Soil	**Pikeville**	**Sanger**	**Porterville**	**Springfield**	**Pikeville** (sterile)	**Sanger** (sterile)
Total Recovery (% AR)	96.7 – 104.7	97.3 – 102.4	96.9 – 101.1	93.5 – 100.3	97.7 – 102.8	91.8 – 98.2
Mean (% AR)	100.0	100.1	99.4	98.4	99.7	96.7
Rel. standard deviation	2.5	1.6	1.5	2.5	2.3	3.5

Bound and extractable residues

Values of extractable radioactivity decreased strongly with time in non-sterile test systems accompanied by formation of NER. Starting from a complete extractability (99.4 to 99.9 % AR) by day zero, values decreased to

8.3 to 25.8 % after 37 days of incubation. In sterile test systems, extractable radioactive residues decreased from 80.5 and 87.6 % AR at day 7 to 47.6 and 53.8 % AR in soils Pikeville and Sanger. In turn, formed amounts of NER increased in non-sterile test systems starting from 0.1 to 0.6 % AR by day zero to 37.6 to 51.3 % AR after 37 days of incubation. In sterile test systems, NER increased to 48.1 and 42.4 % AR in soils Pikeville and Sanger.

Table B.8.1.1.1-26 Extractable and non-extractable residues of ^{14}C-fenoxaprop-P-ethyl (AE F046360) in four US soils (% AR, mean ± SD)

Soil	**Extractable residues** (%)		**Non-extractable residues** (%)	
	(day 0)	(day 37)	(day 0)	(day 37)
Pikeville	99.9 ± 0.8	11.4 ± 0.0	0.1 ± 0.0	51.3 ± 0.1
Sanger	99.8 ± 0.1	6.7 ± 0.2	0.2 ± 0.1	41.0 ± 0.6
Porterville	99.7 ± 0.2	25.8 ± 4.2	0.3 ± 0.1	37.6 ± 1.0
Springfield	99.4 ± 1.2	8.3 ± 0.4	0.6 ± 0.0	38.1 ± 0.6

Volatile radioactivity

Mineralisation of ^{14}C-fenoxaprop-P-ethyl was high and accounted for 42.0 % (soil Pikeville), 49.6 % (soil Sanger), 33.5 % (soil Porterville) and 49.5 % AR (soil Springfield) in non-sterile soils after 37 days of incubation. In sterile soils, mineralisation was low as expected, reaching 0.7 and 4.7 % AR in soils Pikeville and Sanger. Formation of other volatile radioactivity was insignificant (< 0.1 % AR) in sterile and non-sterile soils at any sampling interval.

Transformation of test substance

The active substance was extensively transformed in the course of the study to form fenoxaprop-P-acid (AE F088406), NER and $^{14}CO_2$ as predominant transformation products.

The degradation of fenoxaprop-P-acid (AE F088406) was paralleled by the formation of other metabolites all formed at insignificant level in the course of the study. The biotic character of degradation of fenoxaprop-P-acid (AE F088406) residues in soil is underlined by the formation carbon dioxide including non-extractable (bound) residues that could not be converted fully during the runtime of the study.

Soil sterilisation showed some impact on the rate of NER formation with time. In both soils (Pikeville and Sanger), NER formed were approximately 20 % higher for non-sterile soils when being compared to sterilised samples. This serves as an additional indication that formation of NER is caused by soil biological activity.

For fenoxaprop-P-ethyl (AE F046360) chiral analyses resulted in enantiomer ratios to range from 98:2 (R to S-form) to 100:0 for all samples investigated. No significant change of the enantiomer ratio was therefore observed.

For metabolite fenoxaprop-P-acid (AE F088406), enantiomer ratios were from 94:6 (R to S-form) to 100:0 in all samples of the three soils Pikeville, Sanger and Porterville, while ratios showed some variability for extracts of soil Springfield, i.e. ranging from 94:6 to 79:21. Considering errors in enantiomer-specific analysis there was interconversion between enantiomers of fenoxaprop-P-acid (AE F088406) to a minor extent and for the minority of soils in this study.

It should be noted in this context that the R-enantiomer is the biologically active form. Any interconversion of enantiomers, completely or partly, can therefore be regarded as process contributing to the degradation of the active substance and its relevant metabolite in soil. By taking the values for the active substance and fenoxaprop-P-acid ‘as they are’, i.e. without considering any interconversion of enantiomers, this approach is regarded as worst case and thus conservative for the risk assessment.

Table B.8.1.1.1-27 Results of enantiomer-specific analysis of <u>fenoxaprop-P-ethyl (AE F046360)</u> in soil extracts following application of [UL-phenoxy-^{14}C]-fenoxaprop-P-ethyl (AE F046360) to soil

Soil	Enantiomer ratios	**Sampling interval** (days)						
		0	**0.25**	**0.5**	**1**	**3**	**7**	**15**
Pikeville	Ratio R:S (% AR)	n.a.	66.8:1.4	33.0:0	n.a.	16.4:0	n.a.	n.a.
	Ratio R:S (%)	n.a.	98:2	100:0	n.a.	100:0	n.a.	n.a.

Soil	Enantiomer ratios	Sampling interval (days) 0	0.25	0.5	1	3	7	15
Pikeville	Ratio R:S (% AR)	n.a.	66.8:1.4	33.0:0	n.a.	16.4:0	n.a.	n.a.
	Ratio R:S (%)	n.a.	98:2	100:0	n.a.	100:0	n.a.	n.a.
Sanger	Ratio R:S (% AR)	n.a.	53.7:0.0	n.a.	10.4:0	n.a.	n.a.	n.a.
	Ratio R:S (%)	n.a.	100:0	n.a.	100:0	n.a.	n.a.	n.a.
Porterville	Ratio R:S (% AR)	n.a.	35.1:0.0	22.9:0.0	n.a.	n.a.	n.a.	0.9:0
	Ratio R:S (%)	n.a.	100:0	100:0	n.a.	n.a.	n.a.	100:0
Springfield	Ratio R:S (% AR)	91.0:0.0	n.a.	n.a.	2.4:0.0	0.9:0.0	n.a.	n.a.
	Ratio R:S (%)	100:0	n.a.	n.a.	100:0	100:0	n.a.	n.a.

n.a. = not analysed

Table B.8.1.1.1-28 Results of enantiomer-specific analysis of fenoxaprop-P-acid (AE F088406) in soil extracts following application of [UL-phenoxy-^{14}C]-fenoxaprop-P-ethyl (AE F046360) to soil

Soil	Enantiomer ratios	Sampling interval (days) 0	0.25	0.5	1	3	7	15
Pikeville	Ratio R:S (% AR)	n.a.	29.8:0.8	53.3:1.9	51.2:1:9	44.9:1.8	29.8:0.0	n.a.
	Ratio R:S (%)	n.a.	97:3	97:3	96:4	96:4	100:0	n.a.
Sanger	Ratio R:S (% AR)	n.a.	43.7:2.1	71.1:4.7	71.3:4.8	59.0:5.5	46.0:4.1	24.8:1.0
	Ratio R:S (%)	n.a.	95:5	94:6	94:6	91:9	92:8	96:4
Porterville	Ratio R:S (% AR)	n.a.	61.5:1.8	72.1:2.2	75.9:6.7	77.9:3.9	64.6:4.2	47.8:2.0
	Ratio R:S (%)	n.a.	97:3	97:3	92:8	95:5	94:6	96:4
Springfield	Ratio R:S (% AR)	n.a.	78.5:3.4	77.4:4.8	61.1:7.7	35.8:9.7	23.6:5.7	18.1:2.3
	Ratio R:S (%)	n.a.	96:4	94:6	89:11	79:21	81:19	89:11

n.a. = not analysed

Characterisation of non-extractable residues (NER)

The majority of NER was associated with the humin. After organic matter fractionation, on average 21.1 % AR (Pikeville), 53.3 % (Sanger), 47.6 % (Porterville) and 52.0 % (Springfield) remained in the humin fraction of soil. Thus, even after being exposed to harsh extraction conditions destroying the soil matrix, a significant portion of non-extractable fenoxaprop-P-ethyl-related residues remained bound to soil**.**

Table B.8.1.1.1-29 Non-extractable residue (NER) fractionation (% AR)

Soil	Sampling date (days after application)	Humins (%)	Fulvic acids (%)	Humic acids (%)
Pikeville	15	21.1	51.9	27.0
Sanger	15	53.3	28.6	18.1
Porterville	15	47.5	36.9	15.6
Springfield	15	52.0	29.2	18.8

Conclusion:

[UL-Phenoxy-^{14}C]-fenoxaprop-P-ethyl (AE F046360) was degraded rapidly in aerobic soil to form fenoxaprop-P-acid (AE F088406, maximum: 84.3 % AR, DAT-1, soil Porterville), non-extractable residues (maximum: 51.3 %, DAT-37, Pikeville) and ^{14}C-carbon dioxide (maximum: 49.6 %, DAT-37, soil Sanger) as predominant transformation products of microbial induced degradation. No other metabolites were observed at a significant level.

For the active substance fenoxaprop-P-ethyl (AE F046360) no interconversion was found to occur for from the R-form enantiomer (AE F046360) applied to the biologically inactive S-form (AE F085791). For metabolite fenoxaprop-P-acid (AE F088406) insignificant interconversion was found to occur from the R-form enantiomer (AE F088406) formed in soil to the biologically inactive S-form (AE F088405).

The results confirmed that degradation in aerobic soil therefore contributes significantly to the overall elimination of residues of fenoxaprop-P-ethyl (AE F046360) from the environment.

Comments RMS AT:

- The study follows OECD guideline 307 and is considered reliable.
- The study was re-assessed for degradation rates by Oberdoerster et al. (2016).

Reference:	**Enantioselective environmental behavior of the chiral herbicide fenoxaprop-ethyl and its chiral metabolite fenoxaprop in soil**
Author(s), year:	Zhang, Y., Liu, D., Diao, J., He, Z., Zhou, Z., Wang, P., Li, X. (2010)
Published in:	Journal of Agriculture and Food Chemistry 2010, Volume 58, Issue 24, pp 12878 – 12884
Report/Doc. Number:	M-507961-01-1
Guideline(s):	None
GLP:	No
Validity:	Yes
Status:	**New submission**

Executive Summary:

The degradation behaviour of various forms of the active substance fenoxaprop-ethyl and its metabolite fenoxaprop-acid was investigated in three Chinese soils Neimenggu, Shandong and Jiangxi incubated at 25 °C and about 60 % of the MWHC in the dark for 25 days in maximum. Enantioselective HPLC analysis (chiral column) was performed following incubation of racemic mixtures as well as the separate enantiomers each of fenoxaprop-ethyl and fenoxaprop-acid.

Following application of racemic fenoxaprop-ethyl (AE F033171) to soil, enzymatically induced hydrolytic degradation was slightly faster for the S-form (= enantiomer) fenoxaprop-M-ethyl (AE F085791) than for the R-form fenoxaprop-P-ethyl (AE F046360) to result in a relative enrichment of the (biologically active) R-enantiomer (AE F046360). The composition of residues in residues in terms of enantiomeric ratios (ER) for the ester active substance thus decreased with time from initially 0.98 (racemic) to 0.58 (S : R enantiomer, soil Neimenggu), 0.98 to 0.75 (soil Shandong) and 0.98 to 0.42 for soil Jiangxi. Configuration at the chiral centre of the ester active substance was found to be stable to the enantioselective, microbial-induced enzymatic hydrolysis.

Following separate application of enantiomers of fenoxaprop-acid to soils, both enantiomers of fenoxaprop-acid were significantly degraded. Degradation was faster for the S-enantiomer (AE F088405) than for the R-enantiomer (AE F088406) to result in lower values of the *DT50* for the S- than for the R-enantiomer in soils Neimenggu and Shandong. In case of racemic fenoxaprop-acid (AE F053022) applied the result was a relative enrichment of the R-enantiomer (AE F088406). For soil Jiangxi no clear enantioselectivity in degradation was observed.

Values of the *DT50* in soil were lower for the S-enantiomer of fenoxaprop-acid (2.96 to 5.17 days) than for the R-enantiomer (4.53 to 20.39 days), independent of application of either racemic fenoxaprop-acid or the pure S-enantiomer for two soils Neimenggu and Shandong. Values of the *DT50* in soil ranged from 2.03 to 2.86 days in Jiangxi soil and were thus comparable for the three forms (racemic mixture, R- and S-enatiomer) of fenoxaprop-acid tested.

The data from sterilised control experiments indicated that enantioselective degradation occurred due to microbially mediated processes.

Material and methods:

Test Materials

1. Fenoxaprop-P-ethyl (AE F046360) (R-enantiomer)

Chemical purity: not reported
Ratio of enantiomers: R : S = 98 : 2 (98 % R-enantiomer)
Sample/Batch ID: not reported

2. Fenoxaprop-M-ethyl (AE F085791) (S-enantiomer)

Chemical purity: not reported
Ratio of enantiomers: R : S = 1 : 99 (99 % S-enantiomer)
Sample/Batch ID: not reported, prepared by chiral chromatographic analysis/isolation from racemate

3. Fenoxaprop-ethyl (AE F033171) (racemic mixture)
Chemical purity: 98.0 %
Ratio of enantiomers: R : S = 50 : 50 (50 % R-enantiomer)
Sample/Batch ID: not reported

4. Fenoxaprop-P-acid (AE F088406) (R-enantiomer)
Chemical purity: not reported
Ratio of enantiomers: R : S = 97.5 : 2.5 (97.5 % R-enantiomer)
Sample/Batch ID: not reported, prepared by hydrolysis of fenoxaprop-P-ethyl followed by chiral chromatographic analysis/isolation

5. Fenoxaprop-M-acid (AE F088405) (S-enantiomer)
Chemical purity: not reported
Ratio of enantiomers: R : S = 1 : 99 (99 % S-enantiomer)
Sample/Batch ID: not reported, prepared by hydrolysis of fenoxaprop-M-ethyl followed by chiral chromatographic analysis/isolation

6. Fenoxaprop-acid (AE F053022) (racemic mixture)
Chemical purity: 97.5 %
Ratio of enantiomers: R : S = 50 : 50 (50 % R enantiomer
Sample/Batch ID: not reported, prepared by hydrolysis of fenoxaprop-ethyl followed by chromatographic analysis/isolation

Soils
The publication used three test soils originating from China with physico-chemical characteristics reported as summarised in the table below. Soils had been collected fresh from the top 10 cm and were passed through a 2 mm sieve.

Table B.8.1.1.1-30 Characteristics of test soils

Parameter	Soil		
Sampling site	Neimenggu Chifeng (SC)	Shandong Yanzhou (SY)	Jiangxi Nanchang (SN)
Geographic location (country)	China	China	China
Textural class [A)]	Sandy loam	Silt loam	Clay
Sand (%) [A)]	74.4	41.9	30.2
Silt (%) [A)]	21.9	52.6	28.1
Clay (%) [A)]	3.7	5.5	41.7
*p*H (water)	8.1	6.9	5.0
Organic carbon (%)	1.9	1.1	0.7

[A)] Classification scheme was not specified.

Experimental conditions
Soil samples of 5 g dry weight in polypropylene centrifuge tubes covered with aluminium foil were treated with one of the four test substances each at a concentration of 10 mg/kg soil. The samples were incubated at about 60 % of MWHC and at 25 °C in the dark. Samples of day 0 were fortified for determination of recovery and reproducibility of the extraction method to result in recoveries of > 90 % for fenoxaprop-esters, fenoxaprop-acids and chlorobenzoxazolone (AE F054014). Sterilised soils (10 g dry weight equivalent) were treated and incubated under the same conditions in parallel.

Sampling
Triplicate samples were removed for work-up and analysis after 0, 0.08., 0.17, 0.33, 0.50, 1, 2, 3, 5, 7, 10, 15, 20 and 25 days of incubation.

Analytical procedures
Soil samples were extracted three times successively each by stirring with acidified organic solvent (25 mL ethyl acetate and 0.2 mL 6 M HCl) for 3 min and 10 min ultrasonication. Following centrifugation the organic layer was dried by filtration (anhydrous sodium sulphate). Extracts were combined, concentrated and re-dissolved in 2-propanol for analysis by enantio-selective HPLC coupled with ultraviolet (UV) detection. Chiral analytical method consisted of an amylose tri-(3,5-dimethylphenylcarbamate) chiral column and a n-hexane/2-propanol/trifluoroacetic acid (TFA) (95:5:0.1, by vol.) mobile phase. Quantitation was performed by calibration curves with standard solutions at levels of 0.5, 1, 5, 10 and 50 µg/mL.

The limit of quantification (LOQ) for fenoxaprop esters, fenoxaprop acids and chlorobenzoxazolone (AE F054014) was 0.05 µg/g.

Confirmation of identity of the test items and chlorobenzoxazolone (AE F054014) was achieved by comparison of retention times of peaks with those of pure material of fenoxaprop esters, fenoxaprop acids and chlorobenzoxazolone (AE F054014).

Determination of degradation kinetics
The kinetic evaluation was performed for the fenoxaprop ester and fenoxaprop-acid test substances by applying single first-order (SFO) kinetics.

Results and discussion:

Degradation of fenoxaprop ethyl esters in soil
All of the forms of fenoxaprop ethyl esters, i.e. the racemate, the enantiopure S-(-)- and the R-(+)-form, were degraded rapidly in non-sterilised soils during 25 days of incubation.

With racemic fenoxaprop-ethyl (AE F033171) applied to soil, enzymatically induced hydrolytic degradation of the S-enantiomer (fenoxaprop-M-ethyl, AE F085791) was slightly faster than for the R-form (AE F046360) to result in a relative enrichment of the (biologically active) R-enantiomer. This resulted in a change of enantiomeric ratios (ER) in residues with time from initially 0.98 (racemic) to 0.58 (S : R enantiomer, soil Neimenggu), 0.98 to 0.75 (soil Shandong) and 0.98 to 0.42 for soil Jiangxi. Configuration at the chiral centre was found to be stable to hydrolysis, i.e. no interconversion occurred due to the nature of the process being caused by enantioselective microbial-induced enzymatic hydrolysis. This was confirmed by experiments with sterilised soils with the ER remaining close to 1.00.

Table B.8.1.1.1-31 Enantiomer ratio (ER) following application of racemic fenoxaprop-ethyl (AE F033171) to three Chinese soils

Time (days)	Neimenggu Chifeng soil (SC)		Shandong Yanzhou soil (SY)		Jiangxi Nanchang soil (SN)	
	ER rac-FE	ER rac-FA	ER rac-FE	ER rac-FA	ER rac-FE	ER rac-FA
0	0.98 ± 0.01	n.d.	0.98 ± 0.01	n.d.	0.98 ± 0.01	n.d.
0.08	0.97 ± 0.01	0.94 ± 0.08	0.93 ± 0.01	0.99 ± 0.08	0.87 ± 0.01	1.96 ± 0.08
0.17	0.93 ± 0.01	0.90 ± 0.08	0.92 ± 0.01	0.76 ± 0.08	0.82 ± 0.01	1.54 ± 0.08
0.33	0.82 ± 0.05	0.88 ± 0.07	0.89 ± 0.05	0.76 ± 0.01	0.73 ± 0.05	1.45 ± 0.07
0.50	0.77 ± 0.05	0.86 ± 0.07	0.82 ± 0.05	0.75 ± 0.07	0.57 ± 0.05	1.21 ± 0.07
1	0.69 ± 0.01	0.78 ± 0.06	0.79 ± 0.01	0.66 ± 0.07	0.42 ± 0.01	0.98 ± 0.06
2	0.58 ± 0.01	0.72 ± 0.10	0.75 ± 0.01	0.61 ± 0.06	n.d.	0.95 ± 0.08
3	n.d.	0.62 ± 0.10	n.d.	0.40 ± 0.10	n.d.	0.84 ± 0.08
5	n.d.	0.56 ± 0.08	n.d.	0.33 ± 0.08	n.d.	0.81 ± 0.08
7	n.d.	0.35 ± 0.08	n.d.	0.17 ± 0.08	n.d.	0.72 ± 0.07
10	n.d.	0.31 ± 0.05	n.d.	0.10 ± 0.07	n.d.	0.70 ± 0.07
15	n.d.	0.30 ± 0.07	n.d.	0.07 ± 0.07	n.d.	n.d.
20	n.d.	0.29 ± 0.06	n.d.	0.05 ± 0.06	n.d.	n.d.
25	n.d.	n.d.	n.d.	0.03 ± 0.06	n.d.	n.d.

FE = fenoxaprop-ethyl
FA = fenoxaprop-acid
rac = racemic
ER = enantiomer ratio (S : R enantiomer)
n.d. = not determined

Stability at the chiral centre of fenoxaprop-ethyl in soil

Spiking of sample extracts with pure S- and R-enantiomers of fenoxaprop-ethyl showed that no inversion occurred at the chiral centre throughout the incubation time. Inversion was thus insignificant when being compared to the enantioselective ester hydrolysis.

Formation of metabolites fenoxaprop and chlorobenzoxazolone in soil

Fenoxaprop-acid and chlorobenzoxazolone (AE F054014) were detected as metabolites formed after incubation in soil.

In all soils, the enantioselective hydrolysis of racemic fenoxaprop-ethyl (AE F033171) resulted in fenoxaprop-P-acid (AE F088406) to be formed predominantly, thus decreasing ER values in the course of incubation.

Following application of fenoxaprop-P-ethyl (AE F046360) to soil, only formation of fenoxaprop-P-acid (AE F088406) was observed besides the formation of chlorobenzoxazolone (AE F054014). However, following application of the S-enantiomer (i.e. fenoxaprop-M-ethyl, AE F085791) to soil the formation of the two enantiomers of fenoxaprop-acid was observed in soils Neimenggu and Shandong - besides the formation of chlorobenzoxazolone (AE F054014). For soil Jiangxi only the fenoxaprop-M-acid was formed following application of the S-enantiomer fenoxaprop-M-ethyl, besides the formation of chlorobenzoxazolone (AE F054014).

With the exception of soil Jiangxi, ester cleavage in the R-enantiomer fenoxaprop-P-ethyl (AE F046360) proceeded with retention of absolute configuration, while ester hydrolysis in the corresponding S-enantiomer fenoxaprop-M-ethyl (AE F085791) was via inversion of the configuration.

Table B.8.1.1.1-32 Residues of fenoxaprop-acid and chlorobenzoxazolone (AE F054014) extracted from soil incubated under aerobic conditions

Soil	Compound	Extractable residues (mg/kg)	
		Initial (day 0)	Maximum occurrence
Neimenggu	Fenoxaprop-acid	0.81	9.25 (d 0.5)
Chifeng (SC)	Chlorobenzoxazolone (AE F054014)	0.60	0.91 (d 0.33)
Shandong	Fenoxaprop-acid	2.05	6.75 (d 2)
Yanzhou (SY)	Chlorobenzoxazolone (AE F054014)	1.67	4.04 (d 1)
Jiangxi	Fenoxaprop-acid	2.22	2.25 (d 0.5)
Nanchang (SN)	Chlorobenzoxazolone (AE F054014)	1.76	2.99 (d 0.5)

Enantioselective degradation of fenoxaprop-acid in soil

The kinetics of degradation of racemic, S-enantiomer- and R-enantiomers of fenoxaprop-acid in to non-sterile soils was evaluated by use of the single first-order (SFO) model.

For soils Neimenggu and Shandong, degradation of both enantiomers of fenoxaprop-acid was significant, being faster for the S-enantiomer than for the R-enantiomer to result in lower values of the *DT50* for the S- than for the R-enantiomer. When starting from the racemic mixture of fenoxaprop-acid, the result was a relative enrichment of the R-enantiomer. For soil Jiangxi no clear enantioselectivity in degradation was observed.

Enantiomeric ratios (ER) for fenoxaprop-acid thus decreased from 0.98 (racemic) at the start to about 0.03 (S : R ratio) in Neimenggu soil after 25 days of incubation and from 0.98 to about 0.40 in Shandong soil. ER decrease was less pronounced in Jiangxi soil, i.e. from 0.98 to about 0.69. Results thus revealed degradation of fenoxaprop-acid to be enantioselective in soils Neimenggu and Shandong and to be slightly enantioselective in soil Jiangxi.

Values for the enantioselectivity (ES)[1] of fenoxaprop-acid degradation were 0.09 (Jiangxi), 0.29 (Shandong) and 0.56 (Neimenggu), indicating low to high enantioselective degradation. Enantioselectivity of degradation was thus variable and highest in soil with the highest soil *p*H and sand content (soil Neimenggu) while being lowest in soil Jiangxi (lowest soil *p*H and sand content, highest clay content).

Values of the *DT50* in soil were lower for the S-enantiomer of fenoxaprop-acid (2.96 to 5.17 days) than for the R-enantiomer (4.53 to 20.39 days), independent of application of either racemic fenoxaprop-acid or the pure S-enantiomer for soils Neimenggu and Shandong. Values of the *DT50* in soil ranged from 2.03 to 2.86 days in

[1] calculated from degradation rates by ES = $(k_S - k_R) / (k_S + k_R)$

Jiangxi soil and were thus comparable for the three forms (racemic mixture, R- and S-enatiomer) of fenoxaprop-acid tested.

Table B.8.1.1.1-33 Kinetics of aerobic degradation of fenoxaprop-acid enantiomers in three soils

Soil	Experiment (incubated compound)	Enantiomer	Degradation rate *k* (1/d)	*DT50* (days)	R^2
Neimenggu Chifeng (SC)	racemic FA	S-(-)-FA	0.134	5.17 ± 0.05	0.91
		R-(+)-FA	0.034	20.4 ± 0.03	0.96
	S-(-)-FA	S-(-)-FA	0.154	4.50 ± 0.07	0.96
	R-(+)-FA	R-(+)-FA	0.053	13.1 ± 0.08	0.95
Shandong Yanzhou (SY)	racemic FA	S-(-)-FA	0.280	2.48 ± 0.01	0.94
		R-(+)-FA	0.153	4.53 ± 0.06	0.95
	S-(-)-FA	S-(-)-FA	0.234	2.96 ± 0.03	0.98
	R-(+)-FA	R-(+)-FA	0.132	5.33 ± 0.04	0.92
Jiangxi Nanchang (SN)	racemic FA	S-(-)-FA	0.342	2.03 ± 0.01	0.96
		R-(+)-FA	0.286	2.42 ± 0.01	0.96
	S-(-)-FA	S-(-)-FA	0.290	2.39 ± 0.02	0.98
	R-(+)-FA	R-(+)-FA	0.242	2.86 ± 0.03	0.97

FA = fenoxaprop-acid

Inversion of configuration in soil for fenoxaprop-acid

No inversion of the configuration at the chiral centre was found following separate incubation of S- and R-enantiomers of fenoxaprop-acid and the configuration thus remaining stable in Jiangxi soil.

For soils Neimenggu and Shandong, inversion of the configuration at the chiral centre was observed in case the S-enantiomer of fenoxaprop-acid was applied. However, inversion of the configuration at the chiral centre was insignificant (compared to degradation) when the R-enantiomer was applied to soil. It was thus concluded that fenoxaprop-P-acid (AE F088406) was configurationally stable.

Conclusion:

Based on the published results, racemic fenoxaprop-ethyl can be degraded in soil by enantioselective hydrolysis while enantiomers of fenoxaprop-ethyl esters were configurationally stable.

Enantioselective degradation in soil via the R-enantiomer was also observed when the biologically inactive S-form of fenoxaprop-acid was applied, while configurational stability was found when fenoxaprop-P-acid (AE F088406) was applied to soil.

Comments RMS AT:

- The study indicates that the R-enantiomers ('P') of fenoxaprop-ethyl and fenoxaprop-acid are more slowly degrading in soil than the S-enantiomers ('M'). For that reason degradation rates obtained from the racemic mixture of fenoxaprop-acid and fenoxaprop-acid should in general not be used as a surrogate for the pure R-enantiomers (fenoxaprop-P-ethyl, AE F046360, and fenoxaprop-P-acid, AE F088406).

B.8.1.1.2. Anaerobic degradation

Studies submitted for first Annex I inclusion:

- **Voelkel (2001)**, investigating chlorophenyl labelled fenoxaprop-P-ethyl (AE F046360) and phenoxy labelled racemic fenoxaprop-ethyl (AE F033171) in one soil under anaerobic conditions

New submission by the Fenoxaprop-P-ethyl Task Force:

- **Adam (2008)**, investigating chlorophenyl and phenoxy labelled fenoxaprop-P-ethyl (AE F046360) in one soil under anaerobic conditions

Reference:	**^{14}C-AE F046360/^{14}C-AE F033171: Anaerobic soil degradation**
Author(s), year:	Voelkel, W. (2001a)
Report/Doc. Number:	C024193, M-227834-01-1
Guideline(s):	OECD draft guidance (1998); SETAC (1995); EPA Guidelines 540/9-82-021, Section 162-2 (1982)
GLP:	Yes
Validity:	Yes
Status:	**Previously submitted**

[The following study report is a copy/paste of the original text in the DAR for Annex I inclusion slightly amended in order to meet editorial settings and to improve readability]

Material and methods:

The objective of this study was to investigate the rate and route of degradation of [UL-chlorophenyl-^{14}C]-fenoxaprop-P-ethyl (AE F046360) under the anaerobic conditions of a water-logged agricultural soil (Speyer 2.2) in the laboratory. To describe additionally the fate of the dioxyphenyloxypropionic acid moiety under these conditions, a limited number of samples were generated by applying the ^{14}C-UL-phenoxy labelled racemic parent compound fenoxaprop-ethyl (AE F033171).

100 g dry weight of soil were filled into all-glass metabolism flasks, 300 ml distilled water were added to maintain a layer of 3 cm above the soil surface. Anaerobic conditions were kept by flushing the system with nitrogen. The outcoming nitrogen was passed through a trapping system consisting of one flask of ethylene glycol and one or two flasks of 2N NaOH depending on the amount of CO_2 evolved. Identity of $^{14}CO_2$ formed was checked by precipitation with barium chloride solution. After equilibration of the water-logged samples the test items were applied (dissolved in acetone) to the water surface at a concentration corresponding to 0.25 mg ai/kg soil d.w. The systems were incubated at 20 ± 2° C in the dark. During the acclimation and incubation period, *p*H and oxygen content of the water and redox potential of the water and soil were determined.

At each sampling date the supernatant water was removed from the soil using a glass pipette, without disturbing the soil layer. Practically the total amount of water was separated. However, the radioactivity that remained in the soil residual water after separation was counted for the soil in further processing and balancing. On each sampling day one sample was analysed.

Soil samples were extracted with acetonitrile/water (80:20, v/v), successively until < 2 % AR were recovered for a single extraction step. Aliquots of selected samples (day 45 and day 266) were submitted to Soxhlet extraction using acetonitrile/water (80:20, v/v) for at least four hours, in order to investigate the unextracted residues. Furthermore, addition aliquots of the selected samples were submitted to harsh extraction under reflux condition for about 5 hours using acetonitrile/conc. HCl (9:1, v/v). The soil samples from day 266 were additionally submitted to organic matter fractionation.

Total radioactivity was determined by LSC. Analyses were carried out by HPLC (gradient elution technique, phosphoric acid *p*H 2.5 and acetonitrile) and TLC for confirmation.

Table B.8.1.1.2-34 Soil Characteristics

Soil (USDA)	% Sand	% Silt	% Clay	% OC	*p*H ($CaCl_2$)	CEC (meq / 100g)	MWC (g / 100 g)	Biomass (mg C/kg)
Loamy sand Speyer 2.2	75.8	15.4	8.8	2.11	5.4	10.5	24.1 (40 % MWC: 21.6)	Begin: 420 **Total colonies:** Begin: 26000 End: 31000

Findings:

For the chlorophenyl-labelled (fenoxaprop-P-ethyl, AE F046360) and phenoxy-labelled (racemic fenoxaprop-ethyl, AE F033171) test systems the total mean recoveries were 98 ± 3.0 % and 101.5 ± 3.2 %, respectively.

With the chlorophenyl-label the radioactivity in the water decreased steadily from 92.9 % on day 0 to 5.2 % AR by the end of the study (day 266). For the phenoxy-label values of 99.6 % were determined in the water on day 1 with a decrease to 41.9 % AR by day 266.

For the chlorophenyl-labelled and phenoxy-labelled test systems radioactivity in the soil extracts increased during the study reaching maximum amounts of 36.1 % and 35.6 % AR on days 21 and 14, respectively. Thereafter it steadily decreased to 6.8 % and 15.9 % on day 266 for both label positions, respectively.

The mineralization of fenoxaprop-P-ethyl (AE F046360) was particularly low for the chlorophenyl-labelled system reaching a maximum value of only 7.8 % AR after 266 days. However, less complex and well degradable components were formed in the phenoxy-labelled test system with racemic fenoxaprop-ethyl (AE F033171). A slow rate of mineralization by day 120 (7.8 % AR) was followed by a significant increase to 31.9 % by the end of the study. Other volatiles never exceeded 0.1 % AR.

Fenoxaprop-ethyl is hydrolysed rapidly to the free acid. The different labelling positions reveal that the acid is further degraded by cleavage of the intercyclic ether bond. One degradation product is the propionic acid HOPP-acid (AE F096918) and the other is chlorobenzoxazolone (AE F054014). Chlorobenzoxazolone (AE F054014) revealed to be a compound that either is strongly bound to the soil and be released to a certain extent by acidic extraction or is rapidly further degraded. Both metabolites are further degraded to minor components which are mineralised to CO_2 or adsorbed to soil.

Table B.8.1.1.2-35 Distribution of radioactivity in the test system with chlorophenyl-labelled fenoxaprop-P-ethyl (AE F046360) (% AR)

DAT	Water	Soil			Water + extractables	CO_2	Total
		Extractable	NER	Total			
0	92.9	7.5	0.6	8.1	100.4	-	101.0
0.25	92.3	6.8	0.5	7.3	99.1	< 0.1	99.6
1	90.9	8.5	1.2	9.7	99.4	< 0.1	100.6
2	90.5	9.3	1.4	10.6	99.8	< 0.1	101.1
3	84.6	12.8	2.7	15.4	97.3	< 0.1	100.0
7	70.8	23.9	6.8	30.8	94.7	< 0.1	101.6
14	51.3	32.2	17.2	49.4	83.5	0.1	100.8
21	36.5	36.1	27.8	63.9	72.6	0.2	100.6
28	32.2	31.9	34.2	66.1	64.	0.4	98.7
45	21.4	29.7	48.4	78.1	51.1	0.9	100.4
58	14.6	22.0	58.0	80.0	36.7	1.7	96.4
90	8.4	11.1	71.3	82.3	19.4	4.2	94.9
120	5.9	13.0	76.4	89.5	18.9	0.6	95.9
157	4.8	7.6	77.5	85.0	12.3	3.0	92.8
266	5.2	6.8	73.7	80.5	12.0	7.8	93.5

Table B.8.1.1.2-36 Distribution of radioactivity in the test system with phenoxy-labelled racemic fenoxaprop-ethyl (AE F033171) (% AR)

DAT	Water	Soil			Water + extractables	CO_2	Total
		Extractable	NER	Total			
1	99.6	4.6	0.6	5.1	104.2	< 0.1	104.8
7	79.8	21.2	3.2	24.3	101.0	0.02	104.2
14	57.6	35.6	8.7	44.3	93.2	0.4	102.3
28	52.5	33.4	12.9	46.3	85.8	3.5	102.3
58	52.7	28.7	14.5	43.2	81.4	6.7	102.7
120	55.6	23.5	11.0	34.5	79.0	7.8	97.9
266	41.9	15.9	6.4	22.3	57.8	31.9	96.1

Table B.8.1.1.2-37 Distribution of parent and metabolites in the test system with chlorophenyl-labelled fenoxaprop-P-ethyl (AE F046360) (% AR, numbers shaded in grey indicate exceedance of 5 % AR)

DAT	Fenoxaprop-P-ethyl (AE F046360)			Fenoxaprop-P-acid (AE F088406)			Chlorobenzoxazolone (AE F054014)			Phenol metabolite (AE F040356)		
	Water	Soil extract	Total	Water	Soil extract	Total	Water	Soil extract	Total	Water	Soil extract	Total
0	92.9	4.0	**96.9**	n.d.	3.5	**3.5**	n.d.	n.d.	**n.d.**	n.d.	n.d.	**n.d.**
0.25	55.1	5.7	**60.8**	37.2	1.1	**38.3**	n.d.	n.d.	**n.d.**	n.d.	n.d.	**n.d.**
1	12.1	0.9	**13.0**	78.8	7.6	**86.4**	n.d.	n.d.	**n.d.**	n.d.	n.d.	**n.d.**
2	3.3	0.6	**3.9**	87.2	6.7	**93.9**	n.d.	n.d.	**n.d.**	n.d.	n.d.	**n.d.**
3	n.d.	n.d.	**n.d.**	81.4	12.3	**93.7**	3.1	0.4	**3.5**	n.d.	n.d.	**n.d.**
7	n.d.	n.d.	**n.d.**	66.3	22.1	**88.4**	2.0	0.9	**2.9**	0.4	0.3	**0.7**
14	n.d.	n.d.	**n.d.**	47.0	29.3	**76.3**	2.5	1.3	**3.7**	n.d.	0.3	**0.3**
21	n.d.	n.d.	**n.d.**	32.5	30.8	**63.3**	0.9	1.5	**2.4**	1.7	0.5	**2.2**
28	n.d.	n.d.	**n.d.**	29.4	27.8	**57.2**	0.8	1.3	**2.1**	n.d.	0.2	**0.2**
45	n.d.	n.d.	**n.d.**	19.2	26.5	**54.7**	0.8	1.6	**2.4**	n.d.	n.d.	**n.d.**
58	n.d.	n.d.	**n.d.**	10.8	19.1	**30.0**	0.6	n.d.	**0.6**	n.d.	n.d.	**n.d.**
90	n.d.	n.d.	**n.d.**	2.7	6.2	**8.8**	0.4	0.8	**1.2**	n.d.	n.d.	**n.d.**
120	n.d.	n.d.	**n.d.**	2.4	7.4	**9.8**	0.4	1.2	**1.6**	n.d.	n.d.	**n.d.**
157	n.d.	n.d.	**n.d.**	1.4	3.1	**4.6**	0.3	0.2	**0.6**	n.d.	n.d.	**n.d.**
266	n.d.	n.d.	**n.d.**	n.d.	2.4	**2.4**	1.3	0.5	**1.8**	n.d.	n.d.	**n.d.**

n.d. not detected

Seven additional minor metabolites were observed sporadically never exceeding 5.2 % AR in the water or soil.

Table B.8.1.1.2-38 Distribution of parent and metabolites in the test system with phenoxy-labelled <u>racemic fenoxaprop-ethyl (AE F033171)</u> (% AR, numbers shaded in grey indicate exceedance of 5 % AR)

DAT	Racemic fenoxaprop-ethyl (AE F033171)			Racemic fenoxaprop-acid (AE F053022)			HOPP-acid (racemic mixture) (AE F020686)		
	Water	Soil extract	Total	Water	Soil extract	Total	Water	Soil extract	Total
1	7.5	0.8	**8.3**	92.2	3.8	**96.0**	n.d.	n.d.	**n.d.**
7	n.d	n.d.	**n.d.**	77.0	18.1	**95.1**	n.d.	1.6	**1.6**
14	n.d.	n.d.	**n.d.**	48.2	28..6	**76.8**	7.6	3.6	**11.2**
28	n.d.	n.d.	**n.d.**	19.3	22.3	**41.5**	33.2	8.8	**42.0**
58	n.d.	n.d.	**n.d.**	12.7	13.6	**26.3**	40.0	15.1	**55.1**
120	n.d.	n.d.	**n.d.**	1.6	3.4	**4.9**	54.0	20.1	**74.1**
266	n.d.	n.d.	**n.d.**	n.d.	n.d.	**n.d.**	41.9	15.9	**57.8**

Additionally 4 minor metabolites were observed sporadically never exceeding 3.8 % AR in the whole system. Two of them were not detected in the chlorophenyl labelled system.

Non-extractable residues in soil (chlorophenyl-labelled fenoxaprop-P-ethyl, AE F046360) after ambient extraction were subject to additional investigations by harsher extraction procedures for representative samples. For the Soxhlet extracts of both sampling intervals investigated (day 45 and 266) fenoxaprop-P-acid (AE F088406, max. 5.1 % AR on day 45), chlorobenzoxazolone (AE F054014, max. 8.7 % AR day 45) and an unknown component (max. 3.4 % AR) were found as the main fractions. Two more fractions were detected, not exceeding 3.4 % AR. However, one of these components was detected at 15 % AR in the acidic extract of day 266. It should be considered that the harsh hydrolytic conditions favoured the formation of artefacts. In addition, the absence of distinct peaks allows the conclusion that the radioactivity released consisted of highly disintegrated material. In view of the generally lower level of non-extractable residues only Soxhlet extractions were carried out for a day 266 sample of the phenoxy label. In total 1.5 % AR were found released in the extract.

For both radiolabels used an additional aliquot of extracted soil sample incubated for 266 days was subject to a fractionation of the soil organic matter (NaOH method). About 48.2 % and 4.2 % AR in the soil extracts for the chlorophenyl and phenoxy system, respectively, was bound to the humic acids and humin fraction. The radioactivity associated with the fulvic acids fraction amounted to about 25.5 % and 2.2 % AR for both systems.

<u>Conclusions</u>:

^{14}C-AE F046360/^{14}C-AE F033171-fenoxaprop-ethyl was rapidly converted to the corresponding fenoxaprop-

acid. The different labelling positions revealed that fenoxaprop-acid was further degraded by the cleavage of the heterocyclic ether bond to result in the formation of hydroxyphenoxypropionic acid (racemic mixture of HOPP acid, phenoxy-label) and chlorobenzoxazolone (AE F054014, chlorophenyl-label). Both components, HOPP-acid and chlorobenzoxazolone (AE F054014), were further converted to minor components, being mineralised to $^{14}CO_2$ or adsorbed to the soil. The route of degradation in anaerobic soil did not differ basically from the pathway observed under aerobic conditions.

Comments RMS AT:

- The study broadly follows OECD guideline 307 and is still considered reliable. It may be noted that there was no aerobic incubation phase. Keeping in mind, that fenoxaprop-P-ethyl (AE F046360) is extremely fast degrading under aerobic conditions an aerobic incubation phase is indeed meaningless. Similar to observations made under aerobic conditions fenoxaprop-P-acid (AE F088406) was rapidly formed at significant amounts under anaerobic conditions as well.

- In the study with chlorophenyl-labelled fenoxaprop-P-ethyl (AE F046360) the unknown metabolite fraction 'M8' exceeded 5 % of AR at two consecutive sampling points *in the total system* (see table provided below), thus formally triggering identification and an exposure assessment according to Regulation (EU) No 283/2013. **This is currently not the case.**

Table B.8.1.1.2-39 Occurrence of fraction assigned to M8 (% AR).

DAT	Water	Soil extract	Total
45	1.3	1.6	**2.9**
58	1.4	2.9	**4.3**
90	2.7	2.8	**5.5**
120	1.0	5.2	**6.2**
157	2.0	3.8	**5.8**
266	1.0	1.2	**2.2**

On request by the RMS AT, the applicant *'does not see a reason to assume that M8 should be a potentially hazardous compound requiring risk assessment'*. The applicant argues that M8, based on HPLC retention times, is likely to result from cleavage of the molecule, thus having probably lost herbicidal activity. The applicant also claims that formation of M8 started late in this study (45 DAT and onwards) and there was a clear decline phase towards the end of the study. Finally, the applicant considers an unknown metabolite fraction observed in the second anaerobic soil degradation study (Adam, 2008), also called M8, identical with M8 observed in this study. Maximum residues of M8 in Adam (2008) were 5.4 % AR in the total system (59 DAT), declining thereafter to 3.7 % AR (126 DAT).

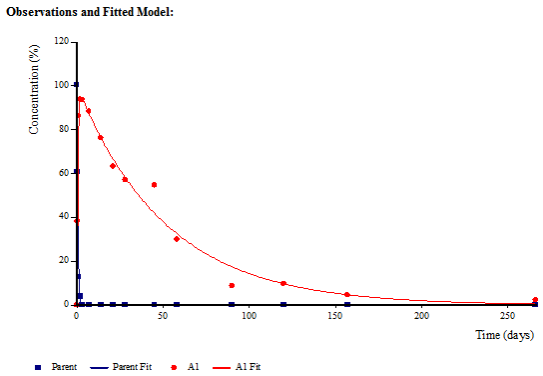
The RMS AT agrees that metabolite fraction M8 in this study is likely to result from substantial brake-down of the parent molecule as its HPLC retention time is in-between HOPP-acid (AE F096918) and chlorobenzoxazolone (AE F054014). However, the RMS AT does not agree that the metabolite fraction M8 in Adam (2008) is necessarily identical with M8 observed in this study as chromatographic conditions in both studies were indeed different. It may be highlighted that formation of metabolite fraction M8 in this study did not start before 45 days of continuous anaerobic conditions, even at 58 DAT M8 was still below 5 % AR. In view of the RMS AT continuous anaerobic conditions for such a long time are extremely unlikely to occur under real outdoor conditions.

- The study was not considered for kinetic re-evaluation by the applicant. Therefore, kinetic analysis for fenoxaprop-P-ethyl (AE F046360) and fenoxaprop-P-acid (AE F088406) in the total system following application of chlorophenyl-labelled fenoxaprop-P-ethyl (AE F046360) was re-done by the RMS AT applying a $P_{SFO} \rightarrow M_{SFO}$ pathway degradation scheme (Cake 3.3). Results are given below.

Table B.8.1.1.2-40 Degradation kinetics of fenoxaprop-P-ethyl (AE F0406360) and fenoxaprop-P-acid (AE F088406) in one soil under anaerobic conditions following application of chlorophenyl labelled fenoxaprop-P-ethyl (AE F046360) – RMS assessment.

Compartment	Kinetics	Substance	DT50 / DT90 (d)	χ^2 error (%)	Prop. > t	ff	Visual assessment
Total system	$P_{SFO} \rightarrow M_{SFO}$	Fenoxaprop-P-ethyl (AE F046360)	0.35 / 1.2	3.8	< 0.01	na	Excellent
		Fenoxaprop-P-acid (AE F088406)	35.7 / 119	7.1	< 0.01	1.00	Good

Table B.8.1.1.2-41 Degradation fit of fenoxaprop-P-ethyl (AE F0406360) and fenoxaprop-P-acid (AE F088406) in one soil under anaerobic conditions following application of chlorophenyl labelled fenoxaprop-P-ethyl (AE F046360) – RMS assessment



- It is noted that in this study anaerobic degradation of racemic fenoxaprop-ethyl (AE F033171) and racemic fenoxaprop-acid (AE F053022) appears to be somewhat faster than degradation of the respective pure R-isomers ('P'), probably due to faster degradation of the S-enantiomer ('M') as already observed under aerobic soil incubation conditions (refer to Zhang et al., 2010). For that reason, degradation rates based on racemic fenoxaprop-ethyl (AE F033171) or racemic fenoxaprop-acid (AE F053022) should in general not be used as a substitute for degradation rates of the pure R-enantiomers (fenoxaprop-P-ethyl, AE F046360, and fenoxaprop-P-acid, AE F088406, respectively).

- Maximum occurrence of racemic HOPP-acid (AE F020686) in the study with racemic fenoxaprop-ethyl (AE F033171) applied was 74.1 % AR. In Adam (2008, next study), applying non-racemic fenoxaprop-P-ethyl (AE F046360), maximum occurrence of (non-racemic) HOPP-acid (AE F096918) was only 49.2 % AR. In view of the low numbers of studies available on anaerobic degradation in soil, the RMS AT considers it defendable to set the overall maximum of HOPP-acid (AE F096918) in anaerobic soils to 74.1 % AR for conservative reasons, irrespective the fact that this value refers to the racemic mixture.

Reference:	**^{14}C-Fenoxaprop-P-ethyl - Degradation and metabolism in one soil incubated under anaerobic conditions**
Author(s), year:	Adam, A. (2008a)
Report/Doc. Number:	266 FPE, M-548193-01-1
Guideline(s):	SETAC (1995), OECD No. 307 (2002), US EPA (1982)
GLP:	Yes
Validity:	Yes
Status:	**New submission**

Executive Summary:

The biotransformation of [UL-chlorophenyl-^{14}C]- and [UL-phenoxy-^{14}C]-fenoxaprop-P-ethyl (AE F046360) was investigated under anaerobic conditions of the laboratory in water-logged samples of soil Speyer 2.2 (loamy sand) following incubation in the dark at 20 °C for 126 days in maximum. A nominal test concentration of 0.24 mg active substance/kg soil was applied thus based on two times the single maximum rate of 90 g a.s./ha in the field.

Total recovery of applied radioactivity (AR) ranged from 94.0 to 100.8 % following application of ^{14}C-

chlorophenyl-label and from 95.6 to 101.5 % for the ^{14}C-phenoxy-label.

Values for total extractable radioactivity decreased from 98.9 % (^{14}C-chlorophenyl-label) and 99.7 % (^{14}C-phenoxy-label) by day zero to 26.2 % and 56.8 %, respectively, by day 126. The decrease of extractable radioactivity was paralleled by formation of non-extractable residues (NER) to account for 63.9 % (^{14}C-chlorophenyl-label) and 26.5 % (^{14}C-phenoxy-label) after 126 days.

Micro-biological degradation finally resulted in ^{14}C-carbon dioxide formation to account for 3.9 % AR (^{14}C-chlorophenyl-label) and 22.7 % (^{14}C-phenoxy-label) in maximum, each by day 126. Formation of other organic volatiles was negligible (< 0.1 % AR). The results confirmed microbial processes to be the predominant factor of influence for the biotransformation of fenoxaprop residues in anaerobic soil.

Following application values of ^{14}C-chlorophenyl-labelled fenoxaprop-P-ethyl (AE F046360) decreased from 98.9 % AR by day 0 to below the LOD of 0.1 % after 14 days of incubation. For samples applied with ^{14}C-phenoxy-labelled active substance values decreased from 99.7 % AR by day 0 to below the LOD of 0.1 % after 14 days of incubation.

Fenoxaprop-P-ethyl (AE F046360) degraded rapidly under the conditions of anaerobic soil testing to form fenoxaprop-P-acid (AE F088406, mean maximum of two positions of radiolabel: 94.3 % AR, DAT-3), non-extractable residues (maximum for ^{14}C-chlorophenyl-label: 63.9 % by DAT-126, maximum for ^{14}C-phenoxy-label: 26.5 % by DAT-126) and ^{14}C-carbon dioxide (maximum for ^{14}C-chlorophenyl-label: 3.9 % by DAT-126, maximum for ^{14}C-phenoxy-label: 22.7 % by DAT-126) as predominant transformation products of microbial induced degradation. In addition, metabolites HOPP-acid (AE F096918) and chlorobenzoxazolone (AE F054014) accounted for 49.2 % (day 59) and 7.5 % AR (day 59) in maximum in the course of the study. Formation of other metabolites was insignificant (individual components occurring at or below 5.4 % in maximum). The biotic character of degradation of fenoxaprop-P-ethyl (AE F046360) residues in soil is underlined by the formation of carbon dioxide including non-extractable (bound) residues.

The overall basic pattern of degradation was thus the same to the one resulting from aerobic incubation.

For the active substance fenoxaprop-P-ethyl (AE F056360) the kinetic evaluation using the SFO model resulted in a *DT50* of 0.36 days (mean of two positions of radiolabel) in total system and a value for the *DT90* of 1.2 days. For metabolite fenoxaprop-P-acid (AE F088406), the half-life was 26.0 days. The corresponding *DT90* was 86.5 days.

Fenoxaprop-P-ethyl (AE F046360) was rapidly degraded in soil forming fenoxaprop-P-acid (AE F088406) as the predominant degradation product. Degradation was paralleled by the formation of metabolites HOPP-acid (AE F096918), chlorobenzoxazolone (AE F054014) and biologically mediated non-extractable residues and carbo dioxide.

Material and methods:

Test Material
[UL-chlorophenyl-^{14}C]-fenoxaprop-P-ethyl (AE F046360)
Specific radioactivity: 6.96 MBq/mg
Radiochemical purity: 98.4 % (HPLC)
Chemical purity: > 98.8 %
Sample/Batch ID: 2382MFO014-3 / 199026/A

[UL-phenoxy-^{14}C]-fenoxaprop-P-ethyl (AE F046360)
Specific radioactivity: 5.39 MBq/mg
Radiochemical purity: 100 % (HPLC)
Chemical purity: not reported
Sample/Batch ID: 2526GAR010-4 / 199044/A

Soil
The soils had been fresh collected from the field followed by sieving to 2 mm.

Table B.8.1.1.2-42 Characteristics of test soil

Soil	Speyer 2.2
Geographic Location (City / State / Country)	Speyer / Hahnhofen Germany
Pesticide use history	None reported
Sampling depth (cm)	Not reported
Textural Class (USDA)	Loamy sand
Sand [50 µm - 2 mm] (%)	81.2
Silt [2 µm - 50 µm] (%)	12.1
Clay [< 2 µm] (%)	6.7
pH in Water	5.8
pH in $CaCl_2$ (0.01 M)	5.4
Organic Matter (%)	3.95
Organic Carbon[(a)] (%)	2.29
CEC (meq/100 g)	10.0
Bulk density (g/mL)	Not reported
MWHC (g/100 g) at pF 0	46.1
MWHC (g/100 g) at 0.1 bar (pF 2.0)	18.7
MWHC (g/100 g) at 0.33 bar (pF 2.5)	12.1
Test moisture (g/100 g)	n.a.
Microbial biomass (mg microbial C/100 g dry weight of soil):	
Initial (Day 0 of anaerobic incubation)	51.2
Final (Day 126)	55.2

(a) % organic carbon = % organic matter / 1.724
CEC: Cation exchange capacity
MWHC: Maximum Water Holding Capacity

Experimental conditions
Samples of 100 g dry weight of sieved (2 mm) soil each were filled into glass incubation flasks and flooded with purified degassed water. The samples were acclimated prior to treatment under anaerobic conditions (darkness, 20 ± 2 °C, purging with nitrogen gas) for about one month.

Upon application the samples were dosed at a nominal concentration of 0.24 mg ^{14}C-labelled test substance/kg soil being equivalent to 180 g a.s./ha, twice the single maximum field-use rate of 90 g a.s./ha. Following application, the samples were purged with nitrogen gas several times per day. The effluent gas was passed through traps to collect ^{14}C-carbon dioxide and other volatile components. Water logged samples were incubated at 20 ± 2 °C in the dark for 126 days in maximum. Untreated soil samples were incubated under the same conditions for determination of soil microbial activity.

Sampling
Single samples of each radiolabel position were removed for analysis after 0, 0.25, 1, 3, 14, 59 and 126 days of incubation.

Analytical procedures
Following separation from the water phase the entire soil sample of each test vessel was extracted up to four times successively with 100 mL aqueous acetonitrile (8:2, by vol.) at ambient temperature (30 min). Ambient temperature extraction was amended by Soxhlet extraction for samples of day 14 and the following using aqueous acetonitrile (8:2, by vol.) for four hours. Each extraction step was followed by centrifugation and filtration of soil extracts. Following separation the water phases were acidified and subject to liquid-liquid partitioning with organic solvent (ethyl acetate). Ambient and Soxhlet extracts were pooled and concentrated prior to analysis by HPLC and TLC.

A full ^{14}C-material balance was established for each sampling interval by determination of radioactivity in soil extracts, volatiles in traps and of non-extractable residues (NER) in soil by combustion. The determination of NER was performed by combustion/LSC of aliquots of the air-dried extracted soil. Following quantitation by LSC, analysis of concentrated extracts was performed by reversed phase HPLC and ^{14}C-flow-through detection techniques as primary analytical method. TLC including phosphor imaging for ^{14}C-detection was used for selected samples as confirmatory analytical method.

The identity of fenoxaprop-P-ethyl (AE F046360), fenoxaprop-P-acid (AE F088406), chlorobenzoxazolone (AE F054014) and HOPP-acid (AE F096918) was confirmed by comparison of HPLC retention-times and retention factors in TLC to reference standards.

Characterisation of NER was performed by harsh extraction of extracted soil using aqueous acetonitrile acidified with 0.1 M hydrochloric acid followed by fractionation of soil organic matter into humic acids, fulvic acids and humins of extracted soil for DAT-126 samples of both radiolabels.

Determination of degradation kinetics

The kinetic evaluation of degradation data was performed for the test substance and its rapidly formed metabolite fenoxaprop-P acid.

Results and discussion:

Table B.8.1.1.2-43 Degradation of [UL-chlorophenyl-^{14}C]-fenoxaprop-P-ethyl (AE F046360) in loamy sand soil Speyer 2.2 under anaerobic conditions (numbers shaded in grey indicate exceedance of 5 % AR)

Component		Sampling interval (days)						
		0	**0.25**	**1**	**3**	**14**	**59**	**126**
Fenoxaprop-P-ethyl (AE F046360)	Water	98.9	59.9	18.6	3.7	-	-	-
	Extracts	n.a.	0.4	0.1	-	-	-	-
	Total	**98.9**	**60.3**	**18.7**	**3.7**	**-**	**-**	**-**
Fenoxaprop-P-acid (AE F088406)	Water	-	35.4	78.7	85.6	46.9	8.0	0.1
	Extracts	-	3.7	1.7	8.2	35.6	33.5	13.3
	Total	**-**	**39.0**	**80.3**	**93.8**	**82.4**	**41.5**	**13.4**
Chlorobenzoxazolone (AE F054014)	Water	-	-	-	-	1.0	0.3	-
	Extracts	-	-	-	0.4	3.4	7.1	3.6
	Total	**-**	**-**	**-**	**0.4**	**4.4**	**7.5**	**3.6**
Others (M3 to M12)[(a)]	Water	-	-	-	-	-	1.5	6.1
	Extracts	-	-	-	0.1	1.5	6.1	3.0
	Total	**-**	**-**	**-**	**0.1**	**1.5**	**7.6**	**9.1**
Total extractable radioactivity	Water	98.9	95.3	97.3	89.3	47.9	9.8	6.2
	Extracts	n.a.	4.1	1.8	8.7	40.5	46.7	19.9
	Total	**98.9**	**99.3**	**99.0**	**97.9**	**88.3**	**56.6**	**26.2**
Non-extractable radioactivity		< 0.1	1.5	0.8	2.7	10.1	38.0	63.9
^{14}C-CO_2 and other volatiles[(b)]		n.a.	< 0.1	< 0.1	< 0.1	< 0.1	1.4	3.9
Total radioactivity (%)		**98.9**	**100.8**	**99.8**	**100.7**	**98.5**	**96.1**	**94.0**

Values given as percentages of initially applied radioactivity (AR)
n.a. = not analysed
(a) No individual peak amount to more than 5.4 % AR in the total system (refer to comment section)
(b) Other volatiles accounted for < 0.1 % AR in the course of the study

Table B.8.1.1.2-44 Degradation of [UL-phenoxy-^{14}C]-fenoxaprop-P-ethyl (AE F046360) in loamy sand soil Speyer 2.2 under anaerobic conditions (numbers shaded in grey indicate exceedance of 5 % AR)

Component		Sampling interval (days)						
		0	**0.25**	**1**	**3**	**14**	**59**	**126**
Fenoxaprop-P-ethyl (AE F046360)	Water	100.4	58.2	14.3	-	-	-	-
	Extracts	-	0.4	-	-	-	-	-
	Total	**100.4**	**58.6**	**14.3**	**-**	**-**	**-**	**-**
Fenoxaprop-P-acid (AE F088406)	Water	-	37.6	81.2	85.7	48.7	5.4	1.5
	Extracts	-	3.8	3.2	10.0	32.3	24.4	9.3
	Total	**-**	**40.2**	**84.3**	**95.7**	**81.1**	**29.8**	**10.8**
HOPP-acid (AE F096918)	Water	-	-	-	1.1	8.5	37.9	30.3
	Extracts	-	-	-	0.5	4.0	11.3	5.3
	Total	**-**	**-**	**-**	**1.6**	**12.5**	**49.2**	**35.7**
Total extractable radioactivity	Water	99.7	95.5	96.4	88.6	56.3	46.0	37.2
	Extracts	n.a.	4.1	2.5	9.7	39.5	46.3	19.6
	Total	**99.7**	**99.6**	**98.8**	**98.3**	**95.8**	**92.4**	**56.8**
Non-extractable radioactivity		< 0.1	1.5	1.5	3.1	5.7	12.2	26.5
^{14}C-CO_2 and other volatiles[(b)]		n.a.	< 0.1	< 0.1	0.2	1.2	7.9	22.7
Total radioactivity (%)		**100.5**	**101.5**	**100.2**	**100.5**	**100.5**	**99.1**	**95.6**

Values given as percentages of initially applied radioactivity (AR)
n.a. = not analysed
(b) Other volatiles accounted for < 0.1 % AR in the course of the study

Mass balance
The values for total mass balances of radioactivity ranged from 94.0 to 100.8 % AR and from 95.6 to 101.5 % for samples incubated with ^{14}C-chlorophenyl- and ^{14}C-phenoxy-fenoxaprop-P-ethyl (AE F046360), respectively, in the course of the study. In conclusion, there were no signs for losses of radioactivity during work-up and processing.

Table B.8.1.1.2-45 Total material balances of radioactivity (% AR) of ^{14}C-fenoxaprop-P-ethyl (AE F046360) in anaerobic soil

Label position	^{14}C-chlorophenyl	^{14}C-phenoxy
Total Recovery (% AR)	94.0 – 100.8	95.6 – 101.5
Mean (% AR)	98.4	99.7
Rel. standard deviation	2.3	1.8

Bound and extractable residues
Values of extractable radioactivity decreased with time accompanied by formation of NER. Starting from a complete extractability (98.9 % AR for chlorophenyl-label and 99.7 % for phenoxy-label) by day zero, values decreased to 26.2 % and 56.8 % after 126 days of incubation, dependent on radiolabel.

In turn, formation of NER was fast starting from less than 0.1 % AR for both radiolabels by day zero to 63.9 % and 26.5 % after 126 days of incubation. The values indicate a strong dependence on position of radiolabel with values of NER being significantly lower for the ^{14}C-phenoxy-label owing to the formation of HOPP-acid from split of the molecule and its mineralisation in the following.

Table B.8.1.1.2-46 Extractable and non-extractable residues (% AR) of ^{14}C-fenoxaprop-P-ethyl (AE F046360) in anaerobic soil

Label position	**Extractable residues** (%)		**Non-extractable residues** (%)	
	(day 0)	(day 126)	(day 0)	(day 126)
^{14}C-chlorophenyl	98.9	26.2	< 0.1	63.9
^{14}C-phenoxy	99.7	56.8	< 0.1	26.5

Volatile radioactivity
Mineralisation of ^{14}C-fenoxaprop-P-ethyl to ^{14}C-carbon dioxide was dependent on position of radiolabel to account for 3.9 % AR (^{14}C-chlorophenyl-label) and 22.7 % (^{14}C-phenoxy-label) in maximum after 126 days of incubation. Formation of other volatile radioactivity was insignificant (< 0.1 % AR) at any sampling interval and the two label positions.

Transformation of test substance
The active substance was hydrolysed to form in a first step fenoxaprop-P-acid (AE F088406, maximum 94.8 %, day 3) to result finally in NER and ^{14}C-carbon dioxide as predominant transformation products. The degradation of fenoxaprop-P acid (AE F088406) was paralleled by the formation of metabolites HOPP-acid (AE F096918) and chlorobenzoxazolone (AE F054014) to account for 49.2 % (day 59) and 7.5 % AR (day 59) in maximum in the course of the study. Formation of other metabolites was insignificant (individual components occurring at or below 5.4 % in maximum). The biotic character of degradation of fenoxaprop-P residues in soil is underlined by the formation carbon dioxide including non-extractable (bound) residues.

Characterisation of non-extractable residues (NER)
The majority of NER was associated with the humin fraction. Following extraction with strong base, an average of 18.9 % AR (^{14}C-chlorophenyl-label) and 5.6 % (^{14}C-phenoxy-label) remained un-extracted in humins supporting the observations of NER by biologically-mediated processes.

Table B.8.1.1.2-47 Non-extractable residue (NER) fractionation

Label position	**Sampling date** (days after application)	**Humins** (%)	**Fulvic acid** (%)	**Humic acid** (%)
^{14}C-chlorophenyl	126	18.9	9.6	20.2
^{14}C-phenoxy	126	5.6	5.9	7.7

Values given as distribution of remaining unextracted radioactivity after harsh extraction

Degradation kinetics

The kinetic evaluation was performed by fitting the degradation data to the kinetic model SFO for the active substance fenoxaprop-P-ethyl (AE F046360) and its metabolite fenoxaprop-P-acid (AE F088406).

For the active substance fenoxaprop-P-ethyl (AE F046360) the evaluation resulted in half-lives of 0.36 days for each of the two radiolabel positions applied. The corresponding values of the *DT90* were 1.20 days (^{14}C-chlorophenyl-label) and 1.21 days (^{14}C-phenoxy-label).

For metabolite fenoxaprop-P-acid (AE F088406) this resulted in *DT50* values of 13.4 days (^{14}C-chlorophenyl) and 26.0 days (^{14}C-phenoxy). The corresponding values of the *DT90* were 43.3 days and 86.5 days.

Table B.8.1.1.2-48 Kinetics of degradation of fenoxaprop-P-ethyl (AE F046360) in anaerobic soil

Label position	Kinetic model	Compartment	*DT50* (days)	*DT90* (days)	r^2
^{14}C-chlorophenyl	SFO	Total system	0.36	1.20	0.998
^{14}C-phenoxy	SFO	Total system	0.36	1.21	0.998

Table B.8.1.1.2-49 Kinetics of degradation of metabolite fenoxaprop-P-acid (AE F088406) in anaerobic soil

Label position	Kinetic model combination	Compartment	*DT50* (days)	*DT90* (days)	r^2
^{14}C-chlorophenyl	SFO	Total system	13.4	43.3	0.998
^{14}C-phenoxy	SFO	Total system	26.0	86.5	0.997

Conclusion:

Fenoxaprop-P-ethyl (AE F046360) degraded rapidly under the conditions of anaerobic soil testing to form fenoxaprop-P-acid (AE F088406, mean maximum of two positions of radiolabel: 94.3 % AR, DAT-3), non-extractable residues (maximum for ^{14}C-chlorophenyl-label: 63.9 % by DAT-126, maximum for ^{14}C-phenoxy-label: 26.5 % by DAT-126) and ^{14}C-carbon dioxide (maximum for ^{14}C-chlorophenyl-label: 3.9 % by DAT-126, maximum for ^{14}C-phenoxy-label: 22.7 % by DAT-126) as predominant transformation products of microbial induced degradation. In addition, metabolites HOPP-acid (AE F096918) and chlorobenzoxazolone (AE F054014) accounted for 49.2 % (day 59) and 7.5 % AR (day 59) in maximum in the course of the study. Formation of other metabolites was insignificant (individual components occurring at or below 5.4 % in maximum). The biotic character of degradation of fenoxaprop-P-ethyl (AE F046360) residues in soil is underlined by the formation carbon dioxide including non-extractable (bound) residues.

Fenoxaprop-P-ethyl (AE F046360) was degraded fast in soil under the anaerobic conditions of the test.

Comments RMS AT:

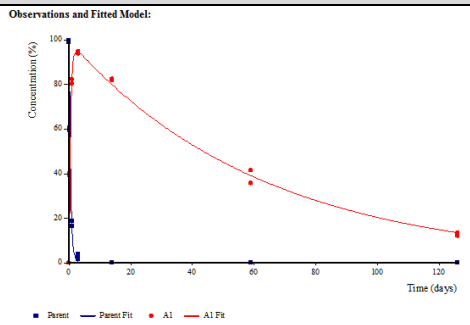
- The study follows OECD guideline 307 and is considered reliable. Similar to Voelkel (2001a) no aerobic pre-incubation phase was applied.
- The RMS AT confirms that unknown metabolite fractions do not exceeded 5 % AR *in the total system* at two consecutive sampling points on individual basis (max. 5.4 % AR for 'M8' at 59 DAT, observed applying chlorophenyl labelled parent only).
- Kinetic analysis for fenoxaprop-P-ethyl (AE F046360) and fenoxaprop-P-acid (AE F088406) in the total system was re-done by the RMS AT applying a $P_{SFO} \rightarrow M_{SFO}$ degradation pathway scheme considering both labels as true replicates (Cake 3.3). Results are given below.

Table B.8.1.1.2-50 Degradation kinetics of fenoxaprop-P-ethyl (AE F0406360) and fenoxaprop-P-acid (AE F088406) in one soil under anaerobic conditions following application of

fenoxaprop-P-ethyl (AE F046360) – RMS assessment

Compartment	Kinetics	Substance	*DT50* / *DT90* (d)	χ^2 error (%)	Prop. > t	ff	Visual assess-ment
Total system	$P_{SFO} \rightarrow M_{SFO}$	Fenoxaprop-P-ethyl (AE F046360)	0.37 / 1.2	4.7	< 0.01	na	Excellent
		Fenoxaprop-P-acid (AE F088406)	43.7 / 145	2.2	< 0.01	1.00	Excellent

Table B.8.1.1.2-51 Degradation fit of fenoxaprop-P-ethyl (AE F0406360) and fenoxaprop-P-acid (AE F088406) in one soil under anaerobic conditions following application of fenoxaprop-P-ethyl (AE F046360) – RMS assessment



B.8.1.1.3. Soil photolysis

Studies submitted for first Annex I inclusion:

- **Sarafin & Jordan (1989)**, investigating racemic fenoxaprop-ethyl (AE F033171) in one soil under conditions of soil photolysis

No new studies were submitted by the Fenoxaprop-P-ethyl Task Force.

Reference:	**Hoe 033171-^{14}C (fenoxaprop-ethyl): Photodegradation on soil**
Author(s), year:	Sarafin, R., Jordan, H. J. (1989)
Report/Doc. Number:	A40297, M-122796-01-1
Guideline(s):	US EPA OPP Guideline No. 161-3
GLP:	Yes
Validity:	Yes
Status:	**Previously submitted**

[The following study report is a copy/paste of the original text in the DAR for Annex I inclusion slightly amended in order to meet editorial settings and to improve readability]

Material and methods:

Photodegradation of [UL-chlorophenyl-^{14}C]-labelled racemic fenoxaprop-ethyl (AE F033171, called Hoe 033171 in the report; 50 % P-isomer fenoxaprop-P-ethyl, AE F046360) was studied on sterilized soil surfaces (sandy clay loam, US) in the laboratory using a xenon arc lamp which closely simulated sunlight. The irradiations were performed under temperature control (25 ± 5 °C).

Air dried soil was passed through a 0.5 mm sieve and then slurried with water. Stainless steel plates (4 cm x 4 cm) were coated with the slurry and then air dried. Prior to the application of the test substance the soil was sterilised by spraying with chloroform. 80 µg of the parent substance per plate were applied as spots on the soil surface (corresponding to 0.5 kg/ha). The experiments were performed in two series of simultaneous irradiations of six plates each in the quartz-topped box. An additional series served as dark control. For absorbing volatiles one trap contained 0.5 g XAD-2 resin in 10 mL bi-distilled water adjusted to *p*H 3 with sulphuric acid. $^{14}CO_2$

was absorbed in 10 mL Carbo-Sorb. To absorb any substances which might pass both stages a cold trap containing a mixture of 20 ml methanol and 1 mL 1 N sodium hydroxide solution was used which was cooled with dry ice.

For the simulation of sunlight radiation an original Hanau Suntest photoreactor (Hanau Quarzlampen GmbH, D-6450 Hanau), equipped with a xenon burner, was used (radiation cut-off at 290 nm). Irradiation was done continuously without day/night intervals.

Soil samples were extracted with acetonitrile/water (adjusted to *p*H 3 with sulphuric acid) 8:2. Concentrated extracts were analysed by HPLC with gradient elution technique (bidest. water *p*H 2.5 and acetonitrile). Metabolites were identified by co-chromatography with reference standards and HPLC/MS.

Table B.8.1.1.3-52 Soil Characteristics

Soil (USDA)	% Sand	% Silt	% Clay	% OM	*p*H ($CaCl_2$)	CEC (meq/100 g)	% Moist. capacity
Sandy clay loam (Arizona, US)	60.2	20.3	19.5	0.45	7.3	11.54	25.8

Findings:

On the basis of outdoor conditions and 52 °N the total duration of irradiation (120 hrs, 5 days) was calculated with the program REALINT to be 35 to 36.8 days.

The material balances for the irradiated samples were in a range of 89.8 % to 100.1 % AR. For dark controls values of 96.4 % to 100.8 % were determined in the course of the study.

^{14}C-CO_2 was formed as the main degradation product of photolysis at about 12 % AR after 120 hrs. Further two components (M1 and M6) can also be assigned to products of photolytic processes which occurred at peak values of 6.0 % after 120 hrs and 6.4 % AR after 72 hrs in the irradiated samples, respectively. Metabolite M6 was characterised by HPLC/MS investigations as a compound with a molecular mass of 407. M1 could not be detected in HPLC/MS. Not extractable residues and very small amounts of other volatiles are also considered as photodegradates. The occurrence of chlorobenzoxazolone (AE F054014) and M2 is attributed to non-photolytic processes.

Table B.8.1.1.3-53 Distribution of radioactivity in % AR (two series, numbers shaded in grey indicate exceedance of 5 % AR)

HAT	Racemic fenoxaprop-ethyl (AE F033171)	Chloro-benz-oxazolone (AE F054014)	M1	M2	M6	CO_2	NER	Total
				Irradiated samples				
0	99.9 / 98.3	0.0 / 2.3	0.0 / 0.0	0.0 / 0.0	0.0 / 0.0	0.0 / 0.0	0.1 / 0.1	100.1 / 99.9
3	97.8 / 95.6	0.0 / 0.0	0.0 / 0.0	0.0 / 0.0	0.0 / 0.0	0.1 / 0.1	1.0 / 1.2	98.9 / 96.9
6	94.9 / 93.3	0.0 / 1.2	0.0 / 0.0	0.0 / 1.1	0.0 / 0.0	0.2 / 0.3	2.1 / 2.3	97.2 / 98.2
24	82.0 / 78.6	0.0 / 6.1	0.0 / 0.0	0.0 / 3.3	6.0 / 2.1	1.8 / 2.6	3.7 / 4.2	93.6 / 97.0
48	62.5 / 69.8	7.5 / 6.0	3.4 / 0.0	6.2 / 6.5	0.0 / 2.4	5.3 / 6.1	6.1 / 5.9	94.3 / 97.1
72	62.9 / 66.6	6.6 / 7.0	4.0 / 4.9	0.0 / 0.0	6.4 / 3.8	7.6 / 8.5	6.3 / 6.0	94.1 / 97.2
120	55.5 / 58.7	3.0 / 5.1	6.0 / 3.3	3.4 / 0.0	4.6 / 2.9	11.9 / 12.2	7.8 / 7.0	92.8 / 89.8
				Dark control				
3	99.2 / 98.0	0.0 / 2.2	0.0 / 0.0	0.0 / 0.0	0.0 / 0.0	0.0 / 0.0	0.2 / 0.2	99.3 / 100.4
6	99.3 / 95.4	0.0 / 2.8	0.0 / 0.0	0.0 / 0.0	0.0 / 0.0	0.0 / 0.0	0.3 / 0.2	99.6 / 98.5
24	96.6 / 93.4	3.7 / 3.3	0.0 / 0.0	0.0 / 3.0	0.0 / 0.0	0.0 / 0.0	0.4 / 0.3	100.7 / 100.1
48	90.8 / 88.9	9.6 / 4.5	0.0 / 0.0	0.0 / 0.0	0.0 / 0.0	0.0 / 0.1	0.4 / 0.4	100.8 / 96.4
72	90.4 / 93.2	4.4 / 6.1	0.0 / 0.0	4.2 / 0.0	0.0 / 0.0	0.0 / 0.1	0.5 / 0.4	99.4 / 99.8
120	90.1 / 87.0	3.5 / 6.5	0.0 / 0.0	6.6 / 5.5	0.0 / 0.0	0.1 / 0.2	0.5 / 0.6	100.8 / 99.7

Other volatiles than CO_2 were found in negligible amounts in the irradiated samples only. Another unknown breakdown product (M4) was detected in one sample, in an amount of 3 % AR.

Assuming 1st order kinetics for the degradation of racemic fenoxaprop-ethyl (AE F033171) the following degradation rates were calculated:

- Irradiation #1: *DT50* = 133 h = 5.5 d (r = -0.939)
- Irradiation #2: *DT50* = 156 h = 6.5 d (r = -0.962)
- Dark control: *DT50* = 750 h = 31 d (r = -0.881)
- Dark control: *DT50* = 835 h = 35 d (r = -0.842)

Although the regressions for the dark controls were not very good they were used to correct the data for non-photolytic degradation. Thus the following values for photolysis half-life were derived:

- Irradiation #1: *DT50* (photolysis) = 162 h (= 6.75 d), corresponding to 596 h of sunshine at 52 °N
- Irradiation #2: *DT50* (photolysis) = 192 h (= 8 d), corresponding to 672 h of sunshine at 52 °N

Conclusions:

For racemic fenoxaprop-ethyl (AE F033171) half-lives for photodegradation on soil surfaces of 50 days and 56 days were calculated (52° N, 12 hours sunshine/day). Compared to microbial degradation this photolytic pathway contributes only to a limited extent to the dissipation of the parent and its metabolites from soil. Metabolites M1 (max. 6.0 % AR) and M6 (max. 6.4 % AR) as well as CO_2 (max. 12.2 % AR) and non-extractable residues (max. 7.8 % AR) were the main photoproducts in this study.

Comments RMS AT:

- The soil photolysis study by Sarafin & Jordan (1989) only partly follows guidance such as OECD draft guidance on phototransformation of chemicals on soil surfaces (2002) or OPPTS guidance 835.2410, photodegradation on soil (2008):
  - Sterilisation of soil is not foreseen in guidance documents
  - Only air-dried samples were exposed (no moist samples as suggested in the OECD draft guidance)
  - Incubation temperature was 25 ± 5 °C instead of 20 ± 2 °C as recommended in the OECD draft guidance

  On overall, deviations observed are not considered to invalidate the study (also refer to next comment).

- The test substance used in this study is the racemic mixture of R/S fenoxaprop-ethyl (AE F033171), consisting of about 50 % fenoxaprop-P-ethyl (AE F046360). However, photolysis is not considered to be sensitive to R/S isomers, thus no impact on the photo-degradation behaviour is expected. In addition, degradation of fenoxaprop-P-ethyl (AE F046360) in aerobic soils is fast at all and irradiation is not expected to significantly enhance dissipation of fenoxaprop-P-ethyl (AE F046360) in terrestrial environments. In this respect, it is also considered defendable to use sterile soils in soil photolysis experiments in order to slow down degradation and to ensure that the test substance is sufficiently exposed to irradiation, allowing formation of possible photolysis degradation products to take place.

- Irradiated, dark and net degradation rates of racemic fenoxaprop-ethyl (AE F033171), considered as an surrogate for non-racemic fenoxaprop-P-ethyl (AE F046360), were recalculated by the RMS AT following pertinent guidance applying CAKE 3.3.

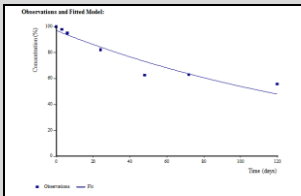
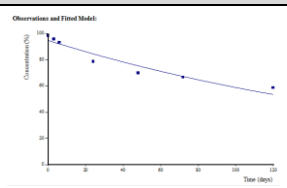
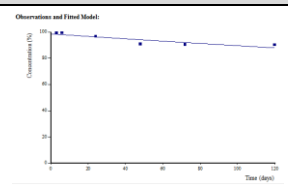
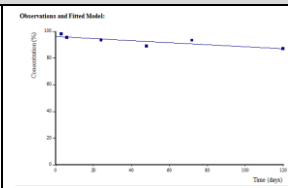
Table B.8.1.1.3-54 Degradation rates of racemic fenoxaprop-ethyl (AE F033171) under conditions of soil photolysis (sterile soils) - RMS AT assessment

Environment	System	Kinetics	*DT50* / *DT90* (d)	χ^2 error (%)	Prop. > t	Visual assessment
Continuous irradiation in the lab	Irradiated #1	SFO	4.9 / 16.3	5.3	< 0.01	Medium
	Irradiated #2	SFO	6.1 / 20.2	4.0	< 0.01	Medium
	Dark #1	SFO	30.3 / 101	1.6	< 0.01	Good
	Dark #2	SFO	34.5 / 115	1.7	0.02	Good
	Net #1		**5.8 / 19.4**			

	Net #2		**7.4 / 24.5**			
Environmental conditions (52 °N)[(a)]	Irradiation #1	-	56.8 / 190	-	-	-
	Irradiation #2	-	68.8 / 228	-	-	-
	Geomean	-	**62.5 / 208**	-	-	-

[(a)] One day continuous irradiation equals 9.8 days (Irr #1) and 9.3 days (Irr #2), respectively, assuming that the daily sun radiation intensity is 75 % of the maximum intensity over a 12-hr period (following paragraph 17 in OECD draft guidance).

Table B.8.1.1.3-55 Fits on degradation rates of racemic fenoxaprop-ethyl (AE F033171) under conditions of soil photolysis (sterile soils) - <u>RMS AT assessment</u>

			
Irradiated #1	**Irradiated #1**	**Dark #1**	**Dark #2**

B.8.1.1.4. Summary on route of degradation in soil

The degradation of fenoxaprop-P-ethyl (AE F046360) under **aerobic soil conditions** proceeds via fast microbial-induced hydrolysis of the ester functional group to form the herbicidal active metabolite fenoxaprop-P-acid (AE F088406). This ester hydrolysis is followed by cleavage at the 'central' heterocyclic ether bond to result in formation of chlorobenzoxazolone (AE F054014) and, in principle, of its counterpart HOPP-acid (AE F096918). However, as indicated by additional dedicated degradation studies (Fitzmaurice, 2010; Stroech & Junge, 2014), HOPP-acid (AE F096918) is degraded almost spontaneously in aerobic soil once formed and the compound is thus too short-living to occur at significant levels in corresponding aerobic soil degradation tests. Cleavage of fenoxaprop-P-acid (AE F088406) at the 'non-central' ether bond (i.e. split at the alkyl ether-phenyl moiety) resulted in the formation of the phenolic metabolite (AE F040356) observed as a minor pathway (< 5 % AR) in the route of degradation in aerobic soil. Formation of non-extractable residues (NER) was significant, particularly for the chlorophenyl label. At study end NER accounted for 63.5 - 68.7 % AR in studies lasting for 37 days and 49.4 - 70.1 % AR in studies lasting for 100 days. Formation of NER for the phenoxy label was somewhat lower with finally 37.6 - 51.3 % AR in studies lasting for 37 days. Formation of CO_2 was significant as well, at study end 8.4 - 16.6 % (37 days studies) and 9.7 - 32.5 % AR (100 days studies), respectively, were observed for the chlorophenyl label. Formation of CO_2 for the phenoxy label accounted for 33.5 - 49.6 % AR (37 days studies only). One study (Buerkle at al., 1986) conducted with racemic fenoxaprop-ethyl (AE F033171) basically gave the same results, but is considered as supplemental information only in this context. An additional study (Buettner et al., 2992) investigating fenoxaprop-P-ethyl (AE F046360) in one soil at 10 and 21 °C is not considered reliable owing to significant data scatter.

In principle, the route of degradation in **anaerobic soil** does not differ from the degradation pathway in aerobic soils. However, HOPP-acid (AE F096918) was found at significant amounts indicating that this metabolite may be considered rather stable under anaerobic soil conditions. As indicated above, HOPP-acid (AE F096918) is degraded spontaneously under aerobic soil conditions. In one anaerobic soil degradation study (Voelkel, 2001a), an unknown metabolite fraction ('M8') exceeded 5 % AR at two consecutive sampling points (max. 6.2 % at 120 DAT, declining thereafter) thus triggering identification and an exposure assessment according to Regulation (EU) No 283/2013. This is currently not the case (data gap). However, as 'M8' appears only in samplings following 45 days of continuous strict anaerobic conditions, the RMS AT considers significant amounts of 'M8' unlikely to occur under real outdoor conditions. Similar to aerobic conditions, formation for NER was significant with 63.9 - 76.4 % AR and 26.5 % AR for the chlorophenyl and phenoxy label, respectively (study end, approx. 120 days). Formation of CO_2 was low for the chlorophenyl label (0.6 - 3.9 % AR) but significant for the phenoxy label (22.7 % AR). It is noted that in one of these anaerobic soil degradation experiments racemic fenoxaprop-ethyl (AE F033171) was applied.

The route of **degradation on irradiated soil surfaces** has been investigated under laboratory conditions in one sterilized and dry soil at 25 °C following application of chlorophenyl labelled racemic fenoxaprop-ethyl (AE F033171). Fenoxaprop-ethyl (AE F033171) was degraded slowly under the conditions of the test when being compared to results of tests performed with microbial active and moist soils. Following continuous irradiation for 120 hours photolytic degradation was found to proceed via formation of non-extractable residues (NER, maximum 7.4 % AR after 120 hours) and CO_2 (maximum of 12.1 % AR after 120 hours). No formation of (racemic) fenoxaprop-acid (AE F053022) was observed in the course of the study. Chlorobenzoxazolone (AE F054014) was observed at maximum amounts of 6.8 % AR. Minor unknown metabolites were observed at levels of 6.4 % AR at maximum, at one sampling time only, thus neither triggering identification nor exposure assessment according to Regulation (EU) No 283/2013. The RMS AT notes that the soil photodegradation study has some deficits as it only investigates racemic fenoxaprop-ethyl (AE F033171) on dry and sterilized soil layers. However, considering the overall fast degradation of fenoxaprop-P-ethyl (AE F046360) in aerobic and anaerobic soils, a significant impact of irradiation on the overall dissipation of fenoxaprop-P-ethyl (AE F046360) in terrestrial systems is not expected at all.

Figure B.8.1.1.4-1: Proposed route of degradation of fenoxaprop-P-ethyl (AE F046360) in aerobic soil

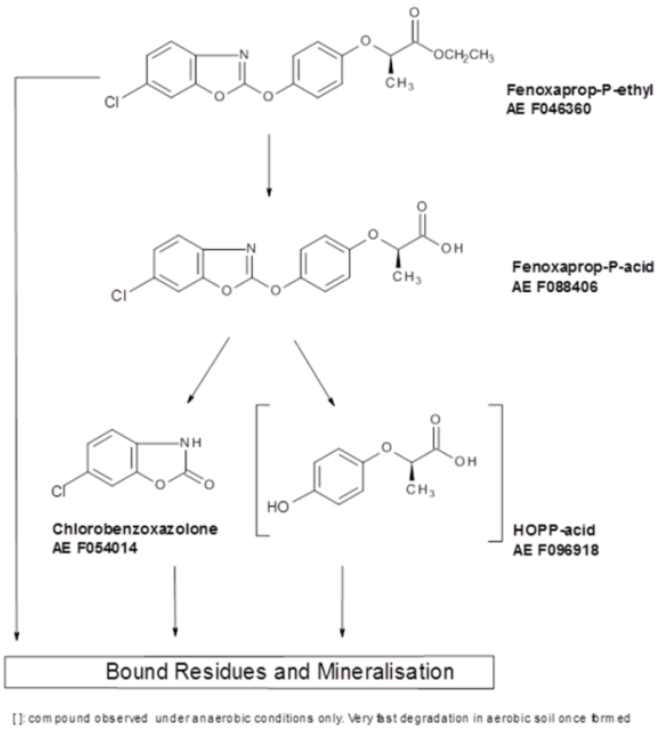


Figure B.8.1.1.4-2: Proposed route of degradation of fenoxaprop-P-ethyl (AE F046360) in anaerobic soil (2-(4-hydroxy-phenoxy)-propionic acid = HOPP acid (AE F096918))

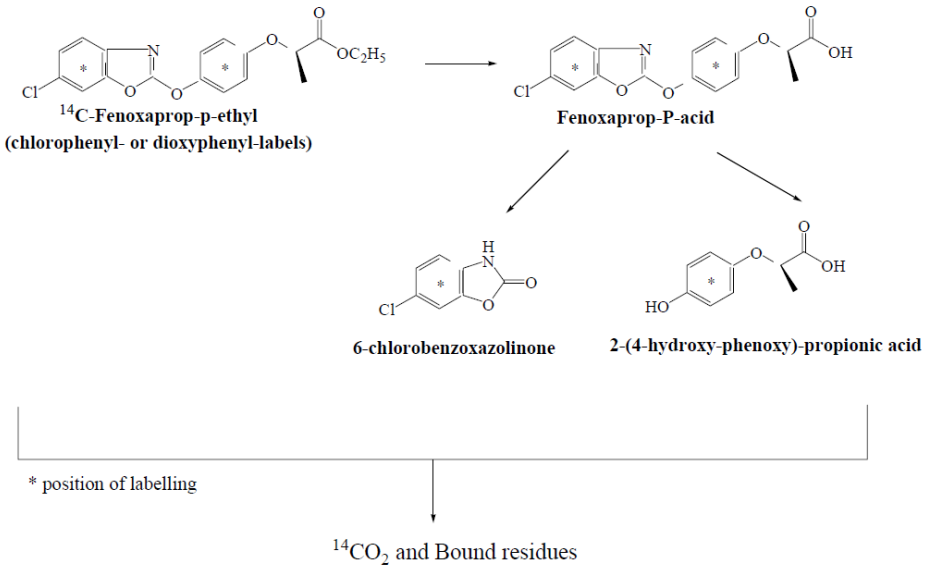


Table B.8.1.1.4-1: Summary on maximum occurrence (% AR) of identified and non-identified (unknown) metabolites in laboratory soil route studies conducted with fenoxaprop-P-ethyl (AE F046360) (metabolites shaded in grey require an exposure assessment in soil, groundwater and surface water)

Compound	Aerobic	Anaerobic	Soil photolysis
Fenoxaprop-P-acid (AE F088406)	85.8[(a)]	94.8[(a)]	no
Chlorobenzoxazolone (AE F054014)	19.1	7.5	6.8[(b)]
HOPP-acid (AE F096918)	no	74.1[(c)]	ni
Phenol metabolite (AE F040356)	1.2	2.2	ni
Unknowns	4.3	6.2[(d)]	6.4[(e)]

ni denotes not investigated
no denotes not observed (but investigated)
(a) Arithmetic mean of ClPh and Ph label applied to the same soil
(b) Racemic fenoxaprop-ethyl (AE F033171) applied (no study available with non-racemic fenoxaprop-P-ethyl (AE F046360)
(c) Racemic mixture (AE F020686) of HOPP-acid (AE F096918) observed after application of racemic fenoxaprop-ethyl (AE F033171); HOPP acid (AE F096918) max. 49.2 % of AR in one study with non-racemic fenoxaprop-P-ethyl (AE F046360) applied
(d) Metabolite fraction 'M8' exceeding 5 % AR at two consecutive sampling points (Voelkel, 2008a), other unknown metabolite fractions max. 5.4 % AR (at one sampling point only)
(e) At one sampling point only

B.8.1.2. Rate of degradation in soil

B.8.1.2.1. Laboratory studies

B.8.1.2.1.1. Aerobic degradation of the active substance

Studies submitted for first Annex I inclusion:

- **Stumpf & Dambach (1988)**, investigating chlorophenyl labelled fenoxaprop-P-ethyl (AE F046360) in four soils, amended by **Schwab (1993a)** and **Tarara (2004a)**
- **Buettner et al. (1992)**, investigating chlorophenyl labelled fenoxaprop-P-ethyl (AE F046360) in one soil at 21 and 11 °C
- **Buerkle et al. (1986)**, investigating phenoxy labelled racemic fenoxaprop-ethyl (AE F033171) in two soils, amended by **Schwab (1993b)** and **Tarara (2004b)**

New studies submitted by the Fenoxaprop-P-ethyl Task Force:

- **Shepherd (2012)**, investigating chlorophenyl labelled fenoxaprop-P-ethyl (AE F046360) in four US soils
- **Shepherd & Ripperger (2012)**, investigating phenoxy labelled fenoxaprop-P-ethyl (AE F046360) in four US soils

All these studies have already been discussed in section B.8.1.1.1 (refer to route of degradation in soil).

A new kinetic analysis of the experimental data in laboratory aerobic soil degradation studies was conducted following the current EC guidance document to derive the rate of degradation of fenoxaprop-P-ethyl (AE F046360) and its metabolites in aerobic soils **(Oberdoerster et al., 2016)**.

Reference:	**Fenoxaprop-P-ethyl and metabolites: Kinetic evaluation of aerobic soil degradation under laboratory conditions**
Author(s), year:	Oberdoerster, C., Boiselle, N., Herrmann, M. (2016)
Report/Doc. Number:	EnSa-15-0391, M-552947-01-1
Guideline(s):	FOCUS, 2006, Sanco/10058/2005 version 2.0; EFSA Journal 2014;12(5):3662 (2014); FOCUS, 2014: Generic guidance for Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration, Version: 1.1; Date: 18 December 2014
GLP:	None
Validity:	Partly (refer to comment section)
Status:	**New submission**

Executive Summary:

For the active substance fenoxaprop-P-ethyl (AE F046360) degradation data from Stump & Dambach (1988), Buettner et al. (1992), Shepherd (2012) and Shepherd & Ripperger (2012) were kinetically evaluated according to actual FOCUS Guidance to derive values for the half-life and the *DT90* in aerobic soil from studies performed at 20 to 22 °C for modelling and trigger endpoints.

A total of four aerobic soil degradation studies performed under laboratory conditions were considered to consist of 13 data sets in total, following application of [UL-chlorophenyl-^{14}C]- or [UL-phenoxy-^{14}C]-fenoxaprop-P-ethyl (AE F046360) to different soils.

The calculations of half-lives in soil followed a stepwise approach. For identification of best fits to the measured data the SFO kinetic model was applied as the initial step. This was followed by application of bi-phasic models, i.e. FOMC or DFOP, in case of unacceptable fits according to the criteria set. The resulting best fits served as the basis to derive non-normalized half-lives for comparison against trigger endpoints. Following again the decision criteria set by FOCUS, fits and their half-lives were identified to serve as the basis for estimation of normalized (reference conditions 20 °C, *p*F2 moisture) values of the *DegT50*.

Trigger endpoints: Non-normalised values of the *DegT50* and the *DegT90* for tests performed at 20 to 22 °C were derived from SFO, FOMC and DFOP kinetic models as best fits.

Non-normalised half-lives of fenoxaprop-P-ethyl (AE F046360) ranged from 0.065 days soil for US Springfield clay loam soil to 0.424 days for German sandy loam while values for the *DegT90* ranged from 0.226 days for US Springfield clay loam soil to 8.52 days for US Pikeville sandy loam soil.

Table B.8.1.2.1.1-1 Comparison against EU triggers: Summary of results of kinetic evaluation of degradation for fenoxaprop-P-ethyl (AE F046360) in aerobic soil in the laboratory

Parameter	Fenoxaprop-P-ethyl (AE F046360)
20 °C, Non-normalised *DT50* , range (days)	0.065 – 0.424
Worst case *DT50* (days)	**0.424**
20 °C, Non-normalised *DT90* , range (days)	0.226 – 8.52
Worst case *DT90* (days)	**8.52**

Modelling endpoints: SFO and FOMC were considered as the visually and statistically best acceptable kinetic models for deriving modelling endpoints. Values were normalised by comparison of study incubation conditions to reference conditions (20 °C, *p*F2 moisture).

For use as modelling endpoint, the overall mean normalised half-life of fenoxaprop-P-ethyl (AE F046360) was estimated to 0.345 days.

Table B.8.1.2.1.1-2 Modelling endpoints: Normalised laboratory DT_{50}-values for fenoxaprop-P-ethyl (AE F046360) in aerobic soil for use as input in environmental exposure assessments

Parameter	Fenoxaprop-P-ethyl (AE F046360)
Normalised (20 °C, *p*F2) DT_{50} , range (days)	0.068 – 1.37
Geometric mean	**0.345**

Material and methods:

For the active substance fenoxaprop-P-ethyl (AE F046360) details on study conduct and its results have been summarised in Section B.8.1.1.1. The degradation data were kinetically evaluated following FOCUS guidance (FOCUS, 2006, amended 2011)[2] with the software KinGUI2.1.

The actual kinetic evaluation considered those data sets that were considered reliable and valid by the RMS during the assessment for Annex I inclusion (Stump & Dambach, 1988, and Buettner et al, 1992) and data sets resulting from new information (Shepherd, 2012, and Shepherd & Ripperger, 2012).

The kinetic evaluation relied on a total set of four aerobic soil degradation studies performed with the active substance at 20 to 22 °C to result in 13 data sets in total including re-assessment of reliability in Section B.1.1.1.

For the data set resulting from tests at 11 °C (Buettner et al, 1992), the reason for exclusion was the incubation at this non-standard test temperature combined with the fact that degradation data were available in the same soil at the test temperature of 20 °C.

The kinetic evaluation derived *DT50*-values according to the respective decision flowchart for the determination of trigger endpoints and for use as input parameters in modelling.

- All data sets were evaluated using simple first order (SFO), first order multi-compartment (FOMC) and double first order in parallel (DFOP) kinetics with free optimisation of parameters.
- The kinetic evaluations and the statistical calculations were conducted with KinGUI (v2.0) using iteratively re-weighted least-square (IRLS) optimization.
- The measured values were taken into account as reported and thus treated as individual replicates. All

[2] 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

sets with their data points were weighted equally.

- For day zero samples, total residues of fenoxaprop-P-ethyl (AE F046360) were set to the amount recovered.

For the evaluation of results the following was considered in addition:

- In a first and major step the assessment of fits was made on the basis of visual inspection. The visual inspection focused on residuals to be minimal compared to the measured data and should randomly distributed around zero. Systematic variations of the residuals can be regarded as an indication for an inappropriate kinetic model. However, in case of sufficiently small, but systematic deviations, a fit may be still qualified to be visually acceptable.
- The quantitative statistical measure for the quality of a fit was expressed in terms of chi square (χ^2) with the latter to be a minimum.
- For a check of parameter significance the evaluation included a test to identify the probability that a parameter is not significantly different from zero, here expressed in terms of a t-test.
- The identification of the most appropriate kinetic model was based on visual inspection and the scaled error (χ^2). Since most exposure models use SFO, this is the kinetic model of choice. If case the SFO fit was visually acceptable and the scaled error χ^2 did not significantly exceed 15 %, the SFO fit and its parameters were regarded as acceptable.
- In case the value of χ^2 was significantly higher than 15 %, other kinetic models were tested and/or model parameters were fixed based on available information (e.g. initial amount). The model with the smaller error is finally chosen as the appropriate model. For metabolite fits also higher values of χ^2 were accepted.
- In case the measured residues of the compound applied were below 10 % at study end, the Gustafson-Holden (FOMC) model was applied as an alternative. Provided the FOMC fit was visually acceptable and significantly better than the SFO fit with a χ^2 error significantly below 15 %, the FOMC fit and its parameters was accepted. An equivalent single first-order half-life was 'back-calculated' on the basis of $DT90_{FOMC}$ / 3.32, while the $DT90_{FOMC} = \beta\ (10^{1/\alpha} - 1)$. The equivalent SFO-curve then meets the FOMC-curve at the time $DT90_{FOMC}$ thus over-predicting the residues at earlier time points as a conservative element.
- In case the measured residues at study end were higher than 10 % of the applied amount, the dual first order in parallel (DFOP) or the hockey stick (HS) model were considered. If the respective fit was acceptable applying the criteria discussed above, the fitted parameter values were considered. Then, a very conservative equivalent single first-order half-life was calculated from the lower of the two kinetic rates. In effect the resulting equivalent SFO-curve over-predicts the residues at all time points.
- In case none of the alternative models had led to a significantly improved fit, the SFO model was chosen, when visually acceptable. The purpose of these rules is to finally avoid over-parameterised models just based on a marginally better fit.
- The value for the scaled error χ^2 of 15 % should not be handled as a threshold and thus as a strict and absolute cut-off criterion since this value is most appropriate only under optimal experimental conditions. While the value of χ^2 may exceed 15 %, the model fit may still describe reasonably well the degradation behaviour. In particular for metabolites it may be justified to accept higher values, due to generally low measurements compared to the mean of all measurements, which strongly influences the results of the χ^2 test.

Table B.8.1.2.1.1-3 Degradation studies performed with fenoxaprop-P-ethyl (AE F046360) in aerobic soil under laboratory conditions including characteristics of soils

Study	Soil	Soil texture	T (°C)	Test moisture (% MWHC)	Sand (%)	Clay (%)	Org. carbon (%)	*p*H ($CaCl_2$)	CEC (meq / 100 g)
Stumpf & Dambach (1988)	SL 2.2	Loamy sand	22	40	79.7	9.1	2.63[(a)]	5.8	10.6
	SL V	Sandy loam	22	40	58.8	6.9	0.74[(a)]	5.6	5.6
	SL 2	Silt loam	22	40	10.8	19.0	0.70[(a)]	5.2	18.4
	SL S	Sandy loam	22	40	55.3	11.6	1.32[(a)]	5.2	5.2
Buettner et al. (1992)	SLV	Sandy loam	21	40	54.4	11.3	0.90[(a)]	5.8	6.9
Shepherd (2012)	Pikeville	Sandy loam	20	26	62.2	7.7	1.4	5.2	6.3
	Porterville	Loamy sand	20	57	79.8	9.7	0.46	6.9	10.3

	Sanger	Sandy loam	20	42	64.4	7.5	0.48	6.2	6.5
	Springfield	Silt loam	20	74	14.8	25.6	1.9	6.6	17.4
Shepherd & Ripperger (2012)	Pikeville	Sandy loam	20	26	62.2	7.7	1.4	5.2	6.3
	Porterville	Loamy sand	20	57	79.8	9.7	0.46	6.9	10.3
	Sanger	Sandy loam	20	42	64.4	7.5	0.48	6.2	6.5
	Springfield	Silt loam	20	74	14.8	25.6	1.9	6.6	17.4

(a) Determined by division of organic matter content by 1.724

Results and discussion:

Trigger endpoint determination

Following the decision criteria and the pathway fit, i.e. the combined evaluation of parent test substance decline along with the formation of metabolites, the bi-phasic models FOMC and DFOP showed improvement over SFO kinetics for some data sets. Best-fits to measured data were derived from use of the SFO kinetic model for four data sets, FOMC for seven data sets and DFOP for two data sets.

The resulting non-normalised values for the *DT50* and the *DT90* were summarised in the tables below.

Table B.8.1.2.1.1-4 Trigger evaluation: Non-normalised best fit *DT50*-values for fenoxaprop-P-ethyl (AE F046360) in aerobic soils at 20 to 22 °C under laboratory conditions

Soil	Label position	Model	*DegT50* (days)	*DegT90* (days)	χ^2 (%)	t-test/ confidence interval	VA[a)]
LS 2.2, loamy sand, 22 °C (Study 1)	1	SFO	0.348	1.16	12.72	k < 0.001	O
SLV, sandy loam, 22 °C (Study 1)	1	SFO	0.332	1.10	11.03	k < 0.001	O
SL 2, silt loam, 22 °C (Study 1)	1	FOMC	0.250	2.99	6.52	-	+
SL S, sandy loam, 22 °C (Study 1)	1	FOMC	0.424	5.90	7.69	-	+
SLV, sandy loam, 21°C (Study 2)	1	FOMC	0.239	4.42	9.51	-	++
Pikeville, sandy loam, 20 °C (Study 3)	1	FOMC	0.316	6.97	5.45	-	++
Porterville, loamy sand, 20 °C (Study 3)	1	SFO	0.215	0.713	10.55	k < 0.001	+
Sanger, sandy loam, 20 °C (Study 3)	1	FOMC	0.129	1.20	2.40	-	++
Springfield, silt loam, 20 °C (Study 3)	1	DFOP	0.065	0.240	1.77	k_1 < 0.001 k_2 = 0.004	+
Pikeville, sandy loam, 20 °C (Study 4)	2	DFOP	0.340	8.52	12.05	k_1 < 0.001 k_2 = 0.005	++
Porterville, loamy sand, 20 °C (Study 4)	2	FOMC	0.143	0.974	6.01	-	++
Sanger, sandy loam, 20 °C (Study 4)	2	SFO	0.236	0.783	10.79	k < 0.001	+
Springfield, silt loam, 20 °C (Study 4)	2	FOMC	0.023	0.226	2.52	-	+

Study 1: Stumpf & Dambach (1988)
Study 2: Buettner et al. (1992)
Study 3: Shepherd (2012)
Study 4: Shepherd & Ripperger (2012)
1 = UL-chlorophenyl-^{14}C; 2 = UL-phenoxy-^{14}C
[a)] VA = Visual Assessment (++ = excellent, + = good, O = acceptable, - = not acceptable)

Modelling endpoint determination

Following the decision criteria and the corresponding pathway fit, i.e. the combined evaluation of parent test substance decline along with the formation of metabolites, the bi-phasic models FOMC showed improvement over SFO kinetics for some data sets. Evaluation of fits resulted in the use of the SFO kinetic model for six data sets and of FOMC for seven data sets.

Following kinetic evaluation the resulting values of half-life for use in environmental modelling were normalised to reference conditions regarding soil moisture (100 % field capacity) and temperature (20 °C). For normalization, the corresponding parameters used in the laboratory tests and the resulting correction factors were summarised in the table below.

Table B.8.1.2.1.1-5 Correction factors for soil temperature and moisture content

Soil	Temperature (°C)	Correction factor Temperature	Incubation moisture (% w/w)	*p*F2 moisture (% w/w)	Correction factor Moisture	Total correction factor
LS 2.2, loamy sand (Study 1)	22	1.0[(a)]	13.2	14[(b)]	0.960	0.960
SL V, sandy loam (Study 1)	22	1.0[(a)]	14.5	19[(b)]	0.827	0.827
SL 2, silt loam (Study 1)	22	1.0[(a)]	18.2	26[(b)]	0.780	0.780

SL S, sandy loam, (Study 1)	22	1.0[(a)]	13.0	19[(b)]	0.767	0.767
SL V, sandy loam (Study 2)	21	1.0[(a)]	12.0	19[(b)]	0.723	0.723
Pikeville, sandy loam (Study 3)	20	1.0	9.5	22.5	0.547	0.547
Porterville, loamy sand (Study 3)	20	1.0	14.2	15.8	0.928	0.928
Sanger, sandy loam (Study 3)	20	1.0	13.1	20.7	0.726	0.726
Springfield, silt loam (Study 3)	20	1.0	32.8	36.4	0.930	0.930
Pikeville, sandy loam (Study 4)	20	1.0	9.5	22.5	0.547	0.547
Porterville, loamy sand (Study 4)	20	1.0	14.2	15.8	0.928	0.928
Sanger, sandy loam (Study 4)	20	1.0	13.1	20.7	0.726	0.726
Springfield, silt loam (Study 4)	20	1.0	32.8	36.4	0.930	0.930

Study 1: Stumpf & Dambach (1988)
Study 2: Buettner et al. (1992)
Study 3: Shepherd (2012)
Study 4: Shepherd & Ripperger (2012)
(a) No correction since study was performed at test temperature of 20 ± 2°C
(b) Focus default value

Table B.8.1.2.1.1-6 Modelling evaluation: Normalised (20 °C and *p*F2) *DT50* values for fenoxaprop-P-ethyl (AE F046360) under laboratory conditions

Soil	Model	Trigger *DegT50* (days)	Trigger *DegT90* (days)	Non-normalised *DegT50* estimate for modelling (days)	*DegT50* (20 °C and *p*F2) (days)
LS 2.2, loamy sand (Study 1)	SFO	0.348	1.16	0.348	0.334
SL V, sandy loam (Study 1)	SFO	0.332	1.10	0.332	0.275
SL 2, silt loam (Study 1)	FOMC	0.250	2.99	0.900	0.702
SL S, sandy loam, (Study 1)	FOMC	0.424	5.90	1.78	1.37
SL V, sandy loam (Study 2)	FOMC	0.239	4.42	1.33	0.962
Pikeville, sandy loam (Study 3)	FOMC	0.316	6.97	2.10	1.15
Porterville, loamy sand (Study 3)	SFO	0.215	0.713	0.215	0.200
Sanger, sandy loam (Study 3)	FOMC	0.129	1.20	0.361	0.263
Springfield, silt loam (Study 3)	SFO	0.073	0.244	0.073	0.068
Pikeville, sandy loam (Study 4)	FOMC	0.351	5.20	1.566	0.859
Porterville, loamy sand (Study 4)	FOMC	0.143	0.974	0.293	0.272
Sanger, sandy loam (Study 4)	SFO	0.236	0.783	0.236	0.171
Springfield, silt loam (Study 4)	SFO	0.075	0.250	0.075	0.070
Geometric mean					**0.345**

Study 1: Stumpf & Dambach (1988)
Study 2: Buettner et al. (1992)
Study 3: Shepherd (2012)
Study 4: Shepherd & Ripperger (2012)

Conclusion:

For comparison with EU trigger endpoints the evaluation of degradation data in aerobic soil from tests performed at 20 to 22 °C according to actual FOCUS kinetic guidance resulted in values for non-normalised half-lives and the *DT90* of the active substance fenoxaprop-P-ethyl. Degradation was found to be adequately described by SFO as kinetic model as best fit for four data sets while it was bi-phasic models FOMC and DFOP for seven and two data sets, respectively. Values of non-normalised half-lives were found to range from 0.023 days for US Springfield silt loam to 0.424 days for a German sandy loam (SLS) soil. The range of values for the *DT90* ranged from 0.226 days (US Springfield silt loam) to 8.52 days for US Pikeville sandy loam soil.

For use as modelling input parameters in environmental risk assessments the evaluation resulted in values for normalised half-lives of the active substance fenoxaprop-P-ethyl in aerobic soil. The approach according to FOCUS resulted in use of the SFO kinetic model for six data sets and the bi-phasic model FOMC for seven data sets. Half-lives were normalised for moisture (*p*F2) and temperature (20°C). The values derived from laboratory tests are regarded as suitable and reliable for use in environmental exposure assessments. For the active substance fenoxaprop-P-ethyl, a normalised geometric mean half-life of 0.345 days was calculated as modelling endpoint.

Comments (RMS AT):

- In view of the extremely fast degradation of fenoxaprop-P-ethyl (AE F406360) in soil, the RMS AT considers different kinetic models for trigger and modelling endpoints for fenoxaprop-P-ethyl (AE F046360) overly complex. The RMS AT agrees with the applicant's kinetic evaluation for deriving *modelling* endpoints for fenoxaprop-P-ethyl (AE F406360), based on SFO and FOMC kinetics only, and recommends using these results as *trigger endpoints* as well. Notice that FOMC fits already give excellent fits (see figures below). Respective endpoints for trigger evaluation (RMS AT assessment) including statistical criteria not stated in the applicant summary are given in the table provided below.

- As discussed more in detail in Buettner et al. (1992) the RMS AT considers residues (parent as well as metabolites) detected in Buettner et al. (1992) not sufficiently robust to allow for kinetic evaluation. This data set is therefore excluded from the final soil degradation data set.

- The study authors calculated individual degradation rates for both labels (ClPh & Ph) in Shepherd (2012) and Shepherd & Ripperger (2012). Ideally, the two labels (with two replicates each) should have been already pooled for kinetic evaluation as the experimental conditions including soil properties seems to be identical in both studies. However, as different labels revealed similar degradation rates (albeit sometimes different kinetic models), the approach by the applicant is considered acceptable in this case.

- The study authors calculated the geometric *DegT50* of fenoxaprop-P-ethyl (AE F046360) on basis of individual labels from Shepherd (2012) and Shepherd & Ripperger (2012). As this gives bias to this particular soil dataset, the RMS AT recommends to first calculating the geometric mean of both labels for each of the four soils and finally calculate the geometric mean of the remaining 8 soils. This comment is also related to the comment given above.

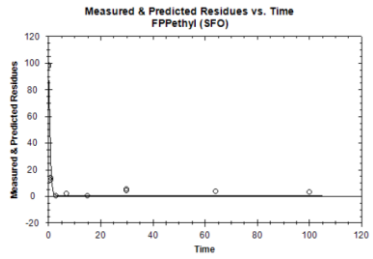
Table B.8.1.2.1.1-7 Trigger & modelling endpoints: Non-normalised best fit *DegT50* and *DegT90* and normalized *DegT50* values for fenoxaprop-P-ethyl (AE F046360) in aerobic soils at 20 to 22 °C under laboratory conditions - applicant fits agreed by the RMS AT

Soil	Label	Model	*DegT50* (days)	*DegT90* (days)	χ^2 error (%)	t-test	VA[a)]	*DegT50* (20 °C and *p*F2) (days)
LS 2.2, loamy sand (Study 1)	ClPh	SFO	0.35	1.2	12.7	k: < 0.001	O	0.33
SL V, sandy loam (Study 1)	ClPh	SFO	0.33	1.1	11.0	k: < 0.001	O	0.28
SL 2, silt loam (Study 1)	ClPh	FOMC	0.25	3.0	6.5	-	+	0.70[(a)]
SL S, sandy loam, (Study 1)	ClPh	FOMC	0.42	5.9	7.7	-	+	1.4[(a)]
Pikeville, sandy loam (Study 3)	ClPh	FOMC	0.32	7.0	5.5	-	++	1.2[(a)]
Porterville, loamy sand (Study 3)	ClPh	SFO	0.22	0.71	10.6	k: < 0.001	+	0.20
Sanger, sandy loam (Study 3)	ClPh	FOMC	0.13	1.2	2.4	-	++	0.26[(a)]
Springfield, silt loam (Study 3)	ClPh	SFO	0.07	0.24	7.3	k: < 0.001	+	0.07
Pikeville, sandy loam (Study 4)	Ph	FOMC	0.35	5.2	12.8	-	++	0.86[(a)]
Porterville, loamy sand (Study 4)	Ph	FOMC	0.14	1.0	6.0	-	++	0.27[(a)]
Sanger, sandy loam (Study 4)	Ph	SFO	0.24	0.78	10.8	k: < 0.001	+	0.17
Springfield, silt loam (Study 4)	Ph	SFO	0.08	0.25	8.6	k: < 0.001	+	0.07

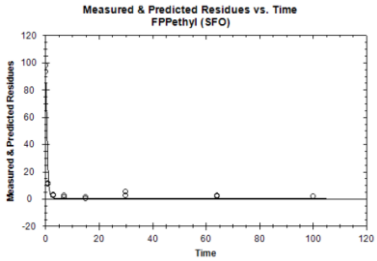
Study 1: Stumpf & Dambach (1988)
Study 3: Shepherd (2012)
Study 4: Shepherd & Ripperger (2012)
(a) Based on non-normalized FOMC-DT90 divided by 3.32

- Figures for the kinetic fits, not provided in the applicant summary, are given in the table below.

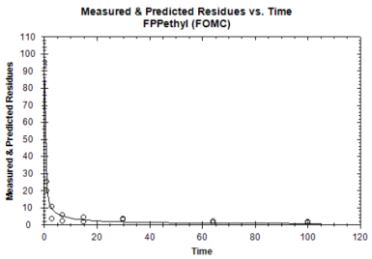
Table B.8.1.2.1.1-8 Kinetic evaluation of degradation of fenoxaprop-P-ethyl (AE F046360) in aerobic soils at 20 to 22 °C under laboratory conditions - residue fits for trigger & modelling endpoints - applicant fits agreed by the RMS AT



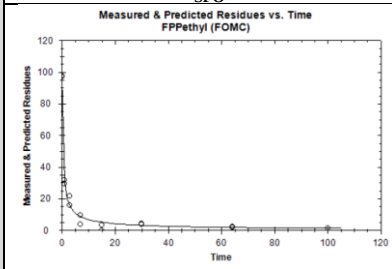
LS2.2, loamy sand (Study 1) - P_{SFO}



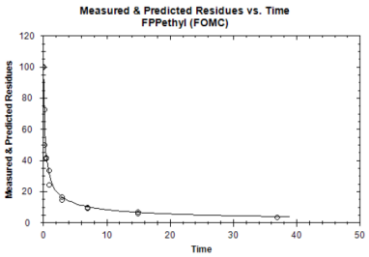
SLV, sandy loam (Study 1) - P_{SFO}



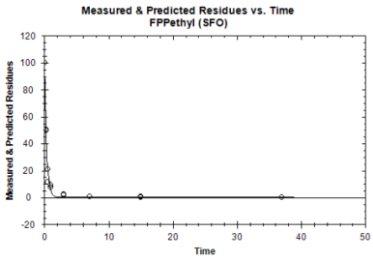
SL2, sandy loam (Study 1) - P_{FOMC}



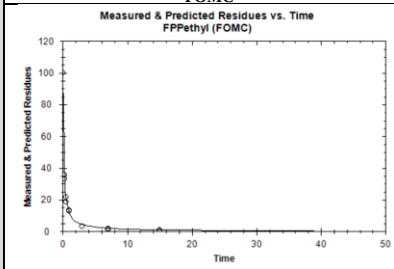
SLS, sandy loam (Study 1) - P_{FOMC}



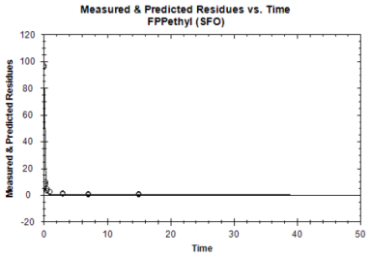
Pikeville, sandy loam (Study 3) - P_{FOMC}



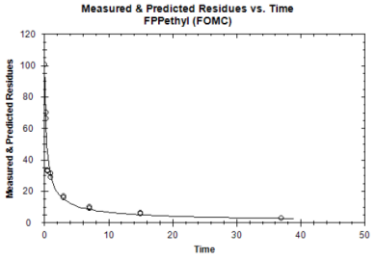
Porterville, loamy sand (Study 3) - P_{SFO}



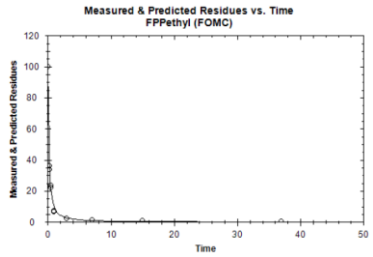
Sanger, sandy loam (Study 3) - P_{FOMC}



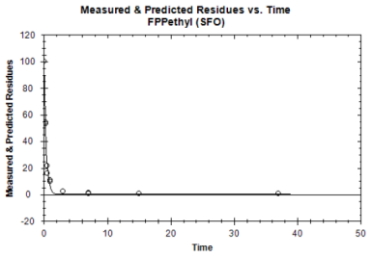
Springfield, silt loam (Study 3) - P_{SFO}



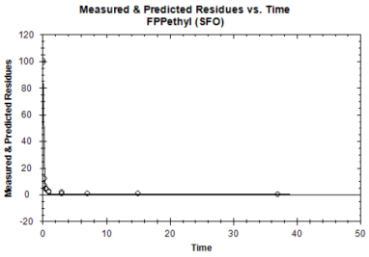
Pikeville, sandy loam (Study 4) - P_{FOMC}



Porterville, loamy sand (Study 4) - P_{FOMC}



Sanger, sandy loam (Study 4) - P_{SFO}



Springfield, silt loam (Study 4) - P_{SFO}

B.8.1.2.1.2. Aerobic degradation of metabolites, breakdown and reaction products

Studies submitted for first Annex I inclusion:

- **Stumpf & Dambach (1988)**, investigating chlorophenyl labelled fenoxaprop-P-ethyl (AE F046360) in four soils, amended by **Schwab (1993a)** and **Tarara (2004a)**
- **Buettner et al. (1992)**, investigating chlorophenyl labelled fenoxaprop-P-ethyl (AE F046360) in one soil at 21 and 11 °C
- **Buerkle et al. (1986)**, investigating phenoxy labelled racemic fenoxaprop-ethyl (AE F033171) in two soils, amended by **Schwab (1993b)** and **Tarara (2004b)**

New studies submitted by the Fenoxaprop-P-ethyl Task Force:

- **Shepherd (2012)**, investigating chlorophenyl labelled fenoxaprop-P-ethyl (AE F046360) in four US soils
- **Shepherd & Ripperger (2012)**, investigating phenoxy labelled fenoxaprop-P-ethyl (AE F046360) in four US soils

All these studies have already been discussed in section B.8.1.1.1 (refer to route of degradation in soil).

New studies on metabolites submitted by the Fenoxaprop-P-ethyl Task Force:

- **Fitzmaurice (2010)**, investigating the rate of radiolabelled HOPP acid (AE F096918) in three soils
- **Stroech & Junge (2014)**, investigating the rate of radiolabelled HOPP acid (AE F096918) in four soils

A new kinetic analysis of the experimental data in laboratory aerobic soil degradation studies was conducted following the current EC guidance document to derive the rate of degradation of fenoxaprop-P-ethyl (AE F046360) and its metabolites in aerobic soils **(Oberdoerster et al., 2016)**.

Reference:	**[^{14}C]-HPPA: Rate of degradation under aerobic conditions in three soils at 20 degree**
Author(s), year:	Fitzmaurice, M. (2010)
Report/Doc. Number:	315 FPE, M-548269-01-1
Guideline(s):	OECD No. 307 (2002)
GLP:	Yes
Validity:	Yes
Status:	**New submission**

Executive Summary:

The degradation rate of [UL-phenyl-^{14}C]-labelled hydroxyphenoxy propanonic acid (HOPP acid, AE F096918) was investigated in three soils under aerobic conditions at 20 °C and soil moisture at 45 % (soil Farditch), 24 % (soil Longwoods) and 41 % (soil Lockington) of the MWHC in the dark. The study was performed at a nominal application rate of 0.18 mg ^{14}C-test substance/kg soil, equivalent to a treatment rate in the field of 67.5 g test substance/ha for a maximum incubation period of 14 days.

Values for ^{14}C-HOPP-acid extractable from soil decreased from 65.6 % (day zero) to 0.7 % (day 1) in soil Farditch, from 83.5 % (day zero) to 0.6 % (day 4) in soil Longwoods and from 78.9 % (day zero) to 0.4 % (day 4) in soil Lockington.

Material and Methods:

Test Material
[UL-phenyl-^{14}C]-(R)-2-(4-hydroxyphenoxy)-propanoic acid (HOPP-acid, AE F096918)
Specific radioactivity: 5.43 MBq/mg (146.6 µCi/mg)
Radiochemical purity: 98.6 % (HPLC)
Chemical purity: 98.7 % (HPLC)
Sample ID: 3420FDG008-4

Soils
The test soils originated from the EU and reflected a range of physico-chemical characteristics. The soils had been collected fresh from the field and were passed through a 2 mm sieve.

Table B.8.1.2.1.2-1 Characteristics of test soils

Soil	Farditch (09/044)	Longwoods (09/045)	Lockington (09/047)
Geographic location (city / state / country)	Longwoods / Derbyshire / United Kingdom	Longwoods Quarry / Lincolnshire / United Kingdom	Lockington Grounds farm / Leicestershire / United Kingdom
OS Map Reference	SK104691	TF056591	SK488304

Textural class [A)]	loam	sandy loam	sandy clay loam
Sand (%) [A)]	36	72	52
Silt (%) [A)]	49	12	18
Clay (%) [A)]	15	16	30
*p*H - water	6.1	7.7	5.9
- 0.01 M $CaCl_2$	5.8	7.4	5.7
Organic matter (%) [B)]	6.2	2.4	5.8
Organic carbon (%)	3.7	1.4	3.4
Microbial biomass (mg microbial C / 100 g soil)			
- Initial	30.5	23.3	102.4
- Final	24.0	21.5	75.4
Cation exchange capacity (meq/100 g)	12.5	12.3	21.1
Water holding capacity at zero bar (*p*F 1) (%)[C)]	73.3	44.5	66.2
Water holding capacity at 0.1 bar (*p*F 2) (%)	36.3	11.7	28.9
Water holding capacity at 0.33 bar (*p*F 2.5) (%)	29.6	9.2	24.9
Actual test moisture (% MWHC)	45.0	23.6	40.6

MWHC = maximum water holding capacity
[A)] USDA classification
[B)] % organic matter = % organic carbon x 1.724
[C)] Equivalent to the Maximum Water Holding Capacity (MWHC)

Experimental conditions
Samples of 100 g dry weight of soil each were filled into glass incubation flasks with each sample to receive 0.18 mg test substance/kg soil, a dose representing a field rate of 67.5 g test substance/ha. Following application the samples were attached to 'flow through' systems with traps to collect each ^{14}C-carbon dioxide and other volatile components. Samples were incubated at 20 ± 2 °C and at 45 % (soil Farditch), 24 % (Longwoods) and 41 % (Lockington) moisture of the maximum water holding capacity (MWHC) in the dark for 14 days in maximum. In addition, untreated soil samples were incubated under the same conditions for determination of soil microbial activity.

Sampling
Duplicate samples were removed for work-up after 0, 1 and 3 hours and 1, 4, 7 and 14 days of incubation. Samples for determination of soil microbial biomass were investigated after 0 days and at the end of incubation. The complete samples were immediately processed by extraction.

Analytical procedures
The entire soil samples were extracted three times by shaking the soil/solvent mixture at ambient temperature for 30 min successively with 270 mL aqueous acetonitrile including formic acid (3.7/92.6/3.7, by vol.), followed by 110 mL aqueous acetonitrile including formic acid (4.5/91/5.5, by vol.) and finally by 100 mL acetonitrile. The extracted soil was extracted with aqueous acetonitrile containing hydrochloric acid (78/20/2, by vol., 102 mL) by boiling the mixture for one hour. Ambient extracts were combined and sub-samples concentrated prior to analysis.

The ^{14}C-material balance was established for each sample by extraction, analysis of volatiles and combustion of non-extractable radioactive residues (NER). Following quantitation of radioactivity in extracts by LSC, analysis was performed by reversed phase HPLC followed and ^{14}C-flow-through detection techniques as primary chromatographic method. The limit of detection (LOD) was 0.1 % AR. In addition, day-0 samples were analysed by liquid chromatography/mass spectroscopic analysis (LC-MS) to confirm the identity of HOPP acid. The NER determination was performed by combustion/LSC of aliquots of the air-dried extracted soil.

Results and Discussion:

Table B.8.1.2.1.2-2 Degradation of [UL-phenyl-^{14}C]-HOPP-acid (AE F096918) in loam soil Farditch under aerobic conditions

Component	Replicate No.	Sampling interval (days) 0	0.04 (1 hr)	0.125 (3 hrs)	1	4	7	14
HOPP-acid (AE F096918)	1	53.57	3.63	6.96	1.07	0.00	n.d.	n.d.
	2	77.69	2.03	3.06	0.41	0.00	n.d.	n.d.
	Mean	**65.63**	**2.83**	**5.01**	**0.74**	**0.00**	**n.a.**	**n.a.**

Others [B)]	1	43.05	20.54	17.78	8.79	3.29	n.d.	n.d.
	2	21.02	22.10	18.87	9.27	3.40	n.d.	n.d.
	Mean	**32.03**	**21.32**	**18.32**	**9.03**	**3.34**	**n.a.**	**n.a.**
Total extractable radioactivity	1	96.62	25.03	25.99	12.03	4.77	3.39	2.94
	2	98.71	24.94	22.92	11.99	5.02	3.66	2.69
	Mean	**97.67**	**24.99**	**24.46**	**12.01**	**4.89**	**3.52**	**2.81**
Non-extractable radioactivity	1	2.88	73.18	61.92	79.28	83.28	72.78	76.21
	2	3.46	80.41	71.97	81.29	88.86	79.20	82.92
	Mean	**3.17**	**76.79**	**66.94**	**80.29**	**86.07**	**75.99**	**79.56**
^{14}C-CO_2 and other volatiles [A)]	1	0.00	0.05	0.04	0.01	0.00	0.04	3.18
	2	0.00	0.05	0.04	0.00	0.01	0.06	3.76
	Mean	**0.00**	**0.05**	**0.04**	**0.01**	**0.01**	**0.05**	**3.47**
Total recovery	1	99.51	98.26	87.94	91.32	88.05	76.21	96.42
	2	102.18	105.39	94.94	93.28	93.88	82.92	84.39
	Mean	**100.84**	**101.83**	**91.44**	**92.30**	**90.97**	**79.56**	**90.40**

Values given as percentages of initially applied radioactivity
n.d.: not determined
n.a.: not applicable
NER = Non-extractable radioactive residues
[A)] Trapped in KOH solution
[B)] Radioactivity distributed into at least four components

Table B.8.1.2.1.2-3 Degradation of [UL-phenyl-^{14}C]-HOPP-acid (AE F096918) in <u>sandy loam soil Longwoods</u> under aerobic conditions

Component	Replicate No.	Sampling interval (days) 0	0.04 (1 hr)	0.125 (3 hrs)	1	4	7	14
HOPP-acid (AE F096918)	1	86.52	2.81	2.00	1.86	0.94	n.d.	n.d.
	2	80.55	2.09	1.62	0.57	0.28	n.d.	n.d.
	Mean	**83.54**	**2.45**	**1.81**	**1.22**	**0.61**	**n.a.**	**n.a.**
Others [B)]	1	16.10	20.80	19.41	6.32	3.20	n.d.	n.d.
	2	22.09	20.27	20.13	8.52	4.13	n.d.	n.d.
	Mean	**19.09**	**20.54**	**19.77**	**7.42**	**3.67**	**n.a.**	**n.a.**
Total extractable radioactivity	1	102.62	25.47	24.37	10.50	5.68	4.32	3.81
	2	102.64	24.18	25.09	11.59	5.86	4.57	3.72
	Mean	**102.63**	**24.83**	**24.73**	**11.05**	**5.77**	**4.45**	**3.77**
Non-extractable radioactivity	1	0.02	80.06	63.58	81.92	83.40	85.94	86.07
	2	0.00	76.30	73.40	84.64	81.04	82.22	85.21
	Mean	**0.01**	**78.18**	**68.49**	**83.28**	**82.22**	**84.08**	**85.64**
^{14}C-CO_2 and other volatiles [A)]	1	0.00	0.03	0.05	0.01	0.01	1.07	3.38
	2	0.00	0.02	0.05	0.00	0.00	1.29	3.71
	Mean	**0.00**	**0.03**	**0.05**	**0.00**	**0.00**	**1.18**	**3.55**
Total recovery	1	102.64	105.56	88.00	92.43	89.09	91.34	93.26
	2	102.64	100.51	98.54	96.23	86.90	88.08	92.64
	Mean	**102.64**	**103.03**	**93.27**	**94.33**	**87.99**	**89.71**	**92.95**

Values given as percentages of initially applied radioactivity
n.d.: not determined
n.a.: not applicable
NER = Non-extractable radioactive residues
[A)] Trapped in KOH solution
[B)] Radioactivity distributed into at least four components

Table B.8.1.2.1.2-4 Degradation of [UL-phenyl-^{14}C]-HOPP-acid (AE F096918) in <u>sandy clay loam soil Lockington</u> under aerobic conditions

Component	Replicate No.	Sampling interval (days) 0	0.04 (1 hr)	0.125 (3 hrs)	1	4	7	14
HOPP-acid AE F096918	1	75.83	2.02	1.72	1.71	0.61	n.d.	n.d.
	2	81.99	1.84	1.69	0.55	0.21	n.d.	n.d.
	Mean	**78.91**	**1.93**	**1.70**	**1.13**	**0.41**	**n.a.**	**n.a.**
Others [B)]	1	21.84	11.67	12.77	4.06	1.45	n.d.	n.d.
	2	18.03	12.57	12.20	4.99	1.93	n.d.	n.d.
	Mean	**19.94**	**12.12**	**12.48**	**4.52**	**1.69**	**n.a.**	**n.a.**

Total extractable radioactivity	1	97.67	14.69	15.80	7.87	3.55	2.96	2.40
	2	100.02	15.35	15.12	7.68	3.65	3.32	2.22
	Mean	**98.85**	**15.02**	**15.46**	**7.78**	**3.60**	**3.14**	**2.31**
Non-extractable radioactivity	1	2.31	82.90	78.08	82.79	94.03	85.90	90.43
	2	2.59	77.25	88.66	80.21	81.95	77.47	82.09
	Mean	**2.45**	**80.07**	**83.37**	**81.50**	**87.99**	**81.69**	**86.26**
^{14}C-CO_2 and other volatiles [A)]	1	0.00	0.04	0.05	0.01	0.01	1.57	4.52
	2	0.00	0.05	0.05	0.00	0.01	1.30	4.68
	Mean	**0.00**	**0.05**	**0.05**	**0.01**	**0.01**	**1.43**	**4.60**
Total recovery	1	99.98	97.64	93.93	90.67	97.58	90.43	87.45
	2	102.61	92.65	103.82	87.90	85.61	82.09	85.61
	Mean	**101.30**	**95.14**	**98.88**	**89.28**	**91.60**	**86.26**	**86.53**

Values given as percentages of initially applied radioactivity
n.d.: not determined
n.a.: not applicable
NER = Non-extractable radioactive residues
[A)] Trapped in KOH solution
[B)] Radioactivity distributed into at least four components

Mass balance
The total recovery of radioactivity ranged from 79.6 to 102.8 % AR for loam soil Farditch, 88.0 to 103.0 % AR for sandy loam soil Longwoods, 86.3 to 101.3 % AR for sandy clay loam soil Lockington. For a number of individual samples the total recovery was thus < 90 % AR, however, the recovery for the corresponding duplicate sample was > 90 % AR. This was probably due to a very high percentage of AR associated with NER and inherent difficulties associated with obtaining high combustion efficiencies for such samples.

Table B.8.1.2.1.2-5 Total material balances of radioactivity of ^{14}C-HOPP-acid (AE F096918) in three aerobic soils

Soil	Farditch	Longwoods	Lockington
Total Recovery (% AR)	79.6 – 102.8	88.0 – 103.0	86.3 – 101.3
Mean (% AR) [A)]	92.5	94.9	92.7
Rel. standard deviation [A)]	8.6	6.5	7.3

Values given as percentages of initially applied radioactivity
[A)] Value includes low recovery samples

Bound and extractable residues
Values of extractable radioactivity decreased rapidly with time accompanied by a strong formation of non-extractable radioactive residues (NER). Starting from a nearly complete extractability given by day zero (97.7 to 102.6 % AR) values decreased to 2.3 to 3.8 % AR at the end of the incubation period of 14 days. In turn, values for NER were low by day zero starting from 0.0 to 3.2 % AR to increase to 79.6 to 86.3 % AR after 14 days of incubation.

Table B.8.1.2.1.2-6 Extractable and non-extractable residues of ^{14}C-HOPP-acid (AE F096918) in three aerobic soils

Soil	**Extractable residues** (%)		**Non-extractable residues** (%)		
	Day 0	**Day 14**	**Day 0**	**Max**	**Day 14**
Farditch	97.7	2.8	3.2	86.1 (d 4)	79.6
Longwoods	102.6	3.8	0.0	85.6 (d 14)	85.6
Lockington	98.9	2.3	2.5	88.0 (d 4)	86.3

Values given as percentages of initially applied radioactivity

Volatile radioactivity
Owing to the overall short incubation time mineralisation of ^{14}C-HOPP-acid (AE F096918) to form ^{14}C-carbon dioxide ranging from 3.5 % to 4.6 % AR in the test soils after 14 days of incubation. Formation of other volatile radioactivity was insignificant at any sampling interval (< 0.1 % AR).

Transformation of test substance
HOPP-acid (AE F096918) was degraded very rapidly in aerobic soil to form NER and ^{14}C-carbon dioxide. Unidentified components were observed at 19.1 to 32.0 % AR in maximum for the total of components in all

soils by day zero. In view of the very fast degradation observed these components showed transient character as indicated by their fast decrease within one day of incubation.

Conclusion:

Following application of ^{14}C-hydroxyphenoxy propanoic acid (HOPP-acid, AE F096918) to three soils degradation was very rapid to form non-extractable residues (NER) as predominant transformation product besides some ^{14}C-carbon dioxide.

Comments (RMS AT):

- The study follows OECD guideline 307 and is considered reliable.
- It is noted that mass balance is sporadically below 90 % AR. However this is not considered to invalidate the study as only later sampling points are affected.
- The RMS AT notes that 'degradation' of HOPP-acid (AE F096918) in soil is driven by almost instantaneous formation of non-extractable residues, accounting for 76.8 - 80.1 % AR already one hour after application hardly changing thereafter. From a scientific point of view it is questionable whether this almost spontaneous formation of NER is attributed to microbial degradation or, more likely, to chemical reaction with the soil matrix.
- The study was re-assessed for degradation kinetics by Oberdoerster et al. (2016).

Reference:	**[Phenyl-UL-^{14}C]AE F096918 (HOPP acid): Degradation in four aerobic soils**
Author(s), year:	Stroech, K., Junge, T. (2014)
Report/Doc. Number:	EnSa-13-0977, M-483333-01-1
Guideline(s):	OECD Test Guideline No. 307 (2002); US EPA OCSPP Test Guideline No. 835.4100 / 835.4200
GLP:	Yes
Validity:	Yes
Status:	**New submission**

Executive Summary:

The degradation rate of [UL-phenyl-^{14}C]-labelled hydroxyphenoxy propanoic acid (HOPP-acid, AE F096918) was investigated in four soils under aerobic conditions at 20 °C and a soil moisture at 34 % (soil Laacherhof Wurmwiese), 29 % (soil Laacher Hof AXXa), 32 % (soil Hoefchen am Hohenseh) and 45 % (soil Dollendorf II) of the MWHC in the dark. The study was performed at a nominal application rate of 0.46 mg ^{14}C-test substance/kg soil, equivalent to a treatment rate in the field of 173 g test substance/ha for a maximum incubation period of 31 days.

Values for ^{14}C-HOPP-acid extractable from soil decreased from 56.8 % (day zero) to 1.1 % (day 31) in soil Wurmwiese, from 52.8 % (day zero) to 1.0 % (day 31) in soil Laacher Hof AXXa, from 33.6 % (day zero) to 0.8 % (day 31) in soil Hoefchen and from 25.9 % (day zero) to 0.8 % (day 31) in soil Dollendorf II.

Material and Methods:

Test Material
[UL-phenyl-^{14}C]-(R)-2-(4-hydroxyphenoxy)-propanoic acid (HOPP acid, AE F096918)
Specific radioactivity: 4.76 MBq/mg (128.65 µCi/mg)
Radiochemical purity: > 99 % (HPLC)
Chemical purity: > 99 % (HPLC)
Sample ID: KML 9553

Soils
The test soils originated from the EU and reflected a range of physico-chemical characteristics. The soils had been collected fresh from the field and were passed through a 2 mm sieve.

Table B.8.1.2.1.2-7 Characteristics of test soils

Soil	Laacher Hof Wurmwiese (WW)	Laacher Hof AXXa (AX)	Hoefchen am Hohenseh (HH)	Dollendorf II (DD)
Geographic location (city / state / country)	Monheim / North Rhine-Westphalia / Germany	Monheim / North Rhine-Westphalia / Germany	Burscheid / North Rhine-Westphalia / Germany	Blankenheim / North Rhine-Westphalia / Germany
GPS Coordinates	N 51° 04.9' E 006° 55.3'	N 51° 04.6' E 006° 53.6'	N 51° 04.0' E 007° 06.3'	N 50° 22.8' E 006° 42.8'
Textural class [A)]	Loam	Sandy loam	Silt loam	Clay loam
Sand (%) [A)]	48	74	16	26
Silt (%) [A)]	33	15	65	41
Clay (%) [A)]	19	11	19	33
*p*H - water	5.5	7.5	6.5	7.4
- 0.01 M $CaCl_2$	5.2	6.9	6.3	7.3
Organic matter (%) [B)]	3.6	2.5	3.3	9.0
Organic carbon (%)	2.1	1.5	1.9	5.2
Microbial biomass (mg microbial C / 100 g soil)				
- Initial (DAT-0)	79.7	105.9	98.0	306.6
- Final (DAT-49)	60.5 [C)] / 58.0 [D)]	69.2 [C)] / 68.2 [D)]	86.9 [C)] / 62.6 [D)]	245.7 [C)] / 243.0 [D)]
Cation exchange capacity (meq/100 g)	10.3	9.2	11.6	20.1
Maximum water holding capacity (MWHC) (g H_2O / 100 g soil)	61.7	53.5	57.7	82.5
Water holding capacity at 0.1 bar (*p*F 2) (%)[3]	25.3	15.9	30.9	47.8

[A)] USDA classification
[B)] % organic matter = % organic carbon x 1.724
[C)] Samples were treated with 200 µL water
[D)] Samples were treated with solvent of application solution (400 µL methanol/water 1/1 [by vol.])

Experimental conditions
Samples of 100 g dry weight of soil each were filled into glass incubation flasks with each sample to receive 460 µg ^{14}C-test substance/kg soil, equivalent to the five-fold maximum single application rate of 90 g fenoxaprop-P-ethyl/ha in the field and an occurrence of approximately 74 % of AR in maximum for HOPP-acid in an anaerobic soil degradation study performed with the active substance (see Voelkel, 2001). Following application, the samples were fitted each with a trap attachment (permeable for oxygen) containing soda lime for absorption of carbon dioxide and a polyurethane (PU) foam plug for adsorption of volatile organic compounds (VOC). Samples were incubated at 20 ± 1 °C and a moisture content of about 34 % (soil WW), 29 % (soil AX), 32 % (soil HH) and 45 % (soil DD) of the MWHC in the dark for 31 days in maximum. In addition, untreated soil samples were incubated under the same conditions for determination of soil microbial activity.

Sampling
Duplicate samples were removed for work-up after 0, 0.08 (2 hours), 0.25 (6 hours), 1, 4, 7, 14 and 31 days after treatment (DAT). Microbial soil biomass was determined at study start and 18 days after the last sampling interval of degradation samples (DAT-0 and DAT-49).The complete samples were immediately processed by extraction.

Analytical procedures
The entire soil sample in each test vessel of DAT-0 to DAT-1 was extracted three times successively each with 80 mL acetonitrile/water solution (4:1, by vol.) by shaking the soil/solvent mixture at ambient temperature for 30 min. Subsequently, soil samples were extracted in a microwave with 80 mL acetonitrile/water solution (1:1, by vol.) at 70 °C followed by a microwave extraction with 80 mL methanol/water solution (1:1, by vol.) at 50 °C. After each extraction step, extract and soil were separated by centrifugation and decantation. The volumes

[3] Equivalent to the Maximum Water Holding Capacity (MWHC)

of the ambient extracts were combined prior to analysis.

Due to the very rapid decline of extractable residues and test item amounts (test item degradation ≥ 90 % AR at DAT 0.25) only one extraction step was performed with 80 mL acetonitrile/water solution (4:1, by vol.) at ambient temperature starting with samples of DAT 4.

The ^{14}C-material balance was established for each sample by extraction, analysis of volatiles and combustion of non-extractable residues (NER). Following quantitation of radioactivity in extracts by liquid scintillation counting (LSC), analysis was performed by normal phase TLC as primary chromatographic method. This was only done for combined ambient/microwave soil extracts derived on DAT 0 to DAT 0.25. Soil extracts from DAT 1 on and PU foam plug extracts were not characterised by chromatographic methods. The LOD of the primary chromatographic method was determined as 0.02 Bq or 0.04 % AR.

Confirmation of the test item identity was performed using HPLC-MS/MS and radio detection. Due to the very rapid and extensive degradation of the test item and the simultaneous formation of NER and carbon dioxide, no identification of degradation products in soil extracts was performed and no isolation procedures were necessary. The NER determination was performed by combustion/LSC of aliquots of the air-dried extracted soil. To characterise the NER, the extracted soils from the DAT 31 interval were fractionated to quantify the amounts of radioactivity associated with humic acids, fulvic acids and humins.

Results and Discussion:

Table B.8.1.2.1.2-8 Degradation of [UL-phenyl-^{14}C]-HOPP-acid (AE F096918) in loam soil Laacher Hof Wurmwiese (WW) under aerobic conditions

Component		Sampling interval (days)							
		0	0.08	0.25	1	4	7	14	31
HOPP-acid (AE F096918)	**Mean** [A)]	**5.7**	**0.4**	**0.2**	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**n.d.**
	SD	±0.9	±0.1	±0.1	n.a.	n.a.	n.a.	n.a.	n.a.
Others [B)]	**Mean** [A)]	**51.1**	**10.1**	**6.5**	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**n.d.**
	SD	±0.9	±0.1	±0.0	n.a.	n.a.	n.a.	n.a.	n.a.
Total extractable radioactivity	**Mean** [A)]	**56.8**	**10.5**	**6.7**	**5.1**	**1.4**	**1.2**	**1.1**	**1.1**
	SD	±0.0	±0.0	±0.1	±0.0	±0.0	±0.0	±0.0	±0.0
Non-extractable radioactivity	**Mean** [A)]	**31.5**	**74.4**	**74.5**	**70.5**	**70.0**	**67.3**	**63.5**	**57.0**
	SD	±0.4	±0.1	±0.2	±1.3	±0.4	±1.8	±1.0	±0.1
^{14}C-CO_2 and other volatiles [C)]	**Mean** [A)]	**n.d.**	**8.4**	**13.0**	**19.0**	**23.0**	**26.6**	**30.8**	**37.2**
	SD	n.a.	±0.5	±0.1	±0.1	±0.2	±0.6	±0.5	±0.4
Total recovery	**Mean** [A)]	**88.3**	**93.3**	**94.2**	**94.5**	**94.4**	**95.1**	**95.5**	**95.2**
	SD	±0.4	±0.3	±0.3	±1.2	±0.6	±1.1	±0.5	±0.5

Values given as percentages of initially applied radioactivity
n.d.: not determined
n.a.: not applicable
SD = standard deviation
[A)] Mean values of duplicate samples analysed
[B)] Total sum of transient components predominantly observed at the first sampling interval, i.e. DAT 0
[C)] Other volatiles accounted for < 0.1 % AR in the course of the study.

Table B.8.1.2.1.2-9 Degradation of [UL-phenyl-^{14}C]-HOPP-acid (AE F096918) in sandy loam soil Laacher Hof AXXa (AX) under aerobic conditions

Component		Sampling interval (days)							
		0	0.08	0.25	1	4	7	14	31
HOPP-acid (AE F096918)	**Mean** [A)]	**9.1**	**1.3**	**0.6**	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**n.d.**
	SD	±0.1	±0.0	±0.2	n.a.	n.a.	n.a.	n.a.	n.a.
Others [B)]	**Mean** [A)]	**43.7**	**10.7**	**7.2**	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**n.d.**
	SD	±0.1	±0.0	±0.0	n.a.	n.a.	n.a.	n.a.	n.a.
Total extractable radioactivity	**Mean** [A)]	**52.8**	**12.0**	**7.7**	**5.4**	**1.5**	**1.3**	**1.2**	**1.0**
	SD	±0.2	±0.0	±0.2	±0.1	±0.0	±0.0	±0.0	±0.0
Non-extractable radioactivity	**Mean** [A)]	**38.9**	**73.0**	**71.9**	**70.3**	**68.5**	**69.1**	**64.1**	**59.1**
	SD	±1.0	±1.7	±1.0	±0.4	±0.9	±0.5	±0.6	±0.2
^{14}C-CO_2 and other volatiles [C)]	**Mean** [A)]	**n.d.**	**8.3**	**13.6**	**18.1**	**22.3**	**24.9**	**28.2**	**36.2**
	SD	n.a.	±0.4	±1.3	±0.1	±0.3	±0.1	±0.4	±0.5

Total recovery	**Mean** [A)]	**91.7**	**93.3**	**93.2**	**93.8**	**92.3**	**95.3**	**93.4**	**96.2**
	SD	±0.8	±1.3	±0.1	±0.4	±0.6	±0.4	±0.2	±0.7

Values given as percentages of initially applied radioactivity
n.d.: not determined
n.a.: not applicable
SD = standard deviation
[A)] Mean values of duplicate samples analysed
[B)] Total sum of transient components predominantly observed at the first sampling interval, i.e. DAT 0
[C)] Other volatiles accounted for < 0.1 % AR in the course of the study.

Table B.8.1.2.1.2-10 Degradation of [UL-phenyl-^{14}C]-HOPP-acid (AE F096918) in silt loam soil Hoefchen am Hohenseh (HH) under aerobic conditions

Component		Sampling interval (days)							
		0	**0.08**	**0.25**	**1**	**4**	**7**	**14**	**31**
HOPP-acid (AE F096918)	**Mean** [A)]	**5.1**	**0.9**	**0.2**	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**n.d.**
	SD	±0.1	±0.1	±0.0	n.a.	n.a.	n.a.	n.a.	n.a.
Others [B)]	**Mean** [A)]	**28.5**	**7.0**	**5.9**	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**n.d.**
	SD	±0.4	±0.2	±0.0	n.a.	n.a.	n.a.	n.a.	n.a.
Total extractable radioactivity	**Mean** [A)]	**33.6**	**7.9**	**6.0**	**4.4**	**1.1**	**1.1**	**0.9**	**0.8**
	SD	±0.3	±0.1	±0.0	±0.0	±0.0	±0.0	±0.1	±0.0
Non-extractable radioactivity	**Mean** [A)]	**62.7**	**75.7**	**75.8**	**74.8**	**73.4**	**71.5**	**67.3**	**64.6**
	SD	±2.5	±0.9	±0.0	±0.4	±0.3	±0.2	±0.1	±0.7
^{14}C-CO_2 and other volatiles [C)]	**Mean** [A)]	**n.d.**	**4.7**	**9.7**	**13.6**	**18.1**	**20.8**	**25.1**	**31.0**
	SD	n.a.	±0.0	±0.1	±0.1	±0.1	±0.0	±0.1	±0.4
Total recovery	**Mean** [A)]	**96.3**	**88.2**	**91.6**	**92.8**	**92.6**	**93.3**	**93.3**	**96.4**
	SD	±2.2	±0.9	±0.1	±0.3	±0.4	±0.2	±0.1	±0.3

Values given as percentages of initially applied radioactivity
n.d.: not determined
n.a.: not applicable
SD = standard deviation
[A)] Mean values of duplicate samples analysed
[B)] Total sum of transient components predominantly observed at the first sampling interval, i.e. DAT 0
[C)] Other volatiles accounted for < 0.1 % AR in the course of the study.

Table B.8.1.2.1.2-11 Degradation of [UL-phenyl-^{14}C]-HOPP-acid (AE F096918) in clay loam soil Dollendorf II (DD) under aerobic conditions

Component		Sampling interval (days)							
		0	**0.08**	**0.25**	**1**	**4**	**7**	**14**	**31**
HOPP-acid (AE F096918)	**Mean** [A)]	**10.8**	**0.8**	**0.3**	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**n.d.**
	SD	±2.8	±0.1	±0.1	n.a.	n.a.	n.a.	n.a.	n.a.
Others [B)]	**Mean** [A)]	**15.1**	**6.8**	**5.4**	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**n.d.**
	SD	±2.8	±0.0	±0.0	n.a.	n.a.	n.a.	n.a.	n.a.
Total extractable radioactivity	**Mean** [A)]	**25.9**	**7.7**	**5.7**	**3.8**	**1.1**	**1.0**	**0.9**	**0.8**
	SD	±0.1	±0.0	±0.1	±0.0	±0.0	±0.0	±0.0	±0.0
Non-extractable radioactivity	**Mean** [A)]	**68.5**	**81.2**	**79.6**	**78.8**	**76.9**	**74.3**	**72.6**	**69.4**
	SD	±0.9	±0.1	±0.8	±0.1	±0.1	±0.1	±0.8	±0.5
^{14}C-CO_2 and other volatiles [C)]	**Mean** [A)]	**n.d.**	**1.8**	**5.7**	**10.8**	**15.2**	**18.7**	**21.8**	**25.5**
	SD	n.a.	±0.1	±0.4	±0.0	±0.2	±0.2	±0.1	±0.4
Total recovery	**Mean** [A)]	**94.4**	**90.7**	**91.0**	**93.4**	**93.2**	**94.0**	**95.3**	**95.8**
	SD	±1.0	±0.2	±0.4	±0.1	±0.1	±0.1	±1.0	±0.9

Values given as percentages of initially applied radioactivity
n.d.: not determined
n.a.: not applicable
SD = standard deviation
[A)] Mean values of duplicate samples analysed
[B)] Total sum of transient components predominantly observed at the first sampling interval, i.e. DAT 0
[C)] Other volatiles accounted for < 0.1 % AR in the course of the study.

Mass balance

The total recovery of radioactivity was complete to range from 88.3 to 95.5 % AR for loam soil WW, 91.7 to 96.2 % AR for sandy loam soil AX, 88.2 to 96.4 % AR for silt loam soil HH and 90.7 to 95.8 % AR for clay loam soil DD. For soil WW and HH, the material balance was slightly below 90 % AR at DAT-0 and DAT-0.08, respectively, presumably due to spontaneous formation of carbon dioxide during the phase where treated flasks

were left open for approx. 15 minutes to allow for evaporation of the application solvent prior to processing (DAT 0 samples) or fitting with traps. However, the samples were used for evaluation of the rate of degradation of the test item.

Table B.8.1.2.1.2-12 Total material balances of radioactivity of ^{14}C-hydroxyphenoxy propanoic acid (HOPP-acid, AE F096918) in four aerobic soils

Soil	Laacher Hof Wurmwiese (WW)	Laacher Hof AXXa (AX)	Hoefchen am Hohenseh (HH)	Dollendor II (DD)
Total Recovery (% AR)	88.3 – 95.5	91.7 – 96.2	88.3 – 96.4	90.7 – 95.8
Mean (% AR) [A)]	93.8	93.6	93.1	93.5
Rel. standard deviation [A)]	2.3	1.5	2.6	1.9

Values given as percentages of initially applied radioactivity; [A)] Value includes low recovery samples

Bound and extractable residues

Values of extractable radioactivity decreased rapidly with time accompanied by formation of ^{14}C-carbon dioxide and non-extractable radioactive residues also decreasing towards the study end. Already at start of the incubation period (0 DAT), amounts of extractable radioactive residues were low ranging from 25.9 to 56.8 % AR. Amounts decreased rapidly until almost no amounts of extractable radioactive residues could be detected at study termination (0.8 to 1.1 % AR). In turn, values for non-extractable radioactivity (NER) were high by day zero starting from 31.5 to 68.5 % AR to increase to 73.0 to 81.2 % AR after 0.08 and 0.25 days. At the end of the study, amounts of NER decreased to 57.0 to 69.4 % AR.

Table B.8.1.2.1.2-13 Extractable and non-extractable residues (% AR) of ^{14}C-hydroxyphenoxy propanoic acid (HOPP-acid, AE F096918) in four aerobic soils

Soil	**Extractable residues** (%)		**Non-extractable residues** (%)		
	Day 0	Day 31	Day 0	Max.	Day 31
Laacher Hof Wurmwiese	56.8	1.1	31.5	74.5 (Day 0.25)	57.0
Laacher Hof AXXa	52.8	1.0	38.9	73.0 (Day 0.08)	59.1
Hoefchen am Hohenseh	33.6	0.8	62.7	75.8 (Day 0.25)	64.6
Dollendorf II	25.9	0.8	68.5	81.2 (Day 0.8)	69.4

NER was further characterized by organic matter fractionation for samples of DAT 31.

Table B.8.1.2.1.2-14 Non-extractable residue (NER) fractionation (% AR)

Soil	Sampling date (days after application)	Humin (%)	Fulvic acid (%)	Humic acid (%)
Laacher Hof Wurmwiese	31	26.6	15.0	13.7
Laacher Hof AXXa	31	24.4	14.9	15.5
Hoefchen am Hohenseh	31	31.5	15.9	14.4
Dollendorf II	31	41.3	9.4	14.7

Volatile radioactivity

Mineralization of ^{14}C-hydroxyphenoxy propanoic acid was significant to range from 25.5 % to 37.2 % AR in the soils tested after 31 days of incubation. Formation of other volatile radioactivity was insignificant at any sampling interval (< 0.1 % AR).

Transformation of test substance

Non-extractable radioactive residues and ^{14}C-carbon dioxide were formed as the predominant transformation product observed in the course of the study. The degradation of HOPP-acid (AE F096918) was accompanied by the formation of unidentified and transient components amounting to 18.7 % AR for a single component in maximum at DAT 0 in soil WW. No identification of degradation products in the soil extracts was performed due to their transient character. The biotic character of HOPP acid (AE F096918) in aerobic soil is underlined by the formation of carbon dioxide including non-extractable (bound) residues that could be converted, at least partly during the runtime of the study.

Conclusion:

Following application of ^{14}C-HOPP-acid (AE F096918) to four soils degradation was rapid to form ^{14}C-carbon

dioxide and non-extractable residues as predominant transformation products underlining the biotic character of conversion of this compound in aerobic soil.

Comments (RMS AT):

- The study follows OECD guideline 307 and is considered reliable.
- Formation of NER was in the same order as observed in Fitzmaurice (2010). Also refer to comments in Fitzmaurice (2010).
- The study was re-assessed for degradation kinetics by Oberdoerster et al. (2016).

Reference:	**Fenoxaprop-P-ethyl and metabolites: Kinetic evaluation of aerobic soil degradation under laboratory conditions**
Author(s), year:	Oberdoerster, C., Boiselle, N., Herrmann, M. (2016)
Report/Doc. Number:	EnSa-15-0391, M-552947-01-1
Guideline(s):	FOCUS kinetics (2006), EFSA Journal 2014;12(5):3662, (2014), FOCUS (2014): Generic guidance for Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration, Version: 1.1
GLP:	Not applicable
Validity:	Partly (refer to comment section)
Status:	**New submission**

Executive Summary:

For metabolites fenoxaprop-P-acid (AE F088406) and chlorobenzoxazolone (AE F054014) degradation data were kinetically evaluated according to FOCUS Guidance originating from four studies performed with ^{14}C-labeled active substance (Stump & Dambach, 1988; Buettner et al., 1992; Shepherd, 2012; Shepherd & Ripperger, 2012). The degradation of ^{14}C-HOPP-acid (AE F096918) was investigated separately in two studies (Fitzmaurice, 2010, and Stroech & Junge, 2014). The data were evaluated to derive trigger and modelling endpoints for use as input parameters for environmental risk assessments.

For metabolite degradation data sets and for trigger endpoint evaluation it was appropriate to apply the SFO kinetic model as best fits to the measured data either from combined fits with the active substance (fenoxaprop-P-acid, AE F088406), decline fits from maximum occurrence (chlorobenzoxazolone, AE F054014) or as decline fit (HOPP-acid, AE F096918).

Following the FOCUS criteria set and for modelling endpoints, non-normalized half-lives were derived from SFO fits to serve as the basis for normalization to reference conditions (20 °C, *p*F2 moisture).

Trigger endpoints
For metabolite fenoxaprop-P-acid (AE F088406), non-normalised values of the *DT50* and the *DT90* were derived from SFO best fits in combination with the active substance (pathway fit).

The non-normalised half-lives ranged from 2.95 days (soil SL 2) to 17.8 days (soil SL V) for fenoxaprop-P-acid (AE F088406), from 7.65 days (soil LS 2.2) to 56.6 days (soil Pikeville) for chlorobenzoxazolone (AE F054014) and from 0.007 days (soil Lockington) to 0.013 days (soil Laacher Hof AXXa) for HOPP-acid (AE F096918). The corresponding values for the *DT90* ranged from 9.80 days (soil SL2) to 59.0 days (soil SLV) for fenoxaprop-P-acid (AE F088406), from 25.4 days (soil LS2.2) to 188 days (soil Pikeville) for chlorobenzoxazolone (AE F054014) and from 0.025 days (soil Lockington) to 0.043 days (soil Laacher Hof AXXa) for HOPP-acid (AE F096918).

Table B.8.1.2.1.2-15 Comparison against EU triggers: Summary of results of kinetic evaluation of

degradation for fenoxaprop-P-acid (AE F088406) in aerobic soil in the laboratory

Parameter	Fenoxaprop-P-acid (AE F088406)
20 °C, Non-normalised *DT50* , range (days)	2.95 – 17.8
Worst case *DT50* (days)	**17.8**
20 °C, Non-normalised *DT90* , range (days)	9.80 – 55.4
Worst case *DT90* (days)	**55.4**

Table B.8.1.2.1.2-16 Comparison against EU triggers: Summary of results of kinetic evaluation of degradation for chlorobenzoxazolone (AE F054014) in aerobic soil in the laboratory

Parameter	Chlorobenzoxazolone (AE F054014)
20 °C, Non-normalised *DT50* , range (days)	7.65 – 56.6
Worst case *DT50* (days)	**56.6**
20 °C, Non-normalised *DT90* , range (days)	25.4 – 188
Worst case *DT90* (days)	**188**

Table B.8.1.2.1.2-17 Comparison against EU triggers: Summary of results of kinetic evaluation of degradation for HOPP-acid (AE F096918) in aerobic soil in the laboratory

Parameter	HOPP-acid (AE F096918)
20°C, Non-normalised DT_{50} , range (days)	0.007 – 0.013
Worst case DT_{50} (days)	**0.013**
20°C, Non-normalised DT_{90} , range (days)	0.025 – 0.043
Worst case DT_{90} (days)	**0.043**

Modelling endpoints

For metabolite fenoxaprop-P-acid (AE F088406), normalised values of the *DT50* and the *DT90* were derived from SFO best fits in combination with the active substance (pathway fit).

For fenoxaprop-P-acid (AE F088406) the range of normalised half-lives was 2.30 days (soil SL 2) to 15.5 days (soil Porterville) to result in a geometric mean normalised half-life of 5.7 days from 13 data sets in total. For chlorobenzoxazolone (AE F054014) the corresponding range was 6.48 days (soil SL S) to 31.0 days (soil Pikeville) to result in a geometric mean normalised half-life of 13.7 days. For HOPP-acid (AE F096918) normalised half-lives ranged from 0.007 days (soils Farditch, Longwoods and Lockington) to 0.012 days (soils Laacher Hof AXXa, Hoefchen and Dollendorf II) to result in a geometric mean normalised half-life of 0.009 days.

Table B.8.1.2.1.2-18 Modelling endpoints: Normalised laboratory *DT50*-values for fenoxaprop-P-acid (AE F088406) in aerobic soil for use as input in environmental exposure assessments

Parameter	Fenoxaprop-P-acid (AE F088406)
Normalised (20 °C, *p*F2) *DT50* , range (days)	2.30 – 15.5
Geometric mean	**5.7**

Table B.8.1.2.1.2-19 Modelling endpoints: Normalised laboratory *DT50*-values for chlorobenzoxazolone (AE F054014) in aerobic soil for use as input in environmental exposure assessments

Parameter	Chlorobenzoxazolone (AE F054014)
Normalised (20 °C, *p*F2) *DT50* , range (days)	6.48 – 31.0
Geometric mean	**13.7**

Table B.8.1.2.1.2-20 Modelling endpoints: Normalised laboratory DT_{50}-values for HOPP-acid (AE F096918) in aerobic soil for use as input in environmental exposure assessments

Parameter	HOPP-acid (AE F096918)
Normalised (20 °C, *p*F2) *DT50* , range (days)	0.007 – 0.012
Geometric mean	**0.009**

Material and Methods:

For metabolite fenoxaprop-P-acid (AE F088406) the kinetic analysis was performed in combination with parent compound data. The evaluation considered degradation data in soil under aerobic conditions of the laboratory from four studies following application of UL-chlorophenyl-^{14}C-labeled and UL-phenoxy-^{14}C-labeled active substance to result in 13 data sets in total. The details on study conduct and their results have been summarised in Section B.1.1.1. In principle, the same set of parent active substance derived data was available for metabolite chlorobenzoxazolone (AE F054014). However, kinetic evaluation could be performed for five data sets owing to the position of radiolabel and its observation at a sufficient number of sampling intervals to allow for the evaluation. For metabolite HOPP-acid (AE F096918) two studies were evaluated to result in seven data sets following separate application of the UL-phenyl-^{14}C-labeled metabolite to aerobic soil.

The degradation data were kinetically evaluated following FOCUS Guidance (FOCUS 2006, amended 2011) with the software KinGui2.1 including the use of iteratively re-weighted least-square (IRLS) optimisation.

The kinetic evaluation derived *DT50* values according to the respective flowcharts for the determination of trigger endpoints and for use as input parameters in modelling.

In following the actual FOCUS guidance, the particular criteria applied were essentially the same as described for the evaluation of the active substance earlier (see Section B.8.1.2.1.1).

The data sets available along with key characteristics of test soils were summarised in Table B.8.1.2.1.1-3 for the active substance. They were also applicable for fenoxaprop-P-acid (AE F088406) and chlorobenzoxazolone (AE F054014). Following separate application to soil for metabolite HOPP-acid (AE F096918), the data sets available along with key characteristics of test soils were summarised in the table below.

Table B.8.1.2.1.2-21 Degradation studies performed with metabolite HOPP-acid (AE F096918) in aerobic soil under laboratory conditions including characteristics of soils

Study	Soil	Soil texture	T (°C)	Test moisture (% MWHC)	Sand (%)	Clay (%)	Org. carbon (%)	*p*H ($CaCl_2$)	CEC (meq/ 100 g)
Fitzmaurice (2010)	Farditch	Loam	20	45	36	15	3.7	5.8	12.5
	Longwoods	Sandy loam	20	25	72	16	1.4	7.4	12.3
	Lockington	Sandy clay Loam	20	41	52	30	3.4	5.7	21.1
Stroech & Junge (2014)	Laacher Hof Wurmwiese	Loam	20	55	48	19	2.1	5.2	10.3
	Laacher Hof AXXa	Sandy loam	20	55	74	11	1.5	6.9	9.2
	Hoefchen am Hohenseh	Silt loam	20	55	16	19	1.9	6.3	11.6
	Dollendorf II	Clay loam	20	55	26	33	5.2	7.3	20.1

Following input of degradation data for fenoxaprop-P-ethyl (AE F046360), fenoxaprop-P-acid (AE F088406), chlorobenzoxazolone (AE F054014) and HOPP-acid (AE F096918) into KinGUI2.1, respectively, SFO kinetics were applied to all datasets according to the flowcharts.

Results and Discussion:

Trigger endpoint determination

For metabolite fenoxaprop-P-acid (AE F088406) and according to the decision criteria, the use of SFO as kinetic model in combination with the corresponding active substance fits (pathway approach) resulted in acceptable fits for all data sets.

For metabolite chlorobenzoxazolone (AE F054014) and according to the decision criteria, the evaluation resulted in SFO fits from maximum as best-fit for all data sets.

For metabolite HOPP-acid (AE F096918) and according to the decision criteria, the evaluation resulted in SFO decline fits as best-fit for all data sets.

Table B.8.1.2.1.2-22 Trigger evaluation: Non-normalised *DegT50* values for fenoxaprop-P-acid (AE F088406) in aerobic soil under laboratory conditions (combined parent/metabolite evaluation)

Soil	Label position	Model	*DegT 50* (days)	*DegT 90* (days)	χ^2 error (%)	t-test/ confidence interval	VA[(a)]
LS 2.2, loamy sand, 22 °C (Study 1)	1	SFO	12.6	41.7	13.37	*k:* < 0.001	O
SL V, sandy loam, 22 °C (Study 1)	1	SFO	4.25	14.1	4.95	*k:* 0.056	O
SL 2, silt loam, 22 °C (Study 1)	1	SFO	2.95	9.80	5.95	*k:* < 0.001	+
SL S, sandy loam, 22 °C (Study 1)	1	SFO	3.96	13.2	12.82	*k:* < 0.001	+
SL V, sandy loam, 21 °C (Study 2)	1	SFO	17.8	59.0	12.12	*k:* < 0.001	O
Pikeville, sandy loam, 20 °C (Study 3)	1	SFO	4.48	14.9	9.95	*k:* < 0.001	O
Porterville, loamy sand, 20 °C (Study 3)	1	SFO	16.7	55.4	2.70	*k:* < 0.001	++
Sanger, sandy loam, 20 °C (Study 3)	1	SFO	9.99	33.2	5.91	*k:* < 0.001	++
Springfield, silt loam, 20 °C (Study 3)	1	SFO	7.87	26.1	6.04	*k:* < 0.001	+
Pikeville, sandy loam, 20 °C (Study 4)	2	SFO	4.75	15.8	8.11	*k:* < 0.001	++
Porterville, loamy sand, 20 °C (Study 4)	2	SFO	16.2	54.0	1.53	*k:* < 0.001	++
Sanger, sandy loam, 20 °C (Study 4)	2	SFO	7.68	25.5	6.66	*k:* < 0.001	++
Springfield, silt loam, 20 °C (Study 4)	2	SFO	4.38	14.5	10.72	*k:* < 0.001	O

Study 1: Stumpf & Dambach (1988)
Study 2: Buettner et al. (1992)
Study 3: Shepherd (2012)
Study 4: Shepherd & Ripperger (2012)
1 = UL-chlorophenyl-^{14}C; 2 = UL-phenoxy-^{14}C
(a) VA = Visual Assessment (++ = excellent, + = good, O = acceptable, - = not acceptable)

Table B.8.1.2.1.2-23 <u>Trigger evaluation</u>: Non-normalised *DegT50* values for <u>chlorobenzoxazolone (AE F054014)</u> in aerobic soil under laboratory conditions (evaluation from maximum occurrence)

Soil	Label position	Model	*DegT 50* (days)	*DegT 90* (days)	χ^2 error (%)	t-test/ confidence interval	VA[(a)]
LS 2.2, loamy sand, 22 °C (Study 1)	1	SFO	7.65	25.4	16.99	*k*: 0.008	O
SL V, sandy loam, 22 °C (Study 1)	1	SFO	23.8	79.2	24.31	*k*: 0.005	+
SL 2, silt loam, 22 °C (Study 1)	1	SFO	17.9	59.6	5.95	*k*: < 0.001	+
SL S, sandy loam, 22 °C (Study 1)	1	SFO	8.45	28.1	19.98	*k*: 0.024	+
Pikeville, sandy loam, 20 °C (Study 3)	1	SFO	56.6	188	4.43	*k*: 0.012	O

Study 1: Stumpf & Dambach (1988)
Study 3: Shepherd (2012)
1 = UL-chlorophenyl-^{14}C; 2 = UL-phenoxy-^{14}C
(a) VA = Visual Assessment (++ = excellent, + = good, O = acceptable, - = not acceptable)

Table B.8.1.2.1.2-24 <u>Trigger evaluation</u>: Non-normalised *DegT50* values for <u>HOPP-acid (AE F096918)</u> in aerobic soil under laboratory conditions (decline fit)

Soil	Label pos-ition	Model	*DegT 50* (days)	*DegT 90* (days)	χ^2 error (%)	t-test/ confidence interval	VA[(a)]
Farditch, loam, 20 °C (Study 1)	1	SFO	0.008	0.027	8.52	*k:* < 0.001	O
Longwoods, sandy loam, 20 °C (Study 1)	1	SFO	0.008	0.026	4.05	*k:* < 0.001	O
Lockington, sandy clay loam, 20 °C (Study 1)	1	SFO	0.007	0.025	3.91	*k:* < 0.001	O
Laacher Hof Wurmwiese, loam, 20 °C (Study 2)	1	SFO	0.010	0.034	0.34	*k:* < 0.001	O
Laacher Hof AXXa, sandy loam, 20 °C (Study 2)	1	SFO	0.013	0.043	0.90	*k:* < 0.001	O
Hoefchen am Hohenseh, silt loam, 20 °C (Study 2)	1	SFO	0.012	0.040	0.31	*k*: 0.008	+
Dollendorf II, clay loam, 20 °C (Study 2)	1	SFO	0.012	0.039	0.48	*k:* < 0.001	+

Study 1: Fitzmaurice (2010)
Study 2: Stroech & Junge (2014)
1 = UL-phenyl-^{14}C
(a) VA = Visual Assessment (++ = excellent, + = good, O = acceptable, - = not acceptable)

Modelling endpoint determination

The FOCUS Kinetics modelling endpoint flowchart (FOCUS, 2006, 2011) was used to evaluate the datasets. The SFO kinetic model was considered visually and statistically acceptable for deriving modelling endpoints for all data sets.

For the use in environmental modelling the degradation half-lives of metabolites fenoxaprop-P-acid (AE

F088406) and chlorobenzoxazolone (AE F054014) were normalised to reference conditions regarding soil moisture (100 % field capacity) and temperature (20 °C). The same key parameters and the respective correction factors were used as derived for the active substance and summarised in Table B.8.1.2.1.1-5. Following separate application of metabolite HOPP-acid (AE F096918) to soil, the key parameters used in the laboratory tests and the respective correction factors were summarised in the table below.

Table B.8.1.2.1.2-25 HOPP-acid (AE F096918): Correction factors for soil temperature and moisture content

Soil	T (°C)	Correction factor Temperature	Incubation moisture (%w/w)	*p*F2 moisture (%w/w)	Correction factor Moisture	Total correction factor
Farditch, loam (Study 1)	20	1.0	33.0	36.3	0.935	0.935
Longwoods, sandy loam (Study 1)	20	1.0	10.5	11.7	0.927	0.927
Lockington, sandy clay loam (Study 1)	20	1.0	26.9	28.9	0.951	0.951
Laacher Hof Wurmwiese, loam (Study 2)	20	1.0	33.9	25.3	1.0	1.0
Laacher Hof AXXa, sandy loam (Study 2)	20	1.0	29.4	15.9	1.0	1.0
Hoefchen am Hohenseh, silt loam (Study 2)	20	1.0	31.7	30.9	1.0	1.0
Dollendorf II, clay loam (Study 2)	20	1.0	45.4	47.8	0.964	0.964

Study 1: Fitzmaurice (2010)
Study 2: Stroech & Junge (2014)

Table B.8.1.2.1.2-26 Modelling endpoints: Normalised (20 °C and *p*F2) *DegT50* values for fenoxaprop-P-acid (AE F088406) in aerobic soil under laboratory conditions (combined parent/metabolite evaluation)

Soil	Model	Trigger *DegT50* (days)	Trigger *DegT90* (days)	Non-normalised *DegT50* estimate for modelling (days)	*DegT50* (20 °C and *p*F2) (days)
LS 2.2, loamy sand (Study 1)	SFO	12.6	41.7	12.6	12.1
SL V, sandy loam (Study 1)	SFO	4.25	14.1	4.25	3.51
SL 2, silt loam (Study 1)	SFO	2.95	9.80	2.95	2.30
SL S, sandy loam (Study 1)	SFO	3.96	13.2	3.96	3.04
SL V, sandy loam (Study 2)	SFO	17.8	59.0	17.8	12.9
Pikeville, sandy loam (Study 3)	SFO	4.48	14.9	4.48	2.45
Porterville, loamy sand (Study 3)	SFO	16.7	55.4	16.7	15.5
Sanger, sandy loam (Study 3)	SFO	9.99	33.2	9.99	7.25
Springfield, silt loam (Study 3)	SFO	8.09	26.86	8.09	7.52
Pikeville, sandy loam (Study 4)	SFO	4.41	14.65	4.41	2.41
Porterville, loamy sand (Study 4)	SFO	16.2	54.0	16.2	15.0
Sanger, sandy loam (Study 4)	SFO	7.68	25.5	7.68	5.58
Springfield, silt loam (Study 4)	SFO	4.50	14.9	4.50	4.18
Geometric mean					**5.7**

Study 1: Stumpf & Dambach (1988)
Study 2: Buettner et al. (1992)
Study 3: Shepherd (2012)
Study 4: Shepherd & Ripperger (2012)

Table B.8.1.2.1.2-27 Modelling endpoints: Normalised (20 °C and *p*F2) *DegT50* values for chlorobenzoxazolone (AE F054014) in aerobic soil under laboratory conditions (evaluation from maximum occurrence)

Soil	Model	Trigger *DegT50* (days)	Trigger *DegT90* (days)	Non-normalised *DegT50* estimate for modelling (days)	*DegT50* [20 °C and pF2] (days)
LS 2.2, loamy sand (Study 1)	SFO	7.65	25.4	7.65	7.34
SL V, sandy loam (Study 1)	SFO	23.8	79.2	23.8	23.8
SL 2, silt loam (Study 1)	SFO	17.9	59.6	17.9	14.0
SL S, sandy loam (Study 1)	SFO	8.45	28.1	8.45	6.48
Pikeville, sandy loam (Study 3)	SFO	56.6	188	56.6	31.0
Geometric mean					**13.7**

Study 1: Stumpf & Dambach (1988)

Study 3: Shepherd (2012)

Table B.8.1.2.1.2-28 Modelling endpoints: Normalised (20 °C and *p*F2) *DegT50* values for HOPP-acid (AE F096918) in aerobic soil under laboratory conditions (decline evaluation)

Soil	Model	Trigger *DegT50* (days)	Trigger *DegT90* (days)	Non-normalised *DegT50* estimate for modelling (days)	*DegT50* (20 °C and pF2) (days)
Farditch, loam (Study 1)	SFO	0.008	0.027	0.008	0.007
Longwoods, sandy loam, (Study 1)	SFO	0.008	0.026	0.007	0.007
Lockington, sandy clay loam (Study 1)	SFO	0.007	0.025	0.008	0.007
Laacher Hof Wurmwiese, loam (Study 2)	SFO	0.010	0.034	0.010	0.010
Laacher Hof AXXa, sandy loam (Study 2)	SFO	0.013	0.043	0.012	0.012
Hoefchen am Hohenseh, silt loam (Study 2)	SFO	0.012	0.040	0.012	0.012
Dollendorf II, clay loam (Study 2)	SFO	0.012	0.039	0.013	0.012
Geometric mean					**0.009**

Study 1: Fitzmaurice (2010)
Study 2: Stroech & Junge (2014)

Conclusion:

For comparison with EU trigger endpoints the evaluation of aerobic soil degradation data according to actual FOCUS kinetic guidance resulted in non-normalised half-lives to range from 2.95 days to 16.7 days for metabolite fenoxaprop-P-acid (AE F088406), from 7.65 days to 56.6 days for chlorobenzoxazolone (AE F054014) and from 0.007 days to 0.013 days for HOPP-acid (AE F096918).

The corresponding range of values of the *DegT90* was 9.80 days to 55.4 days for metabolite fenoxaprop-P-acid (AE F088406), from 25.4 days to 188 days for chlorobenzoxazolone (AE F054014) and from 0.025 days to 0.043 days for HOPP-acid (AE F096918).

Degradation was found to be adequately described by SFO as kinetic model for the various data sets to fit best with experimental data.

For use as modelling input parameter in environmental risk assessments and following the criteria set by FOCUS the fitting with experimental data resulted in the use of the SFO kinetic model to derive non-normalised values for the *DegT50* followed by normalisation for moisture (*p*F2) and temperature (20 °C). The evaluation resulted in geometric mean normalized half-lives of 5.7 days for fenoxaprop-P-acid (AE F088406), 13.7 days for chlorobenzoxazolone (AE F054014) and 0.009 days for HOPP-acid (AE F096918).

The values derived are regarded as suitable and reliable for use in environmental exposure assessments.

Comments RMS AT:

- The RMS AT agrees with the applicant's kinetic pathway degradation scheme linking fenoxaprop-P-acid (AE F088406) to fenoxaprop-P-ethyl (AE F046360) and to stay with decline fits in case of chlorobenzoxazolone (AE F054014). As already mentioned the RMS AT considers $P_{SFO} \rightarrow M_{SFO}$ and $P_{FOMC} \rightarrow M_{SFO}$ pathway fits sufficient to obtain robust degradation endpoints for fenoxaprop-P-ethyl (AE F046360) and fenoxaprop-P-acid (AE F088406). In view of the RMS AT trigger and modelling endpoints are considered to be the same in this case.

- Decline fits on chlorobenzoxazolone (AE F054014) (all SFO) provided by the applicant are accepted by the RMS AT (also refer to figures given below).

- As discussed more in detail in Buettner et al. (1992) the RMS AT considers residues (parent as well as metabolites) detected in Buettner et al. (1992) not sufficiently robust to allow for kinetic evaluation. This data set is therefore excluded from the final soil degradation data set.

- In case of fenoxaprop-P-acid (AE F088406) the study authors calculated individual degradation rates

for both labels in Shepherd (2012) and Shepherd & Ripperger (2012). Ideally, the two labels (with two replicates each) should have been already pooled for kinetic evaluation as the experimental conditions including soil properties seems to be identical in both studies. However, as different labels revealed similar degradation rates, the approach by the applicant is considered acceptable in this case.

- The study authors calculated the geometric *DegT50* of fenoxaprop-P-acid (AE F088406) on basis of individual labels from Shepherd (2012) and Shepherd & Ripperger (2012). As this gives bias to this particular soil dataset, the RMS AT recommends to first calculating the geometric mean of both labels for each of the four soils and finally calculate the geometric mean of the remaining 8 soils. This comment is also related to the comment given above.

- Formation fractions of fenoxaprop-P-acid (AE F088406) and statistical criteria following application of the parent-metabolite-pathway fit ($P_{SFO} \rightarrow M_{SFO}$ or $P_{FOMC} \rightarrow M_{SFO}$) are not given in the applicant study summary. This information is provided here.

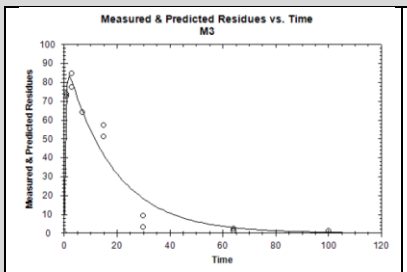
Table B.8.1.2.1.2-29 **<u>Trigger & modelling endpoints:</u> Non-normalised best fit *DegT50* and *DegT90* and normalized *DegT50* values for <u>fenoxaprop-P-acid (AE F088406)</u> in aerobic soil at 20 and 22 °C under laboratory conditions (parent-metabolite pathway fits) - <u>applicant fits agreed by the RMS AT</u>**

Soil	Label	Model	*DegT50* (days)	*DegT90* (days)	χ^2 error (%)	t-test	ff (-)	VA	*DegT50* (20 °C and *p*F2) (days)
LS 2.2, loamy sand (Study 1)	ClPh	$P_{SFO} \rightarrow M_{SFO}$	12.6	41.7	13.4	< 0.001	0.95	o	12.1
SL V, sandy loam (Study 1)	ClPh	$P_{SFO} \rightarrow M_{SFO}$	4.3	14.1	5.0	< 0.056	0.90	o	3.5
SL 2, silt loam (Study 1)	ClPh	$P_{FOMC} \rightarrow M_{SFO}$	3.0	9.8	6.0	< 0.001	0.66	+	2.3
SL S, sandy loam (Study 1)	ClPh	$P_{FOMC} \rightarrow M_{SFO}$	4.0	13.2	12.8	< 0.001	0.79	+	3.0
Pikeville, sandy loam (Study 3)	ClPh	$P_{FOMC} \rightarrow M_{SFO}$	4.5	14.9	10.0	< 0.001	0.76	o	2.5
Porterville, loamy sand (Study 3)	ClPh	$P_{SFO} \rightarrow M_{SFO}$	16.7	55.4	2.7	< 0.001	0.93	++	15.5
Sanger, sandy loam (Study 3)	ClPh	$P_{FOMC} \rightarrow M_{SFO}$	10.0	33.2	5.9	< 0.001	0.93	++	7.3
Springfield, silt loam (Study 3)	ClPh	$P_{SFO} \rightarrow M_{SFO}$	8.1	26.9	6.4	< 0.001	0.88	o	7.5
Pikeville, sandy loam (Study 4)	Ph	$P_{FOMC} \rightarrow M_{SFO}$	4.4	14.7	10.5	< 0.001	0.84	+	2.4
Porterville, loamy sand (Study 4)	Ph	$P_{FOMC} \rightarrow M_{SFO}$	16.2	54.0	1.5	< 0.001	0.95	++	15.0
Sanger, sandy loam (Study 4)	Ph	$P_{SFO} \rightarrow M_{SFO}$	7.7	25.5	6.7	< 0.001	0.90	++	5.6
Springfield, silt loam (Study 4)	Ph	$P_{SFO} \rightarrow M_{SFO}$	4.5	14.9	10.9	< 0.001	0.86	o	4.2

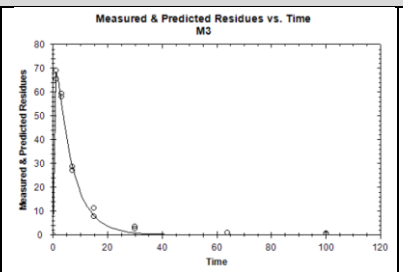
Study 1: Stumpf & Dambach (1988)
Study 3: Shepherd (2012)
Study 4: Shepherd & Ripperger (2012)

- Figures on kinetic fits of fenoxaprop-P-acid (AE F088406) and chlorobenzoxazolone (AE F046360), not provided in the applicant summary, are provided in the tables below. Fits on HOPP-acid (AE F096918) are not shown here as *DegT50* of HOPP-acid (AE F096918) is extremely low (<< 1 day) and SFO fits are considered suitable in any case.

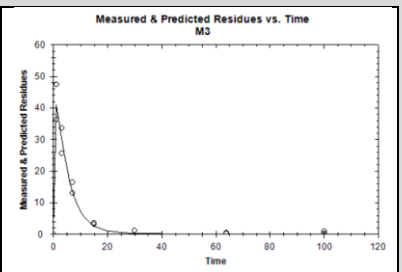
Table B.8.1.2.1.2-30 **Kinetic evaluation of degradation of fenoxaprop-P-acid (AE F088406) in aerobic soils at 20 to 22 °C under laboratory conditions (parent-metabolite pathway fits) - <u>fits for trigger & modelling endpoints agreed by the RMS AT</u>**



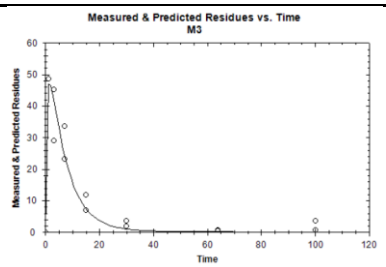
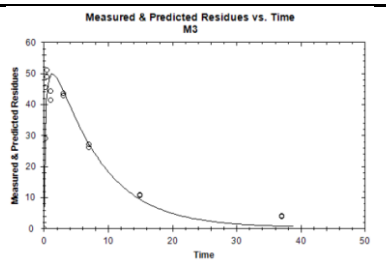
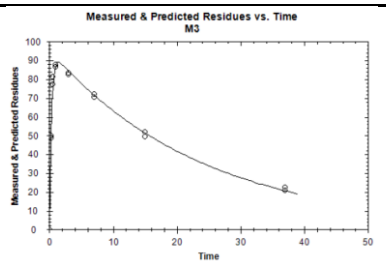
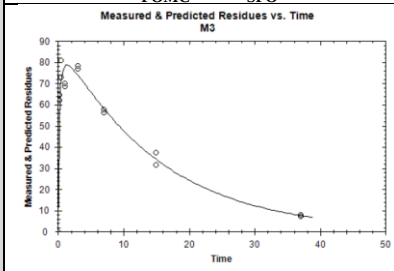
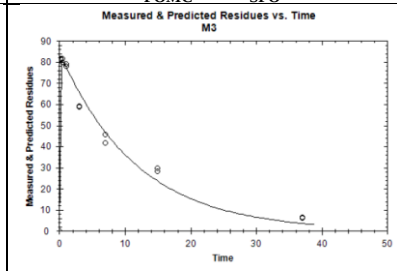
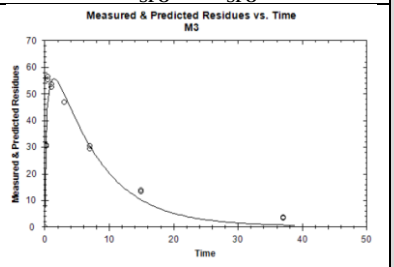
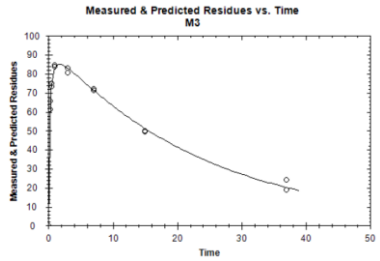
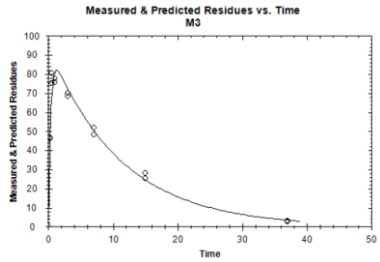
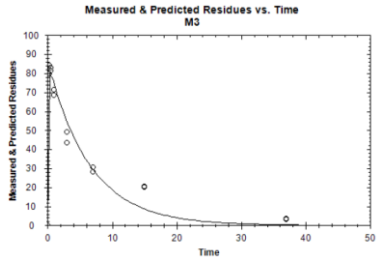
LS 2.2, loamy sand (Study 1) - $P_{SFO} \rightarrow M_{SFO}$



SL V, sandy loam (Study 1) - $P_{SFO} \rightarrow M_{SFO}$

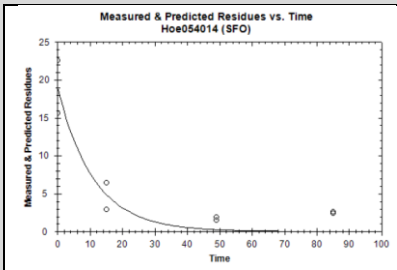
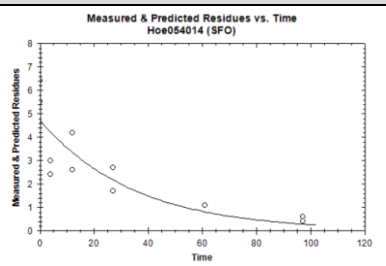
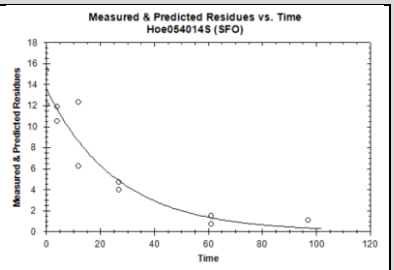
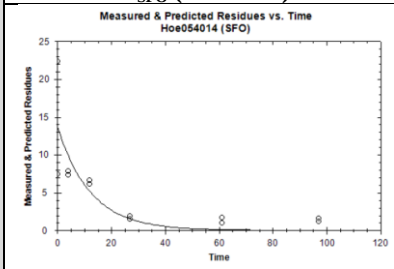
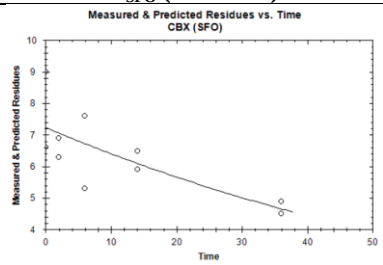


SL 2, sandy loam (Study 1) - $P_{FOMC} \rightarrow M_{SFO}$

 **SL S, sandy loam (Study 1) - $P_{FOMC} \rightarrow M_{SFO}$**	 **Pikeville, sandy loam (Study 3) - $P_{FOMC} \rightarrow M_{SFO}$**	 **Porterville, loamy sand (Study 3) - $P_{SFO} \rightarrow M_{SFO}$**
 **Sanger, sandy loam (Study 3) - $P_{FOMC} \rightarrow M_{SFO}$**	 **Springfield, silt loam (Study 3) - $P_{SFO} \rightarrow M_{SFO}$**	 **Pikeville, sandy loam (Study 4) - $P_{FOMC} \rightarrow M_{SFO}$**
 **Porterville, loamy sand (Study 4) - $P_{FOMC} \rightarrow M_{SFO}$**	 **Sanger, sandy loam (Study 4) - $P_{SFO} \rightarrow M_{SFO}$**	 **Springfield, silt loam (Study 4) - $P_{SFO} \rightarrow M_{SFO}$**

Study 1: Stumpf & Dambach (1988)
Study 3: Shepherd (2012)
Study 4: Shepherd & Ripperger (2012)

Table B.8.1.2.1.2-31 Kinetic evaluation of degradation of <u>chlorobenzoxazolone (AE F054014)</u> in aerobic soils at 20 to 22 °C under laboratory conditions - <u>decline fits for trigger & modelling endpoints agreed by the RMS AT</u>

 **LS 2.2, loamy sand (Study 1) - M_{SFO} (decline fit)**	 **SL V, sandy loam (Study 1) - M_{SFO} (decline fit)**	 **SL 2, sandy loam (Study 1) - M_{SFO} (decline fit)**
 **SL S, sandy loam (Study 1) -**	 **Pikeville, sandy loam (Study 3) -**	No reliable fit, low occurrence (< 2 % AR) **Porterville, loamy sand (Study 3)**

M_{SFO} (decline fit)	M_{SFO} (decline fit)	
No reliable fit, low occurrence (< 5 % AR) **Sanger, sandy loam (Study 3)**	No reliable fit, low occurrence (< 3 % AR) **Springfield, silt loam (Study 3)**	

Study 1: Stumpf & Dambach (1988)
Study 3: Shepherd (2012)
Study 4: Shepherd & Ripperger (2012)

B.8.1.2.1.3. Anaerobic degradation of the active substance

Degradation rates of fenoxaprop-P-ethyl (AE F046360) assessed in two anaerobic soils were 0.35 and 0.37 days (both SFO kinetics, for details refer to Voelkel, 2001, and Adam, 2008).

B.8.1.2.1.4. Anaerobic degradation of metabolites, breakdown and reaction products

Degradation rates of the herbicidal active metabolite fenoxaprop-P-acid (AE F088406) assessed in two anaerobic soils were 35.7 and 43.7 days (both SFO kinetics, for details refer to Voelkel, 2001, and Adam, 2008).

In general anaerobic degradation rate studies with metabolites of fenoxaprop-P-ethyl (AE F046360) are not considered necessary as degradation rates obtained under aerobic conditions are used for environmental exposure modelling.

B.8.1.2.1.5. Summary on laboratory degradation rates in soil

The rate of degradation in soil of fenoxaprop-P-ethyl (AE F046360) and metabolites has been assessed in laboratory studies and is summarised in the tables below.

Table B.8.1.2.1.5-1 Summary on aerobic degradation rates for fenoxaprop-P-ethyl (AE F046360) in laboratory studies - trigger & modelling endpoints

Soil name	Soil type (USDA)	Label	*p*H ($CaCl_2$)	T (°C)	Water content (% MWHC)	*DegT 50* (d)	*DegT 90* (d)	*DegT50* (d) 20 °C, *p*F2	χ^2 err. (%)	Kinetic model	Reference
LS 2.2	Loamy sand	ClPh	5.8	22	40	0.35	1.2	0.33	12.7	SFO	Stumpf & Dambach (1988)
SL V	Sandy loam	ClPh	5.6	22	40	0.33	1.1	0.28	11.0	SFO	
SL 2	Silt loam	ClPh	5.2	22	40	0.25	3.0	0.70[(a)]	6.5	FOMC	
SL S	Sandy loam	ClPh	5.2	22	40	0.42	5.9	1.4[(a)]	7.7	FOMC	
Pikeville	Sandy loam	ClPh	5.2	20	26	0.32	7.0	1.2[(a)]	5.5	FOMC	Shepherd (2012)
Porterville	Loamy sand	ClPh	6.9	20	57	0.22	0.71	0.20	10.6	SFO	
Sanger	Sandy loam	ClPh	6.2	20	42	0.13	1.2	0.26[(a)]	2.4	FOMC	
Springfield	Silt loam	ClPh	6.6	20	74	0.07	0.24	0.07	7.3	SFO	
Pikeville	Sandy loam	Ph	5.2	20	26	0.35	5.2	0.86[(a)]	12.8	FOMC	Shepherd & Ripperger (2012)
Porterville	Loamy sand	Ph	6.9	20	57	0.14	1.0	0.27[(a)]	6.0	FOMC	
Sanger	Sandy loam	Ph	6.2	20	42	0.24	0.78	0.17	10.8	SFO	
Springfield	Silt loam	Ph	6.6	20	74	0.08	0.25	0.07	8.6	SFO	
					Maximum (n = 8)[(b)]	**0.42**	**5.9**	**-**		FOMC[(c)]	
					Geometric mean (n = 8)[(b)]	**-**	**-**	**0.36**		SFO	
					pH-dependency: y/n	**y[(d)]**					

(a) Based on non-normalized FOMC-DT90 divided by 3.32
(b) Different labels in Shepherd (2012) and Shepherd & Ripperger (2012) averaged (geometric mean) before averaging different soils or calculating maximum
(c) FOMC $\alpha = 0.771$, $\beta = 0.305$
(d) Refer to text below

Table B.8.1.2.1.5-2 Summary on aerobic degradation rates for fenoxaprop-P-acid (AE F088406) in laboratory studies - trigger and modelling endpoints

Soil name	Soil type (USDA)	Label	*p*H (Ca-Cl_2)	T (°C)	WC (% MWHC)	*DegT 50* (d)	*DegT 90* (d)	*ff* (-)	*DegT50* (d) 20 °C, *p*F2	χ^2 err. (%)	Kinetic model	Ref.
LS 2.2	Loamy sand	ClPh	5.8	22	40	12.6	41.7	0.95	12.1	13.4	$P_{SFO} \rightarrow M_{SFO}$	1)
SL V	Sandy loam	ClPh	5.6	22	40	4.3	14.1	0.90	3.5	5.0	$P_{SFO} \rightarrow M_{SFO}$	
SL 2	Silt loam	ClPh	5.2	22	40	3.0	9.8	0.66	2.3	6.0	$P_{FOMC} \rightarrow M_{SFO}$	
SL S	Sandy loam	ClPh	5.2	22	40	4.0	13.2	0.79	3.0	12.8	$P_{FOMC} \rightarrow M_{SFO}$	
Pikeville	Sandy loam	ClPh	5.2	20	26	4.5	14.9	0.76	2.5	10.0	$P_{FOMC} \rightarrow M_{SFO}$	2)
Porterville	Loamy sand	ClPh	6.9	20	57	16.7	55.4	0.93	15.5	2.7	$P_{SFO} \rightarrow M_{SFO}$	
Sanger	Sandy loam	ClPh	6.2	20	42	10.0	33.2	0.93	7.3	5.9	$P_{FOMC} \rightarrow M_{SFO}$	
Springfield	Silt loam	ClPh	6.6	20	74	8.1	26.9	0.88	7.5	6.4	$P_{SFO} \rightarrow M_{SFO}$	
Pikeville	Sandy loam	Ph	5.2	20	26	4.4	14.7	0.84	2.4	10.5	$P_{FOMC} \rightarrow M_{SFO}$	3)
Porterville	Loamy sand	Ph	6.9	20	57	16.2	54.0	0.95	15.0	1.5	$P_{FOMC} \rightarrow M_{SFO}$	
Sanger	Sandy loam	Ph	6.2	20	42	7.7	25.5	0.90	5.6	6.7	$P_{SFO} \rightarrow M_{SFO}$	
Springfield	Silt loam	Ph	6.6	20	74	4.5	14.9	0.86	4.2	10.9	$P_{SFO} \rightarrow M_{SFO}$	
					Maximum (n = 8)[(a)]	**16.4**	**54.7**	**-**	**15.2**	**-**		
					Geometric mean (n = 8)[(a)]	**-**	**-**	**-**	**5.0**	**-**		
					Arithmetic mean (n = 8)[(b)]	**-**	**-**	**0.85**	**-**	**-**		
					***p*H-dependency: y/n**	**y[(c)]**						

Ref. 1) Stumpf & Dambach (1988)
Ref. 2) Shepherd (2012)
Ref. 3) Shepherd & Ripperger (2012)
(a) Different labels in Shepherd (2012) and Shepherd & Ripperger averaged (geometric mean) before averaging different soils
(b) Different labels in Shepherd (2012) and Shepherd & Ripperger averaged (arithmetic mean) before averaging different soils
(c) Refer to text below.

Table B.8.1.2.1.5-3 Summary on aerobic degradation rates for chlorobenzoxazolone (AE F054014) in laboratory studies - trigger and modelling endpoints

Soil name	Soil type (USDA)	Label	*p*H ($CaCl_2$)	T (°C)	WC (% MWHC)	*DegT 50* (d)	*DegT 90* (d)	*ff* (-)	*DegT50* (d) 20 °C, *p*F2	χ^2 err. (%)	Kinetic model	Ref.
LS 2.2	Loamy sand	ClPh	5.8	22	40	7.7	25.4	na	7.3	17.0	SFO[(a)]	1)
SL V	Sandy loam	ClPh	5.6	22	40	23.8	79.2	na	23.8	24.3	SFO[(a)]	
SL 2	Silt loam	ClPh	5.2	22	40	17.9	59.6	na	14.0	6.0	SFO[(a)]	
SL S	Sandy loam	ClPh	5.2	22	40	8.5	28.1	na	6.5	20.0	SFO[(a)]	
Pikeville	Sandy loam	ClPh	5.2	20	26	56.6	188	na	31.0	4.4	SFO[(a)]	2)
Porterville	Loamy sand	ClPh	6.9	20	57	Low occurrence (< 2 % AR)						
Sanger	Sandy loam	ClPh	6.2	20	42	Low occurrence (< 5 % AR)						
Springfield	Silt loam	ClPh	6.6	20	74	Low occurrence (< 3 % AR)						
					Maximum (n = 5)	**56.6**	**188**	**-**	**-**			
					Geometric mean (n = 5)	**-**	**-**	**-**	**13.7**			
					Arithmetic mean (n = 5)	**-**	**-**	**na**	**-**			
					***p*H-dependency: y/n**	**n[(b)]**						

(a) Decline fit
(b) No *p*H dependent degradation can be deduced from the available degradation rate data set. However, OECD 106 batch studies indicate that chlorobenzoxazolone is less stable under more alkaline conditions (refer to text below)
Ref. 1) Stumpf & Dambach (1988)
Ref. 2) Shepherd & Ripperger (2012)

Table B.8.1.2.1.5-4 Summary on aerobic degradation rates for HOPP-acid (AE F096918) in laboratory studies - trigger and modelling endpoints

Soil name	Soil type (USDA)	Label	*p*H ($CaCl_2$)	T (°C)	WC (% MWHC)	*DegT 50* (d)	*DegT 90* (d)	*ff* (-)	*DegT50* (d) 20 °C, pF2	χ^2 err. (%)	Kinetic model	Ref.
Farditch	Loam	Ph	5.8	20	45	0.01	0.03	na	0.01	8.5	SFO[(a)]	1)
Longwoods	Sandy loam	Ph	7.4	20	24	0.01	0.03	na	0.01	4.1	SFO[(a)]	
Lockington	Sandy clay loam	Ph	5.7	20	41	0.01	0.03	na	0.01	3.9	SFO[(a)]	
Wurmwiese	Loam	Ph	5.2	20	34	0.01	0.03	na	0.01	0.3	SFO[(a)]	2)
AXXa	Sandy loam	Ph	6.9	20	29	0.01	0.04	na	0.01	0.9	SFO[(a)]	
Hoefchen	Silt loam	Ph	6.3	20	32	0.01	0.04	na	0.01	0.3	SFO[(a)]	
Dollendorf	Clay loam	Ph	7.3	20	45	0.01	0.04	na	0.01	0.5	SFO[(a)]	
					Maximum (n = 7)	**0.01**	**0.04**	**-**	**-**			
					Geometric mean (n = 7)	**-**	**-**	**-**	**0.01**			
					Arithmetic mean (n = 7)	**-**	**-**	**na**	**-**			
					***p*H-dependency: y/n**	**n**						

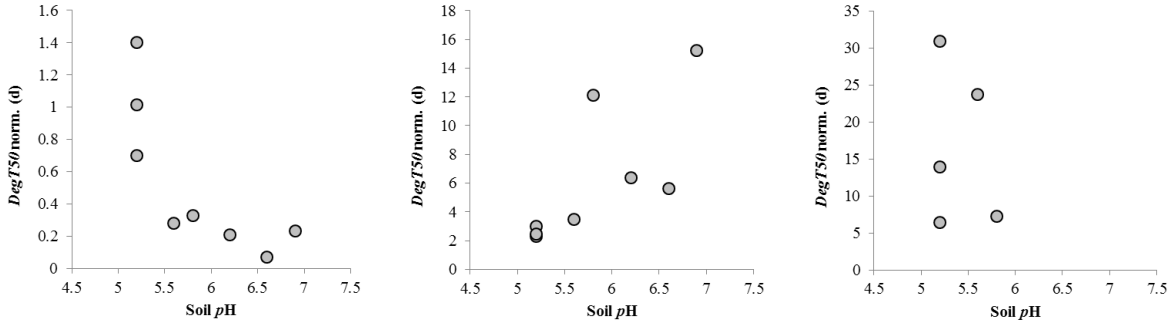
na denotes not applicable
(a) Metabolite applied
Ref. 1) Fitzmaurice (2010)
Ref. 2) Stroech & Junge (2014)

The RMS AT notes that with the exception of HOPP-acid (AE F096918) lab degradation studies do not cover alkaline soils at all. This is considered particularly critical in case of fenoxaprop-P-acid (AE F088406) as degradation rates available for acidic and neutral soils (see figure below) as well as data from batch sorption studies conducted with fenoxaprop-P-acid (AE F088406) (Rupprecht, 1999; Voelkel, 2008a) indicate that fenoxaprop-P-acid (AE F088406) is more stable to degradation in alkaline soils. Unless degradation rates are available for alkaline soils as well, the RMS AT therefore recommends applying the worst case *DegT50* of fenoxaprop-P-acid (AE F088406) observed in acidic and neutral soils in the environmental exposure assessment for conservative reasons.

Degradation rates available for the parent fenoxaprop-P-ethyl (AE F046360) in acidic and neutral soils indicate some *p*H-dependent degradation as well, with possibly faster degradation in more alkaline soils (see figure below). This observation is somewhat in contrast to results from (abiotic) hydrolysis, where fenoxaprop-P-ethyl (AE F046360) was most stable under neutral conditions (*p*H 7). As degradation of fenoxaprop-P-ethyl (AE F046360) is fast in any case (*DegT50* ≤ 1.4 days) the RMS AT does not consider it necessary applying a more conservative approach in this case.

OECD 106 batch experiments conducted with chlorobenzoxazolone (AE F054014) (Allan, 2004; Voelkel, 2008b) indicate that chlorobenzoxazolone (AE F054014) is less stable under alkaline soil conditions. Thus degradation rates available for acidic soils only (*p*H in $CaCl_2 \leq 5.8$) are considered sufficiently conservative for the groundwater and aquatic exposure assessment.

Degradation rates (at reference conditions) in relation to the soil *p*H are given in Figure B.8.1.2.1.5-1.



Fenoxaprop-P-ethyl (AE F046360) **Fenoxaprop-P-acid (AE F088406)** **Chlorobenzoxazolone (AE F054014)**

Figure B.8.1.2.1.5-1: Normalized *DegT50 vs* soil *p*H for fenoxaprop-P-ethyl (AE F046360) and metabolites (different labels from Shepherd, 2012, and Shepherd & Ripperger, 2012, averaged)

The rate of degradation of fenoxaprop-P-ethyl (AE F046360) in anaerobic soil is rapid as well (*DegT50* of 0.35 and 0.37 days in two soils). Degradation of the herbicidal active metabolite fenoxaprop-P-acid (AE F088406) is somewhat lower under anaerobic conditions compared to aerobic conditions (*DegT50* of 35.7 and 43.7 days in two soils).

The rate of degradation of racemic fenoxaprop-ethyl (AE F033171), used as a surrogate for fenoxaprop-P-ethyl (AE F046360), under conditions of photolysis on a (sterile) soil surface is relatively slow (*DegT50* of 62.5 days under environmental conditions, 52 °N). On overall, photolysis is not considered to significantly contribute to the overall dissipation of fenoxaprop-P-ethyl (AE F046360) in terrestrial systems.

B.8.1.2.2. Field studies

B.8.1.2.2.1. Soil dissipation studies

Studies submitted for first Annex I inclusion:

- **Carringer & O'Grodnick, (1993a)**, amended by **Clayton & Parkes (1996a)**, investigating formulated fenoxaprop-P-ethyl (AE F046360) in a US peanut field soil
- **Carringer & O'Grodnick (1993b)**, amended by **Clayton & Parkes (1996b)**, investigating formulated fenoxaprop-P-ethyl (AE F046360) in a US soybean field soil
- **Belyk & Gadsby (1991a),** investigating formulated fenoxaprop-P-ethyl (AE F046360) in a Canadian bare soil
- **Belyk & Gadsby (1991b)**, investigating formulated fenoxaprop-P-ethyl (AE F046360) in a Canadian spring wheat field

No new studies have been submitted by the Fenoxaprop-P-ethyl Task Force.

Reference:	**Field dissipation of Super Whip 0.67EC [Bugle® Herbicide] (Fenoxaprop-P-ethyl) applied to peanuts in North Carolina**
Author(s), year:	Carringer, R. D., O´Grodnick, J. S. (1993a)
Report/Doc. Number:	A51887, M-132786-02-1
Guideline(s):	EPA Pesticide Assessment Guidelines, 164-1
GLP:	Yes
Validity:	Supplemental information (refer to comment section)
Status:	**Previously submitted**

including

Reference:	**Report Amendment no. 1 to final report**
Author(s), year:	Clayton, B., Parkes, R. L. (1996a)
Report/Doc. Number:	A55848, M-132786-02-1
Guideline(s):	Not applicable
GLP:	Yes
Validity:	Supplemental information (refer to comment section)
Status:	**Previously submitted**

[The following study report is a copy/paste of the original text in the DAR for Annex I inclusion slightly amended in order to meet editorial settings and to improve readability]

Material and methods:

The objective of this study were to evaluate the persistence and mobility of fenoxaprop-P-ethyl (AE F046360), formulated as Super Whip 0.67EC (HOE 046360 00 EC09 A1212, batch C0131MO19), and its metabolites fenoxaprop-P-acid (AE F088406) and chlorobenzoxazolone (AE F054014) in peanut field soil when applied to peanut plants 20-25 cm in diameter. One application at a rate equivalent to 896 g fenoxaprop-P-ethyl/ha (equivalent to 1008 g fenoxaprop-P-ethyl plus fenoxaprop-N-ethyl[4]/ha) was made to field plots near Lucama, Wilson County, NC (35.3 °N) in July 1991. The formulation contains 80.3 g fenoxaprop-P-ethyl/l or 89.9g fenoxaprop-P-ethyl plus fenoxaprop-N-ethyl/l.

The site had a slope of 1.0 % with a depth to the water table of 1.2-1.8 m. One plot of 7.2 × 27 m was established as the untreated plot and the treated plot was subdivided into four subplots of the same size. Peanuts were maintained following normal agronomic practices.

The site received an average of 176 % total water during the test based on the 10 year norm.

At each sampling event five soil cores were collected from the control plot and five cores from each treated

[4] Fenoxaprop-N-ethyl = S-enantiomer of fenoxaprop-ethyl (also called fenoxaprop-M-ethyl, AE F085791)

subplot. Soil cores were obtained as 0-15.2 cm and 15.2-106.7 cm sections. Immediately after coring the samples were cut into 15.2 cm increments. All samples were frozen within two hours after collection. Application cards were prepared by placing 15.2 cm diameter filter papers inside glass petri dishes.

Soil samples were initially screened for total fenoxaprop-P-ethyl related residues of concern according to EN-CAS analytical method ENC-8/91 with a LOQ of 0.01 ppm. Soil samples which were first shown to contain total residues ≥ 0.05 ppm, which is the sum of the limits of quantitation of the methods of the individual analytes ppm, were further analysed by the individual analyte method, EN-CAS analytical method ENC-4/92, with a LOQ of 0.02 ppm for each of the components. Application cards were analysed according to EN-CAS analytical method ENC-7/91. Quantification was carried out by reversed phase HPLC with UV-detection.

In-lab storage stability data for individual fenoxaprop-P-ethyl indicated that although degradation of fenoxaprop-P-ethyl is evident in soil by the 18-month interval, the sum of fenoxaprop-P-ethyl and the breakdown products, fenoxaprop-P-acid and chlorobenzoxazolone, quantitatively yields acceptable recovery (80 % and 81 %) after frozen storage for 26 months. In-lab storage stability data for individual acid and chlorobenzoxazolone demonstrates stability in soil after 26 months of frozen storage (recoveries were 105 % and 114 % for the acid and 78 % and 80 % for chlorobenzoxazolone).

Table B.8.1.2.2.1-1 Soil Characteristics

Soil	% Sand	% Silt	% Clay	% OM	*p*H	CEC (meq/100 g)	Field capacity (% moisture at 1/3 bar)
Norfolk sandy loam							
0 - 15.2 cm	73.3	19.2	7.5	0.8	6.1	5.8	21.6
15.2 - 30.5 cm	57.3	23.2	19.5	0.0	4.6	6.2	24.2

Findings:

Table B.8.1.2.2.1-2 Monthly air temperatures in °C

Month	Average minimum	Average maximum
July	22.2	33.9
August	21.1	31.1
September	15.0	28.9
October	8.9	23.3
November	2.2	13.9

Table B.8.1.2.2.1-3 Rainfall and irrigation (monthly totals)

Month	Water (mm)
July 11-31	295
August	154
September	90
October	87
November 1-11	69
Total	**695**

Table B.8.1.2.2.1-4 Summary of average residues for the 0-15.2 cm soil layer (four replicates) in mg/kg

DAT	Total method (parent equivalents)	---------- Individual method ----------			Sum of individual analytes
		Fenoxaprop-P-ethyl (AE F046360)	Fenoxaprop-P-acid (AE F088406)	Chlorobenz-oxazolone (AE F054014)	
1 hour	0.15	< 0.02	0.13	0.02	0.15
4-6 hours	0.14	< 0.02	0.18	0.02	0.20
1	0.16	< 0.02	0.14	0.03	0.17
2	0.19	< 0.02	0.15	0.02	0.17
4	0.11	< 0.02	0.11	< 0.02	0.11
6	0.16	< 0.02	0.10	0.04	0.14
8	0.19	< 0.02	0.10	0.03	0.13
10	0.09	< 0.02	0.08	0.02	0.10
14	0.07	< 0.02	0.05	0.03	0.08

DAT	Total method (parent equivalents)	---------- Individual method ----------			Sum of individual analytes
		Fenoxaprop-P-ethyl (AE F046360)	Fenoxaprop-P-acid (AE F088406)	Chlorobenz-oxazolone (AE F054014)	
28	0.02	< 0.02	< 0.02	< 0.02	< 0.02

Analyses of the 0-15.2 cm soil layers for fenoxaprop-P-ethyl (AE F046360) and its metabolites by the total method indicated average soil residues between 1 hour after application and 8 days after application in the range of 0.11 to 0.19 mg/kg soil. The residues dissipated to 0.09 mg/kg by day 10, 0.02 mg/kg by day 28 and 0.01 mg/kg by day 90. The half-life for the total residues was found to be 9.6 days (r^2 = 0.84) in this soil segment.

No residues were found in samples from the 15.2-30.5 cm soil layer except for a residue of 0.01 mg/kg in one out of the four replicates at day 90. No residues were found in the 30.5-45.7 cm layer, 45.7-76.2 cm layer or 76.2-106.7 cm soil layer. All control samples analysed for total residues yielded results below the LOQ of 0.01 ppm. Procedural recoveries ranged from 69 to 97 % with a mean of 78 % and a standard deviation of 7.2 % (n = 51).

Results of individual fenoxaprop-P-ethyl (AE F046360) samples were all below the LOQ of 0.02 mg/kg in the 0-15.2 soil layer. The half-life of the parent compound was estimated to be less than 1 hour. Fenoxaprop-P-acid (AE F088406) was found to be the major residue present in the soil. Average residues of this metabolite between 1 hour after application and 8 days after application ranged from 0.10 to 0.18 mg/kg. Fenoxaprop-P-acid (AE F088406) had dissipated to 0.05 mg/kg at day 14 and < 0.02 mg/kg at day 28. The half-life for this metabolite was calculated as 9.4 days (r^2 = 0.97). It was not possible on the basis of the available data to calculate a reliable half-life for metabolite chlorobenzoxazolone (AE F054014).

Procedural recoveries (n = 10) for the parent compound ranged from 89 to 107 % (95 % ± 6.7), those for the acid were between 77 and 109 % (88 % ± 11) and those for chlorobenzoxazolone (AE F054014) were 79-116 % (93 % ± 15).

Results for fenoxaprop-P-ethyl (AE F046360) total residues in/on the application cards from the treated plots ranged from 746 to 1417 µg with an average recovery of 1010 µg. Based on the treatment rate of 1008g/ha the theoretical content is 1831µg/card.

Conclusions:

In a field study conducted in the USA (Wilson County, NC) where Super Whip 0.67EC (HOE 046360 00 EC09 A1212) was applied to peanut plants at a rate equivalent to 896 g fenoxaprop-P-ethyl/ha (1008 g fenoxaprop-P-ethyl plus fenoxaprop-N-ethyl/ha) fenoxaprop-P-ethyl (AE F046360) was immediately converted to fenoxaprop-P-acid (AE F088406). For the acid a *DT50* of 9.4 days (r^2 = 0.97) was calculated on the basis of 1st order kinetics. Degradation product chlorobenzoxazolone (AE F054014) was found in very low amounts and no *DT50* value could be calculated. No residues were found below 15 cm in the soil. For total fenoxaprop-P-related residues the calculated *DT50* value was 9.6 days (r^2 = 0.84).

Comments (RMS AT):

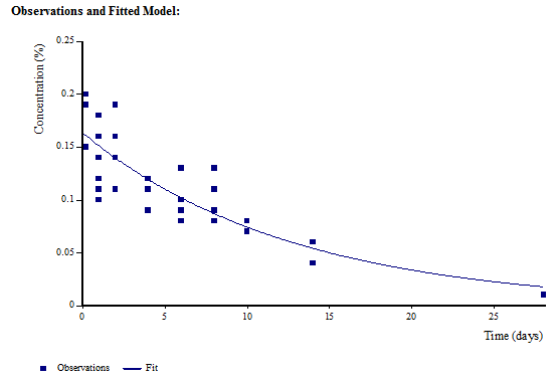
- Study results do not allow calculating a dissipation half-life for fenoxaprop-P-ethyl (AE F046360). Dissipation half-life of fenoxaprop-P-acid (AE F088406) was reassessed by the RMS AT (see tables below) applying a SFO decline fit (CAKE 3.3). Results obtained are well in line with results from lab studies. On overall these **results are considered as supplemental information only**.

Table B.8.1.2.2.1-5 Dissipation rate of fenoxaprop-P-acid (AE F088406) in a peanut field trial (SFO, decline fit) - RMS AT assessment

Field trial	*DisT50* (d)	*DisT90* (d)	χ^2 error	Prop. < t	VA
Wilson County, NC, peanut field	8.8	29.2	9.2	< 0.001	+

Table B.8.1.2.2.1-6 Fit on dissipation of fenoxaprop-P-acid (AE F088406) in a peanut field trial (SFO,

decline fit) - RMS AT assessment



Reference:	**Field dissipation of Super Whip 0.67EC [Bugle® Herbicide] (Fenoxaprop-P-ethyl) applied to soybeans in Iowa**
Author(s), year:	Carringer, R. D., O´Grodnick, J. S. (1993b)
Report/Doc. Number:	A51888, M-132787-02-1
Guideline(s):	EPA Pesticide Assessment Guidelines, 164-1
GLP:	Yes
Validity:	Supplemental information (refer to comment section)
Status:	**Previously submitted**

including

Reference:	**Report Amendment no. 1 to final report**
Author(s), year:	Clayton, B., Parkes, R.L (1996b)
Report/Doc. Number:	A55847, M-132787-02-1
Guideline(s):	Not applicable
GLP:	Yes
Validity:	Supplemental information (refer to comment section)
Status:	**Previously submitted**

[The following study report is a copy/paste of the original text in the DAR for Annex I inclusion slightly amended in order to meet editorial settings and to improve readability]

Material and methods:

The objective of this study were to evaluate the persistence and mobility of Super Whip 0.67EC (HOE 046360 00 EC09 A1212, batch C0131MO19) and its metabolites fenoxaprop-P-acid (AE F088406) and chlorobenzoxazolone (AE F054014) in soybean field soil when applied to soybean plants in the trifoliate stage. One application at a rate equivalent to 818 g fenoxaprop-P-ethyl (AE F046360)/ha (equivalent to 919 g fenoxaprop-P-ethyl (AE F046360) plus fenoxaprop-N-ethyl[5]/ha) was made to field plots in Danville, Iowa (40.8 °N) in July 1991. The formulation contains 80.3 g fenoxaprop-P-ethyl (AE F046360)/l or 89.9 g fenoxaprop-P-ethyl (AE F046360) plus fenoxaprop-N-ethyl/l.

The site had a slope of 1.0 % with a depth to the water table of 0.9 m. One plot of 3 × 57 m was established as the untreated plot and the treated plot was subdivided into four subplots of the same size. Soybeans were planted in June in 76 cm rows. The soybeans were cut and removed from the plots 27 days prior to the last sampling event. No maintenance chemicals or fertilizers were applied during the test period and the plot was not tilled after the formulation was applied.

The site received an average of 163 % total water during the test based on the 10 year norm (monthly ten-year

[5] Fenoxaprop-N-ethyl = S-enantiomer of fenoxaprop-ethyl (also called fenoxaprop-M-ethyl, AE F085791)

av. rainfall).

At each sampling event five soil cores were collected from the control plot and five cores from each treated subplot. All soil cores from the untreated control plot and soil cores taken from the treated subplots at day 60, 91 and 121 were collected as continuous 0-106.7 cm. Soil cores were obtained as 0-15.2 cm and 15.2-106.7 cm sections for the sampling intervals up to and including day 28. Immediately after coring the samples were cut into 15.2 cm increments. All samples were frozen within two hours after collection. Application cards were prepared by placing 15.2 cm diameter filter papers inside glass petri dishes.

Soil samples were initially screened for total fenoxaprop-P-ethyl (AE F046360) related residues of concern according to EN-CAS analytical method ENC-8/91 with a LOQ of 0.01 ppm. Soil samples which were first shown to contain total residues ≥ 0.05 ppm, which is the sum of the limits of quantitation of the methods of the individual analytes ppm, were further analysed by the individual analyte method, EN-CAS analytical method ENC-4/92, with a LOQ of 0.02 ppm for each of the components. Application cards were analysed according to EN-CAS analytical method ENC-7/91. Quantification was carried out by reversed phase HPLC with UV-detection.

Half-lives were calculated based on 1st order reaction kinetics.

In-lab storage stability data for total fenoxaprop-P-acid (AE F088406) demonstrates that the substance is stable in soil (recoveries were 93 % and 94 %) after 20 months of frozen storage. In-lab storage stability data for individual fenoxaprop-P-ethyl (AE F046360) indicated that although degradation of fenoxaprop-P-ethyl (AE F046360) is evident in soil by the 18-month interval, the sum of fenoxaprop-P-ethyl (AE F046360) and the breakdown products, fenoxaprop-P-acid (AE F088406) and chlorobenzoxazolone (AE F054014), quantitatively yields recoveries of 68 % after frozen storage for 26 months. In-lab storage stability data for individual acid and chlorobenzoxazolone (AE F054014) demonstrates stability in soil after 26 months of frozen storage (recoveries were 79 % and 97 % for the acid and 66 % and 78 % for chlorobenzoxazolone, AE F054014).

Table B.8.1.2.2.1-7 Soil Characteristics

Soil	% Sand	% Silt	% Clay	% OM	*p*H	CEC (meq/100 g)	Field capacity (% moisture at 1/3 bar)
Mahaska							
0-15.2 cm (silt loam)	15.3	59.2	25.5	3.2	5.8	18.6	34.8
15.2-30.5 cm (silty clay loam)	11.3	61.2	27.5	3.1	6.0	18.4	35.6

Findings:

Table B.8.1.2.2.1-8 Monthly air temperatures in °C

Month	Average minimum	Average maximum
July	20.0	30.6
August	18.9	29.4
September	13.3	25.0
October	6.7	17.8
November	-3.3	6.1

Table B.8.1.2.2.1-9 Rainfall and irrigation (monthly totals)

Month	Water (mm)
July 11-31	108
August	177
September	118
October	196
November 1-11	254
Total	**624**

Table B.8.1.2.2.1-10 Summary of average residues for the 0-15.2 cm and 15.2-30.5 cm soil layers (four replicates) in mg/kg

DAT	Total method	Individual method	Sum of

	(parent equivalents)	Fenoxaprop-P-ethyl (AE F046360)	Fenoxaprop-P-acid (AE F088406)	Chlorobenz-oxazolone (AE F054014)	individual analytes
			0 - 15.2 cm soil depth		
1 hour	0.31	0.02	0.11	0.06	0.19
4-6 hours	0.25	0.02	0.17	0.05	0.24
1	0.25	0.02	0.16	0.05	0.23
2	0.26	0.01	0.16	0.03	0.20
4	0.41	0.01	0.18	0.07	0.26
6	0.26	0.03	0.18	0.06	0.27
8	0.36	< 0.01	0.20	0.09	0.29
10	0.35	< 0.01	0.19	0.10	0.29
14	0.24	< 0.01	0.12	0.04	0.16
28	0.06	< 0.01	0.02	0.02	0.04
			15.2 - 30.5 cm soil depth		
4-6 hours	0.06	< 0.01	0.03	0.01	0.04

Analysis of the 0-15.2 cm soil samples for fenoxaprop-P-ethyl (AE F046360) and its metabolites by the total method indicated average soil residues from 3 hours after application to 14 days after application in the range of 0.24-0.41 mg/kg soil. Increases in soil concentrations were noted at day 4 and day 8 following irrigation which resulted in wash-off of plant residues on July 13 and July 17. The residues dissipated to 0.06 mg/kg by day 28, 0.02 mg/kg by day 60 and 0.01 mg/kg by day 90. The half-life for the total residues was found to be 14.3 days in the 0-15.2 cm segment (r^2 = 0.60). Soil samples from the 15.2-30.5 sol layers were found to contain an average of 0.04 mg/kg soil for the 1 hour and 4-6 hours samples which dissipated to < 0.01 mg/kg by day 1. Except for residues of 0.02 mg/kg in one of the four replicates at day 4 and one replicate at day 28 and 0.01 mg/kg in two of the replicates at day 10, all other analyses for the 15.2-30.5 soil layers were below the LOQ of 0.01 mg/kg. No residues were found in the deeper soil layers.

All control soil samples yielded results below the LOQ. Procedural recoveries for the total fenoxaprop-P-ethyl (AE F046360) residues ranged from 69 to 120 % with a mean of 84 % and a standard deviation of ± 9.9 % (n = 60).

Average fenoxaprop-P-ethyl (AE F046360) concentrations (individual analytes method) for the 0-15.2 cm soil layers ranged from 0.01 to 0.03 mg/kg for 1 hour after application to 6 days after application and dissipated to < 0.01 mg/kg by day 8. The half-life for the parent compound was estimated to be < 1 hour. Concentrations in the 15.2-30.5 cm soil layer were below the LOQ of 0.01 mg/kg 4-6 hours after application. Fenoxaprop-P-acid (AE F088406) was found to be the major residue. Average residues of this metabolite between 1 hour and 10 days after application ranged from 0.11-0.20 mg/kg soil. This compound had dissipated to 0.12 mg/kg at day 14 and 0.02 mg/kg at day 28. The half-life of the acid in soil was calculated to be 10.8 days (r^2 = 0.64). Chlorobenzoxazolone (AE F054014) was found in low amounts and no reliable half-life could be calculated.

Procedural recoveries (n = 12) for the parent compound ranged from 75 to 95 % (87 % ± 6.3), those for the acid were between 61 and 101 % (79 % ± 13) and those for chlorobenzoxazolone (AE F054014) were 73-123 % (85 % ± 13).

Results for total residues in/on the application cards from the treated plots ranged from 928 to 1562 µg with an average recovery of 1249 µg. The theoretical content based on the treatment rate of 919 g/ha is 1677 µg/card.

Conclusions:

In a field study conducted in the USA (Danville, Iowa) where Super Whip 0.67EC (HOE 046360 00 EC09 A1212) was applied to soybean plants at a rate equivalent to 818 g fenoxaprop-P-ethyl/ha (equivalent to 919 g fenoxaprop-P-ethyl (AE F046360) plus fenoxaprop-N-ethyl/ha) fenoxaprop-P-ethyl (AE F046360) was very quickly converted to fenoxaprop-P-acid (AE F088406). On the basis of 1st order reaction kinetics a *DT50* of 10.8 days was calculated (r^2 = 0.64). Degradation product chlorobenzoxazolone (AE F054014) was found in very low amounts and no reliable *DT50* value could be calculated. No residues were found below 15 cm in the soil. For total fenoxaprop-P-related residues the calculated *DT50* value was 14.3 days (r^2 = 0.60).

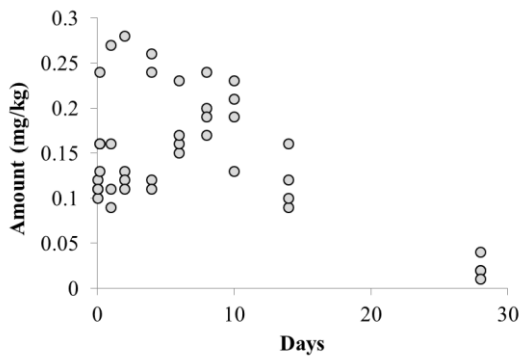
Comments (RMS AT):

- Study results do not allow calculating a dissipation half-life for fenoxaprop-P-ethyl (AE F046360). Dissipation half-life of fenoxaprop-P-acid (AE F088406) was reassessed by the RMS AT (see tables below) applying a SFO decline fit (CAKE 3.3). As residues of fenoxaprop-P-acid (AE F088406) showed quite a scatter in the initial phase, only sampling points within a clear decline phase (starting with 8 DAT) were considered (see figures below). Results obtained are well in line with results from lab studies. On overall these **results are considered as supplemental information only**.

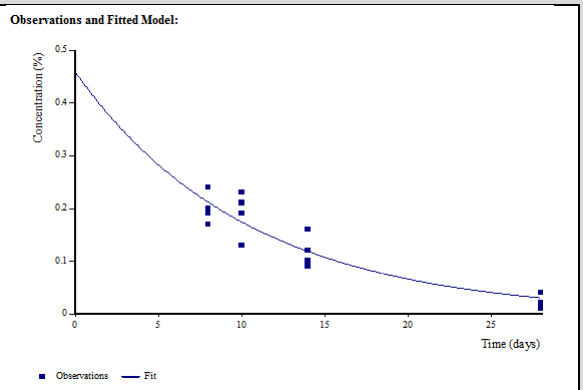
Table B.8.1.2.2.1-11 Dissipation rate of fenoxaprop-P-acid (AE F088406) in a soybean field trial (SFO, decline fit) - RMS AT assessment

Field trial	*DisT50* (d)	*DisT90* (d)	χ^2 error	Prop. < t	VA
Iowa, US, soybeans	7.2	23.8	6.5	< 0.001	+

Table B.8.1.2.2.1-12 Fit on dissipation of fenoxaprop-P-acid (AE F088406) in a soybean field trial (SFO, decline fit) - RMS AT assessment



All sampling points



Sampling points considered for fitting (decline phase)

Reference:	**A comparative field dissipation study of HOE 046360 (EXCEL SUPER) and HOE 046360 + HOE 070542 (PUMA SUPER) in a dry-land Saskatchewan soil**
Author(s), year:	Belyk, M. B., Gadsby, M. C. (1991a)
Report/Doc. Number:	C000912, M-181455-01-1
Guideline(s):	Arizona Terrestrial Field Dissipation
GLP:	Yes
Validity:	Non-reliable (refer to comments)
Status:	**Previously submitted**

[The following study report is a copy/paste of the original text in the DAR for Annex I inclusion slightly amended in order to meet editorial settings and to improve readability]

Material and methods:

The purpose of this study was to compare the dissipation of fenoxaprop-P-ethyl (AE F046360) applied by itself (formulated as EXCEL SUPER) to the dissipation of fenoxaprop-P-ethyl (AE F046360) applied in the presence of the safener HOE 70542[6] (formulated as PUMA SUPER) in a dry-land Saskatchewan soil. This report addresses the fenoxaprop-P-ethyl (AE F046360) results only and not the safener.

A one year study was established at Rosthern, approximately 50 km north of Saskatoon (52 °N), Saskatchewan. In June 1990 a single application of EXCEL SUPER and PUMA SUPER was applied onto bare soil plots (two replicates) at rates equivalent to 300 g ai/ha.

[6] Fenchlorazole-ethyl (AE F070542)

Soil core samples (6.25 cm diameter) were collected with a Back-Saver Probe immediately following application and at 1, 4, 11, 20, 43 and 78 days after treatment. The soil from a 30 cm soil core was carefully split into 0-7.5, 7.5-15 and 15-30 cm depths. On the same day all samples were weighed and an oven-dry moisture content determined. Each sample was sieved through a 2 mm screen, mixed thoroughly, subdivided into foil-lined paper bags and store in a freezer at -20 °C.

The analytical method used in this study was Hoechst-Roussel Agri-Vet Analytical Method number HRAV-4. The active substance (AE F046360) and its metabolites chlorobenzoxazolone (AE 054014) and fenoxaprop-P-acid (AE F088406, active metabolite, free acid form) were extracted from soil by refluxing with a mixture of acetonitrile/water/HCl (90/50/10). The extract was diluted and any undissolved material was removed by filtration. An aliquot of the filtrate was transferred to an Extrelut QE column, which was then washed with n-hexane to remove co-extracted substances. The hydrolysis product chlorobenzoxazolone (AE F054014) was then eluted from the column and eluate evaporated down. Chlorobenzoxazolone (AE F054014was derivatized with acetic anhydride/pyridine at 130 °C. The resulting acetyl derivative Hoe 083312 was cleaned up and samples were analysed by gas chromatography with ECD for the detection of the acetyl derivative. Residue data are expressed as fenoxaprop-P-ethyl (AE F046360) equivalents.

The mean recovery of this method was 80.8 %. The limit of detection for the total residues was 0.025 mg/kg.

Table B.8.1.2.2.1-13 Soil Characteristics

Soil	% Sand	% Silt	% Clay	% OM	*p*H	CEC (meq / 100g)	% FMC (w/w) at 0.03 MPa
Black Chernozem, silty clay loam							
0 - 7.5 cm	19.1	49.9	31.0	7.7	6.0	31.9	42.1
7.5 - 15 cm	19.8	48.9	31.3	6.4	6.5	30.9	37.3
15 - 30 cm	18.9	54.1	27.0	3.9	6.9	26.6	33.8

Findings:

During the 78 day monitoring period in 1990 (June 7 to August 24) the highest daily maximum temperature of 33.5 °C and the lowest daily minimum temperature of 5.0 °C occurred on August 6 and August 9, respectively. Of the 78 days monitored, 31 days had daily maximum temperatures ≥ 25 °C. A total of 25 rainfall events occurred with a cumulative amount of 206 mm. The average maximum and minimum daily temperature and total rainfall for the first 7 days after application were 21 °C, 9.4 °C and 25.2 mm, respectively. Throughout the monitoring period water infiltration below the soil surface layer was greatly reduced due to the relatively small amounts of rainfall combined with a high evaporative rate. Results are summarised in the table below:

Table B.8.1.2.2.1-14 Residue levels of fenoxaprop-P-ethyl (AE F046360) equivalents in soil samples (adjusted for % recovery)

Soil layer (cm)	PUMA SUPER		EXCEL SUPER	
	DAT	mg/kg residues	DAT	mg/kg residues
0-7.5	0	0.256	0	0.153
	1	0.256	1	0.180
	4	0.113	4	0.096
	11	0.07	11	0.104
	20	0.09	20	0.059
	43	0.04	43	n.d.
	79*	n.d.	-	-
7.5-15	4	0.03	4	n.d.
	8*	n.d.	-	-
	11*	0.037	11	0.029
	20	n.d.	20	n.d.
	43	n.d.	43	n.d.
15-30	20	n.d.	20*	n.d.
	43	n.d.	43*	n.d.

* only one replicate

Degradation rates were calculated considering 1st order reaction kinetics. The number of days to reach the limit

of detection was determined from a straight line fit of the data (log transformed). From this, a rate constant and a half-life value were calculated for each treatment (0-7.5 cm soil layer). The calculated half-life was 15.5 and 14.4 days for EXCEL SUPER and PUMA SUPER, respectively. Correlation coefficients were not given.

Conclusions:

Fenoxaprop-P-ethyl (AE F046360) was applied onto bare soil at a rate equivalent to 300 g ai/ha formulated either as EXCEL SUPER (without safener) or PUMA SUPER (including safener HOE 70542). The test site was located near Saskatoon, province of Saskatchewan (Canada). Calculated half-lives for fenoxaprop-P-ethyl (AE F056360) equivalents were 15.5 and 14.4 days. In the 7.5-15 cm soil layer only very low amounts of residues were found sporadically. No residues were detected in the 15-30 cm soil layer.

Comments (RMS AT):

- The RMS AT notes that the analytical methodology applied (HRAV Analytical Method: HRAV-4B) is not capable to differentiate between fenoxaprop-P-ethyl (AE F046360), fenoxaprop-P-acid (AE F088406) and chlorobenzoxazolone (AE F054014) as in the soil extraction step (reflux in a mixture of acetonitrile/HCl/water (90:10:50) for 6 hours) fenoxaprop-P-ethyl (AE F046360) and fenoxaprop-P-acid (AE F088406) are quantitatively converted into chlorobenzoxazolone (AE F054014) which is derivatized and finally measured by gas chromatography. Thus results on residues refer to fenoxaprop-P-ethyl (AE F046360) *equivalents* always. Keeping this in mind, **the study is considered non-reliable**.

Reference:	**Field persistence and dissipation of HOE 046360 and HOE 070542 over a one, two and three year period**
Author(s), year:	Belyk, M. B., Gadsby, M. C. (1991b)
Report/Doc. Number:	C000913, M-181457-01-1
Guideline(s):	Arizona Terrestrial Field Dissipation
GLP:	Yes
Validity:	Non-reliable (refer to comment section)
Status:	**Previously submitted**

[The following study report is a copy/paste of the original text in the DAR for Annex I inclusion slightly amended in order to meet editorial settings and to improve readability]

Material and methods:

The purpose of this study was to examine the dissipation and persistence of fenoxaprop-P-ethyl (AE F046360) and its safener fenchlorazole-ethyl (AE F070542, called Hoe 070542 in the study report) in crop and non-crop subplots over a three year period. This report addresses the fenoxaprop-P-ethyl (AE F056360) results only and not the safener.

The experiment was located at Southey (50 °N), province of Saskatchewan (Canada). The climatic data were given only for one of the three years period. Fenoxaprop-P-ethyl (AE F046360) formulated as PUMA SUPER (7.5 % w/w fenoxaprop-P-ethyl and 3.75 % w/w of the safener) was applied at rates equivalent to 200 g a.i./ha to the plots, either two times (1988 and 1989) or three times (1988, 1989 and 1990) post emergence to spring wheat.

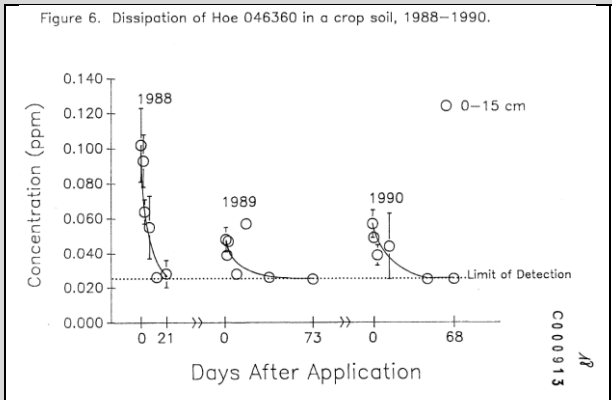
Prior to seeding in these years plant material covering both crop and non-crop plots was worked under by cultivator. In late fall the entire experimental area was moved down, the stubble was left standing over winter.

Soil samples were taken before, immediately after application and up to 5 times more, at the latest 68 days after application. Samples were taken up to a depth of 30 cm with a 6.25 cm diameter Back-Saver Probe and portioned to two horizons (0-15 cm and 15-30 cm). The analytical methodology was the same as described in the study above (Document C000912). The mean recovery of this method was 81.5 %. The limit of detection for the total residues was 0.025 mg/kg.

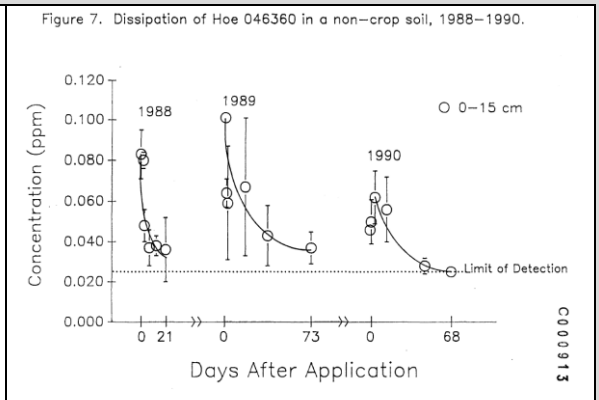
Comments (RMS AT):

- The RMS AT notes that the analytical methodology applied (HRAV Analytical Method: HRAV-4B) is not capable to differentiate between fenoxaprop-P-ethyl (AE F046360), fenoxaprop-P-acid (AE F088406) and chlorobenzoxazolone (AE F054014) as in the soil extraction step (reflux in a mixture of acetonitrile/HCl/water (90:10:50) for 6 hours) fenoxaprop-P-ethyl (AE F046360) and fenoxaprop-P-acid (AE F088406) are quantitatively converted into chlorobenzoxazolone (AE F054014) which is finally derivatized and measured by gas chromatography. Thus results on residues refer to fenoxaprop-P-ethyl (AE F046360) *equivalents* always. Keeping this in mind, **the study is considered non-reliable**.

- Results have not been summarised in a common way in the study report. However, two figures given in the report may give an impression of the results obtained (total residues expressed as fenoxaprop-P-ethyl (AE F046360) equivalents):



Cropped soil



Non-cropped soil

B.8.1.2.2.2. Soil accumulation studies

No studies submitted. Values for the *DT90* of fenoxaprop-P-ethyl (AE F046360) and its metabolites from laboratory and field tests were all significantly less than one year thus with no indication for accumulation of fenoxaprop residues in the soil environment.

B.8.1.2.2.3. Summary on field studies

Field dissipation studies with formulated fenoxaprop-P-ethyl (AE F046360) were conducted in the US (two studies) and in Canada (two studies, one of them with repeated application over 3 years). Results from the Canadian field trials are expressed on basis of parent equivalents only, thus these two studies are considered non-reliable. In the two studies conducted in the US (one peanut and one soybean field trial) amounts of fenoxaprop-P-ethyl (AE F046360) in soil close to the LOQ do not allow calculating dissipation half-lives for the parent. Dissipation half-lives for fenoxaprop-P-acid (AE F088406) re-calculated by the RMS AT were 8.8 days in Wilson County, NC (peanut field) and 7.2 days in Iowa (soybeans), thus well in line with observations made in the laboratory studies. Results from these two field studies are considered supplemental information only.

B.8.1.3. Adsorption and desorption in soil

B.8.1.3.1. Adsorption and desorption

B.8.1.3.1.1. Adsorption of the active substance

Studies submitted for first Annex I inclusion:

- **Goerlitz & Rutz (1988)**, investigating adsorption/desorption of fenoxaprop-P-ethyl (AE F046360) and fenoxaprop-P-acid (AE F088406) in four soils
- **Reynolds (1992)**, investigating adsorption/desorption of fenoxaprop-P-ethyl (AE F046360), fenoxaprop-P-acid (AE F088406) and chlorobenzoxazolone (AE F054014) in four soils

No new studies were submitted by the Fenoxaprop-P-ethyl Task Force.

Reference:	**Hoe 046360, adsorption/desorption in the system soil/water and Hoe 088406 adsorption in the system soil/water**
Author(s), year:	Goerlitz, G., Rutz. U. (1988)
Report/Doc. Number:	A38826, M-120443-01-1
Guideline(s):	US-EPA Guidelines N, 163-1 (1982)
GLP:	Yes
Validity:	Non-reliable (refer to comment section)
Status:	**Previously submitted**

[The following study report is a copy/paste of the original text in the DAR for Annex I inclusion slightly amended in order to meet editorial settings and to improve readability]

Material and methods:

The objective of this study was the determination of the adsorption/desorption behaviour of non-labelled fenoxaprop-P-ethyl (AE F046360, called Hoe 046360 in the study report) using the batch-equilibrium method.

In a first experiment an adsorption kinetic was determined. After 8 hours equilibrium was reached. After 32 hours the concentration of fenoxaprop-P-ethyl (AE F046360) in the aqueous phase decreased again while the concentration of the acid (AE F088406, called Hoe 088406 in the study report) increased at the same time, indicating significant degradation of fenoxaprop-P-ethyl (AE F046360). In order to ensure that adsorption equilibrium is reached, without incurring too much degradation of the active substance the equilibration time of all adsorption experiment was fixed at 14 hours. For experimental reasons all desorption experiment were carried out with 24 hours equilibration time. As it was shown that some degradation of fenoxaprop-P-ethyl (AE F046360) to the corresponding acid fenoxaprop-P-acid (AE 088406) in prior sterilised soil was unavoidable the adsorption of fenoxaprop-P-acid (AE F088406) on the soils was determined in a separate experiment, at a concentration level of 0.31 mg/L. During all the experiments also the concentration of the degradation product was monitored. Measurements of adsorption and desorption of fenoxaprop-P-ethyl (AE F046360) were then corrected for degradation during the experiments. Adsorption isotherms according to Freundlich were determined for fenoxaprop-P-ethyl (AE F046360) on each soil by using four different initial concentrations between 0.03 mg/L and 0.3 mg/L (nominal). At one concentration level following to the adsorption experiment two consecutive desorption steps were performed by adding 0.01 M $CaCl_2$ solution to the soil. In a further step a similar desorption experiment was performed with acetonitrile and the mass balance was calculated for the total extractable test substance. For the adsorption experiments a soil/solution ratio of 1:5 was chosen. The tests were carried out at 21 °C in the dark.

Aqueous solutions were acidified with HCl and extracted with methylene chloride. After methylene chloride was removed by evaporation under a stream of nitrogen a solution containing 60 % acetonitrile and 40 % aqueous phosphoric acid was added and the resulting sample solution transferred to the HPLC system. Since fenoxaprop-P-ethyl (AE F046360) is stable under acidic conditions no degradation could occur after sampling. Recovery rate between 61.9 % (at 7 µg/L) and 101.4 % (at 0.361 mg/L) were found for fenoxaprop-P-ethyl (AE F046360). For fenoxaprop-P-acid (AE F088406) the recovery rates were between 99.2 % and 104.4 % in the whole range between 5 µg/L and 0.249 mg/L.

Table B.8.1.3.1.1-1 Soil Characteristics

Soil	% Sand	% Silt	% Clay	% OM	% OC[(a)]	*p*H ($CaCl_2$)	CEC (meq/100 g)	MWHC (g/100 g)
SL 2, silty loam, Leland (USA)	16.1	65.6	18.3	1.06	0.62	5.4	16.11	39.0
SL S, sandy loam, Leland (USA)	63.8	31.1	5.1	1.51	0.89	6.3	3.90	30.3
SL V, sandy loam, Germany	58.8	31.6	9.6	2.17	1.26	5.9	6.3	36.2
LS 2.2, loamy sand, Speyer	79.7	18.2	9.1	4.53	2.66	5.8	10.59	33.0

(a) OC = OM / 1.724

Findings:

The results for the adsorption/desorption behaviour can be summarized as follows:

Soil SL 2

Adsorption A = 83.9 % of total, K_d = 79.5 L/kg
Desorption (1st step) D = 71.9 % of adsorbed substance, K_{des} = 328.4 L/kg
Desorption (2nd step) D = 21.0 % of adsorbed substance, K_{des} = 100.3 L/kg
Material accounted for: 81.5 % (the difference to 100 % is material still strongly adsorbed to the soil)

Soil SL S

Adsorption A = 87.7 % of total, K_d * = 71.8 L/kg
Desorption (1st step) D = 56.0 % of adsorbed substance, K_{des} = 369.0 L/kg
Desorption (2nd step) D = 19.5 % of adsorbed substance, K_{des} = 136.7 L/kg
Material accounted for: 77.1 % (the difference to 100 % is material still strongly adsorbed to the soil)

Soil SL V

Adsorption A = 86.8 % of total, K_d * = 102.6 L/kg
Desorption (1st step) D = 75.0 % of adsorbed substance, K_{des} could not be evaluated
Desorption (2nd step) D = 37.3 % of adsorbed substance, K_{des} = 83.4 L/kg
Material accounted for: 87.7 % (the difference to 100 % is material still strongly adsorbed to the soil)

Soil LS 2.2

Adsorption A = 88.4 % of total, K_d = 234.9
Desorption (1st step) D = 32.1 % of adsorbed substance, K_{des} = 275.9 L/kg
Desorption (2nd step) D = 26.0 % of adsorbed substance, K_{des} = 93.5 L/kg
Material accounted for: 107.9 %

Results indicate that generally adsorption is not completely reversible. The accuracy of desorption measurements however were very much reduced by the degradation of the test substance. Desorption values D include material desorbed in the form of the degradation product fenoxaprop-P-acid (AE F088406).

The results from the single level adsorption experiment with the metabolite fenoxaprop-P-acid (AE F088406, Hoe 088406) are as tabled below:

Table B.8.1.3.1.1-2 Adsorption coefficients for fenoxaprop-P-acid (AE F088406)

Soil	K_d (L/kg)	K_{oc} (L/kg)
SL 2	1.2	188
SL S	1.0	113
SL V	1.4	109
LS 2.2	4.3	161

These values were used to correct the adsorption/desorption measurement of fenoxaprop-P-ethyl (AE F046360) for amounts of fenoxaprop-P-acid (AE F088406) adsorbed on soil.

Isotherms for fenoxaprop-P-ethyl (AE F046360) were determined from the molar concentrations in soil and aqueous phase according to the Freundlich equation. The *b* values (1/*n*) differed significantly from unity. Therefore these values were not used for the adsorption coefficient *K*. K_f-values were calculated as the mean

values of K_d over the range of the isotherm.

Table B.8.1.3.1.1-3 Adsorption parameters for the parent compound fenoxaprop-P-ethyl (AE F046360)

Soil	*p*H of soil	% OC in soil	Freundlich coefficients *a* (K_f)	*b* (1/*n*)	r^2	K_d (L/kg)	K_{oc} (L/kg)
SL 2	5.4	0.62	343	1.27	0.99	104	16774
SL S	6.3	0.89	262	1.42	0.98	57	6404
SL V	5.9	1.28	139	1.14	0.96	82	6406
LS 2.2	5.8	2.66	8340	1.88	0.95	149	5602

Conclusions:

In this batch equilibrium study fenoxaprop-P-ethyl (AE F046360) showed strong adsorption to soil. K_{oc} values between 5602 and 16774 L/kg were calculated. K_{oc} values decreased with increasing organic matter content of the soils but were fairly constant within three soils. The very high adsorption constant determined for soil SL 2 may indicate a contribution of clay to the adsorption of fenoxaprop-P-ethyl (AE F046360).

As fenoxaprop-P-ethyl (AE F046360) hydrolyses very rapidly to fenoxaprop-P-acid (AE F088406) the concentrations of fenoxaprop-P-ethyl (AE F046360) in soil had been corrected for the amount of fenoxaprop-P-ethyl (AE F046360) which degraded during the adsorption step. Nevertheless, adsorption parameters determined in this way are subject to some uncertainty and can only be an estimate for the specific time range chosen in the experiment. Estimated Freundlich coefficients had been calculated all above 1.0 (1.14 - 1.88). The calculated values for 1/*n* are not considered realistic. But as a conclusion from the available data, fenoxaprop-P-ethyl (AE F046360) is considered to be of low mobility.

Comments RMS AT:

- The study only roughly follows OECD guideline 106. Major deficits are:
  - No pre-equilibrium phase (i.e. shaking of soil with pure $CaCl_2$ solution overnight). In principle, this invalidates the study with respect to recommendations given in OECD guidance 106.
  - Optimum soil-to-solution ratio has not been checked (1:5 used without justification)
  - Only two orders of magnitude in concentration of test item applied (0.03 - 0.3 mg/L)
  - In order to calculate the mass of the test item (fenoxaprop-P-ethyl (AE F046360)) adsorbed to the soil, the study authors applied a correction procedure on basis of K_d values obtained for the degradation product fenoxaprop-P-acid (AE F088406) in the same soil and concentrations of fenoxaprop-P-acid (AE F088406) measured in the liquid phase of the parent experiment. Although this correction is scientifically defendable under certain conditions (refer to text below), such a correction procedure is neither mentioned nor described in the OECD guideline 106.

- As can be expected from aerobic soil degradation experiments, the study authors observed significant degradation of fenoxaprop-P-ethyl (AE F046360) in the batch experiment. For that reason, the equilibrium time was restricted to 14 hrs and soils have been sterilized. As there were still significant amounts of the degradation product fenoxaprop-P-acid (AE F088406) found in the liquid phase after the adsorption phase (and even more after the desorption phases) the study authors applied a correction method on basis of the concentration of fenoxaprop-P-acid (AE F088406) measured in the liquid phase and the K_d of fenoxaprop-P-acid (AE F088406) measured in an separate batch experiment in the same soil. From a scientific point of view this approach is only valid, if it can be ensured that there are no other degradation products present and non-extractable residues are negligible in both batch systems. Both requirements have not been checked by the study authors, neither in batch experiments with fenoxaprop-P-ethyl (AE F046360) nor with fenoxaprop-P-acid (AE F088406), as they only investigated the liquid phases (following the *indirect* method according to OECD guideline 106) applying cold (non-labelled) material without investigating other possible degradation products. In view of results obtained in other batch studies with fenoxaprop-P-ethyl (AE F046360) and fenoxaprop-P-acid (AE F088406) (refer to next studies) the approach used by the study authors

(*indirect* method in combination with a correction procedure) is not considered appropriate to derive robust sorption coefficients for both, fenoxaprop-P-ethyl (AE F0463609 and fenoxaprop-P-acid (AE F088406). On overall, the RMS AT considers this **study and results obtained non-reliable**.

Reference:	**Adsorption and desorption of ^{14}C-fenoxaprop-P-ethyl in four soils**
Author(s), year:	Reynolds, J.L. (1992), revised 1993
Report/Doc. Number:	A51332, M-137847-02-3
Guideline(s):	US EPA, subdivision N, § 163-1 (1982)
GLP:	Yes
Validity:	Partly (refer to comment section)
Status:	**Previously submitted**

[The following study report is a copy/paste of the original text in the DAR for Annex I inclusion slightly amended in order to meet editorial settings and to improve readability]

Material and methods:

The objective of this study was to examine the adsorption/desorption behaviour of UL-chlorophenyl-^{14}C labelled fenoxaprop-P-ethyl (AE F046360, called Hoe 046360 in the study report) and the corresponding free acid fenoxaprop-P-acid (AE F088406) according to the batch equilibrium method, and to determine the Freundlich constants in four different agricultural soils. The actual treatment solution concentrations were 0.36, 0.17, 0.08 and 0.04 mg/l 0.01 M $CaCl_2$. Preliminary testing with ^{14}C-fenoxaprop-P-ethyl (AE F046360) using Arizona clay soil and a 0.35 ppm treatment rate indicated that a soil/solution ratio of 1:5 was appropriate. As an optimum equilibration time 6 hours was determined with exception of the Mississippi Soil, where 24 hours were found to be appropriate. Preliminary work further indicated that ^{14}C-fenoxaprop-P-ethyl (AE F046360) binds to glass tubes. In order to minimize the adsorption, the glass tubes were pre-coated with unlabelled fenoxaprop-P-ethyl (AE F046360). Selected adsorption solutions were also subjected to HPLC analyses to determine the extent of the active substance degradation. After the adsorption step one desorption step was carried out.

A total of 16 tubes, 3 tubes per soil type and 2 positive controls (blank tubes plus treatment solution) and 2 negative controls (soil plus untreated $CaCl_2$ solution) were prepared for the 0.35 mg/L rate. For each remaining treatment rate a total of 2 tubes per soil type were prepared. After the shaking period of 6 or 24 hours followed by centrifugation, the supernatants were subjected for LSC. One tube (replicate 'C') per soil type from the 0.35 mg/L samples was removed and the supernatant and solids were extracted as described below. After the desorption procedure, followed by centrifugation, the supernatants were assayed by LSC. The supernatants and solids from one tube (replicate 'A') per soil type and treatment rate were extracted as follows: Supernatants were acidified with HCl and then directly partitioned with methylene chloride yielding an organosoluble fraction (Fraction I) and an aqueous fraction (Fraction II). The soils were blended with acetonitrile/acidified water (1 % 1N HCl; 4:1) followed by vacuum filtration. The filtrate was partitioned with CH_2Cl_2 yielding an organosoluble fraction (Fraction III) and a polar aqueous fraction (Fraction IV). The resulting solid residues were designated as post extraction solids (PES).

The desorbed soil from the other replicate were removed, air-dried and subsampled for combustion analyses. Concentrated organosoluble fractions ("Fractions I" and "III") and reference standards were analysed by TLC. Representative organosoluble fractions from selected samples were also analysed by reverse phase HPLC. Levels of radioactivity in the soil after extraction (PES) and the desorbed soils were determined by combusting and LSC.

Average recoveries obtained throughout the study were determined to be 91.4 - 103.8 %.

Table B.8.1.3.1.1-4 Soil characteristics

Soil	% Sand	% Silt	% Clay	% OM	% OC	*p*H	CEC (meq/100 g)	FC at 1/3 bar (%)
Clay, Arizona	32	25	43	0.4	0.23	7.6	23.9	26.80
Silty clay loam, Mississippi	14	47	39	1.4	0.81	6.5	17.1	32.10
Sandy loam, Maryland, Pillsville	75.6	13.0	11.4	4.40	2.55	6.4	9.40	12.88

Soil	% Sand	% Silt	% Clay	% OM	% OC	*p*H	CEC (meq/100 g)	FC at 1/3 bar (%)
Clay loam, Michigan	34.6	33.0	32.4	4.56	2.65	6.8	17.14	25.89

Findings:

The distribution of applied radioactivity for each soil type and treatment rate is summarised in the table below:

Table B.8.1.3.1.1-5 Distribution of applied radioactivity (%)

Soil	Test conc. (ppm)	Supernatant (ads.)	Supernatant (des.)	Extractable soil	Remaining radioactivity in soil	Sample recovery
Clay Arizona	**0.35 'C'**	49.0	na	50.2	1.5	100.7
	0.35 'A'	49.0	28.7	24.0	1.2	102.9
	0.17	53.6	29.0	25.1	0.8	108.5
	0.08	52.7	27.3	21.2	3.1	104.3
	0.04	50.2	27.6	23.0	1.9	102.7
Silty clay loam Mississippi	**0.35 'C'**	31.1	na	66.4	4.0	101.3
	0.35 'A'	32.7	18.9	42.0	7.3	100.9
	0.17	28.5	19.3	46.7	8.4	102.9
	0.08	29.0	20.0	46.8	8.5	104.2
	0.04	24.4	16.9	44.3	7.7	93.4
Sandy loam Maryland, Pillsville	**0.35 'C'**	24.5	na	69.4	7.3	101.2
	0.35 'A'	24.8	13.2	54.7	7.7	100.4
	0.17	24.3	12.5	56.5	10.3	103.6
	0.08	19.3	9.6	58.6	13.2	100.7
	0.04	18.5	7.5	61.3	17.1	104.3
Clay loam Michigan	**0.35 'C'**	39.3	na	55.0	6.8	101.1
	0.35 'A'	39.7	20.3	35.0	7.5	102.5
	0.17	38.8	18.4	36.1	10.1	103.4
	0.08	36.6	16.5	36.8	13.0	102.8
	0.04	38.6	14.3	36.8	16.7	106.5

na denotes not applicable

The stability of fenoxaprop-P-ethyl (AE F046360) under the test conditions was examined by TLC analyses of the organosoluble extract from the adsorption solution and extracts from the residual solids from all four soils at 0.35 mg/L.

Table B.8.1.3.1.1-6 Summary of distribution of parent compound and degradates (% of total) - final adsorption k_d values are based on the concentrations in supernatant and solids shaded in grey

Test conc. (ppm)	Fraction	Fenoxa-prop-P-ethyl (AE F046360)	Fenoxa-prop-P-acid (AE F088406)	Chloro-benz-oxazolone (AE F054014)	Un-knowns	Fenoxa-prop-P-ethyl (AE F046360)	Fenoxa-prop-P-acid (AE F088406)	Chloro-benz-oxazolone (AE F054014)	Un-knowns
		---------- Soil Arizona ----------				---------- Soil Mississippi ----------			
0.35 'C' ads.	Supernatant	13.21	31.96	3.38	0.43	0.31	13.48	14.19	3.09
	Solids	37.41	12.74	2.16	-	15.06	31.11	12.47	11.55
0.35 'A' des.	Supernatant	5.98	19.28	2.12	1.27	nd	6.26	7.61	5.05
	Solids	10.99	12.83	1.03	0.34	7.00	29.21	4.44	8.63
0.17	Supernatant	6.18	20.30	1.59	0.89	nd	0.44	11.71	7.14
	Solids	10.75	13.58	0.33	1.23	9.46	29.59	4.85	11.18
0.08	Supernatant	4.62	17.71	2.69	2.27	nd	12.54	5.65	1.78
	Solids	7.92	12.07	1.12	3.18	5.40	18.96	8.25	22.59
0.04	Supernatant	10.41	14.75	0.99	1.49	nd	nd	12.25	4.64
	Solids	8.71	2.33	0.83	3.04	9.41	26.26	4.53	11.82
		---------- Soil Maryland[(a)] ----------				---------- Soil Michigan ----------			
0.35 'C' ads.	Supernatant	0.17	8.44	11.48	4.41	0.27	37.55	0.98	0.47
	Solids	16.22	44.98	4.99	10.53	10.63	42.75	0.60	7.81
0.35 'A' des.	Supernatant	0.07	9.81	3.03	0.30	0.10	9.16	0.63	0.41
	Solids	3.99	12.46	8.85	37.13	5.51	28.15	0.35	8.53

0.17	Supernatant	0.22	9.87	1.71	0.72	0.20	16.69	0.68	0.87
	Solids	nd	2.54	11.45	52.78	5.13	28.44	0.90	11.65
0.08	Supernatant	0.34	7.43	0.86	0.95	nd	14.97	1.04	0.49
	Solids	8.47	26.22	10.80	26.32	6.13	27.13	1.24	15.21
0.04	Supernatant	nd	3.09	3.59	0.84	0.61	0.35	7.15	6.23
	Solids	7.37	19.55	13.76	37.66	5.11	27.61	2.04	18.73

nd denotes < 0.01 % of total applied radioactivity
(a) One to four unknowns were found. The maximum one detected at R_f of 0.00 accounted for 21.04 % of the total applied radioactivity in the 0.17 mg/L rate.

Adsorption and desorption constants according to the Freundlich equation were calculated based on the total radiocarbon measurements in soils and supernatants over the range of test concentrations:

Table B.8.1.3.1.1-7 Adsorption/desorption constants based on <u>total radiocarbon</u>

Soil	Adsorption				Desorption			
	K_f (L/kg)	K_{foc} (L/kg)	1/*n* (-)	r^2	K_f (L/kg)	K_{foc} (L/kg)	1/*n* (-)	r^2
Arizona, Clay	4.10	1767	0.9881	0.9975	4.28	1843	1.004	1.000
Mississippi, Silty clay loam	6.55	807	0.8362	0.9994	8.31	1023	0.8488	0.9966
Maryland, Sandy loam	9.77	383	0.8385	0.9998	11.0	432	0.7660	0.9976
Michigan, Clay loam	5.91	223	0.9180	0.9995	5.57	210	0.7826	0.9999

Distribution coefficients were calculated for fenoxaprop-P-ethyl (AE F046360), fenoxaprop-P-acid (AE F088406) and chlorobenzoxazolone (AE F054014) based on the concentrations in soil and supernatants of the 0.35 mg/L test samples. Desorption constants according to the Freundlich equation were also calculated for these compounds based on the concentrations in soils and supernatants over the range of test concentrations:

Table B.8.1.3.1.1-8 Adsorption/desorption constants based on concentrations of the parent compound and its metabolites.

Soil	---- Adsorption ----		---------- Desorption ----------			
	K_d (L/kg)	K_{oc} (L/kg)	K_f (L/kg)	K_{foc} (L/kg)	1/*n* (-)	r^2
Fenoxaprop-P-ethyl (AE F046360)						
Arizona clay	12.8	5419	25.89	11157	1.257	0.957
Mississippi Silty clay loam	212	26207	na	na	na	na
Maryland Sandy loam	443	17352	188[(a)]	7379	na	na
Michigan Clay loam	176	6667	9.33E+25[(b)]	3.53E+27	7.8077	0.9117
Fenoxaprop-P-acid (AE F088406)						
Arizona clay	1.77	763	2.59	1116	0.9156	0.9981
Mississippi Silty clay loam	10.11	1245	0.11[(c)]	13.2	-0.1896	0.2325
Maryland Sandy loam	24.7	969	0.27	10.6	0.2898	0.3977
Michigan Clay loam	5.1	193	10.9	413	1.0847	0.9988
Chlorobenzoxazolone (AE F054014)						
Arizona clay	2.84	1223	0.46	196	0.7466	0.8825
Mississippi Silty clay loam	3.85	474	2.29	282	0.9074	0.8403
Maryland Sandy loam	2.02	79	84	3297	1.2829	0.9235
Michigan Clay loam	2.74	104	0.002	0.07	-0.1651	0.3779

(a) Average value from the K_d values from the 0.08 and 0.35 mg/L rate data
(b) 0.08 mg/L data not used for regression
(c) 0.04 mg/L data not used for regression

<u>Conclusions</u>:

Based on K_{oc} values which were derived from single distribution coefficients of the 0.35 mg/L test concentration fenoxaprop-P-ethyl (AE F046360) can be classified as immobile in soil (K_{oc} 5419 - 26207 L/kg). Fenoxaprop-P-acid (AE F088406) showed low to medium mobility (K_{oc} 193 – 1245 L/kg). Considering the K_d values of the free acid, these values decreased with increasing *p*H. Chlorobenzoxazolone (AE F054014) showed high to low mobility considering its K_{oc} values, which were 79 - 1223 L/kg, pending on the clay content.

<u>Comments RMS AT:</u>

- In this study no pre-equilibrium phase (i.e. shaking of soil with pure $CaCl_2$ solution overnight) was accounted for. In principle this invalidates the study with respect to recommendations given in OECD guideline 106. However, batch sorption experiments with fenoxaprop-P-ethyl (AE F046360) will always be somehow limited due to the distinct instability of fenoxaprop-P-ethyl (AE F046360) in these test systems. In this respect, the RMS AT considers results obtained in this study (following corrections as proposed below) sufficiently robust to give at least an estimate of the sorption coefficient of fenoxaprop-P-ethyl (AE F046360) in soils even without pre-equilibrium phase. However, results for fenoxaprop-P-acid (AE F088406) and chlorobenzoxazolone (AE F054014) are not considered further as dedicated batch adsorption studies are available for these two metabolites which adequately account for a pre-equilibrium phase.

- Aside from the missing pre-equilibration phase the study broadly follow OECD guideline 106 with some deviations:
  - The range of concentration for determination of Freundlich adsorption isotherms does not cover 3 orders of magnitude (0.04 - 0.36 mg/L only) with only 4 instead of 5 different concentrations investigated. However, final adsorption results for all three substances are based on the highest concentration only (so no Freundlich adsorption isotherm was deduced from the experiment).
  - The soils investigated do not always fulfil soil selection criteria related to *p*H, organic carbon content, clay content and soil texture as given in OECD guideline 106. Additionally, the *p*H value of the soils is in a rather narrow range of 6.4 - 7.6. However, keeping in mind that fenoxaprop-P-ethyl (AE F046360) is a non-dissociating substance *p*H dependent sorption is *a priori* not expected.
  - The adsorption phase (replicate 'C') was not conducted in replicates.

  On overall the RMS AT is of the opinion that deviations observed are minor and do on overall not invalidate the study.

- Fenoxaprop-P-ethyl (AE F046360) as well as its major soil metabolites fenoxaprop-P-acid (AE F088406), chlorobenzoxazolone (AE F054014) and HOPP-acid (AE F096918) are prone to significant formation of non-extractable residues (NER) in aerobic soil degradation experiments as well as in batch sorption experiments. The table below gives an overview on NER found in soil degradation experiments already at early stage (24 hrs of incubation) and in sorption experiments (6 - 48 hrs adsorption phase).

Table B.8.1.3.1.1-9 Non-extractable residues (NER) found in aerobic lab degradation (1 day of incubation) and in batch adsorption experiments (preliminary or screening experiments) conducted with fenoxaprop-P-ethyl (AE F046360) or its major soil metabolites - <u>RMS AT assessment</u>

Substance	Aerobic lab degradation experiments		Batch adsorption experiments (preliminary phase)		Reference
	NER (% AR)	HAT[(a)]	NER (% AR)	HAT[(a)]	
Fenoxaprop-P-ethyl (AE F046360)	2.3 - 17.3[(b)]	24	-	-	Several studies[(c)]
	-	-	Up to 22.9[(d)]	-	Goerlitz & Rutz, 1988
	-	-	1.5 - 7.3	6	Reynolds, 1992
Fenoxaprop-P-acid (AE F088406)	-	-	9.3 - 32.7	24	Rupprecht, 1999
	-	-	26.1 - 39.5	48	Voelkel, 2008a
Chlorobenzoxazolone (AE F054014)	-	-	7.1 - 27.6	22	Allan, 2004
	-	-	3.3 - 46.3	48	Voelkel, 2008b
HOPP-acid (AE F096918)	70.3 - 83.3	24	-	-	Fitzmaurice, 2010; Stroech & Junge, 2014

(a) Hours after treatment
(b) NER data from different labels (Shepherd, 2012, and Shepherd & Ripperger, 2012) averaged
(c) Stumpf & Dambach (1988), Buettner et al. (1992), Shepherd (2012), Shepherd & Ripperger (2012)
(d) Difference to 100 % mass balance (may also include degradation products other than fenoxaprop-P-acid (AE F088406))

Beside degradation, formation of NER mainly contributes to the low test item mass balances observed in all batch adsorption experiments with fenoxaprop-P-ethyl (AE F046360) and its major soil metabolites. It is noted that OECD guideline 106 explicitly excludes NER from the test item mass balance (see Eq. 10 in OECD guideline 106). Quite often, study authors ignore this and fully include

NER in their mass balance, thus only accounting for degradation and other losses but not for NER. However, this approach is not in line with OECD guideline 106 and finally leads to a systematic overestimation of adsorption coefficients obtained. Following recommendations of OECD guideline 106, a test item mass balance (according to Eq. 10) below 90 % requires the *direct* method to be used also for the advanced Freundlich isotherms experiments. The *direct* method ensures that NER can be adequately excluded from the calculation of the adsorption coefficients and degradation is accounted for in both, the liquid phase as well as in the soil extract. This recommendation has not been followed in any of the adsorption studies in this dossier. Therefore, the RMS AT considers **Freundlich sorption isotherms** (K_{foc} and $1/n$) obtained by the *indirect* method for fenoxaprop-P-ethyl (AE F046360) and its major soil metabolites in general **non-reliable** as they are systematically overestimated.

It may be recalled that NER are already accounted for in calculating degradation rates in soil. From a conceptual point of view this implies that NER also have to be accounted for in calculation of equilibrium sorption coefficients in a batch experiment. Otherwise, exposure models systematically underestimate the substance present in the soil pore water, thus underestimating the leaching potential of this substance. It is scientifically not defendable to assume that substances 'hidden' within NER substantially contribute to the equilibrium sorption in a batch experiment. The RMS AT is aware that NER in a typical 24-hrs batch sorption experiments may be negligible in many cases as they are usually low. However, in case of fenoxaprop-P-ethyl (AE F046360) and its major soil metabolites, NER in the sorption batch studies are significant and must not be ignored. As amounts of NER depend on the extraction efficiency, extraction methods used in the soil degradation and in the batch sorption study should be ideally the same (or at least comparable).

In contrast to the 'advanced Freundlich isotherm experiments' (applying the *indirect* method and ignoring formation of NER), the RMS AT considers the so called 'preliminary' or 'screening' experiments (applying the *direct* method, including quantification of NER) suitable for deriving robust adsorption coefficients. As these preliminary experiments where performed at one concentration only (usually the highest one) no Freundlich isotherms can be deduced. Instead a linear sorption is assumed ($1/n = 1$).

In case of this study (Reynolds, 1992) no advanced Freundlich isotherm experiment on fenoxaprop-P-ethyl (AE F046360) was performed at all. However, the study authors did not adequately account for NER in the calculation of the adsorption coefficient, which is not considered acceptable as already mentioned above. Therefore, the RMS AT re-calculated K_{oc} values on basis of extractable amounts in soil only (as recommended by OECD guideline 106). The correction factor needed to account for non-extractable residues can be directly obtained from the amount of extractable and non-extractable radioactivity measured in the adsorption experiment (see tables below).

Table B.8.1.3.1.1-10 Correction factors to account for non-extractable residues in the calculation of the sorption coefficient (adsorption phase) - RMS AT assessment

Soil	Extractables (% AR)[(a)]	Non-extractables (% AR)[(a)]	Correction factor[(b)]
Clay	50.2	1.5	0.97
Silty clay loam	66.4	4.0	0.94
Sandy loam	69.4	7.3	0.90
Clay loam	55.0	6.8	0.89

(a) Raw data from the report (also refer to Table B.8.1.3.1.1-5)
(b) Correction factor = extractables / (extractables + non-extractables)

Table B.8.1.3.1.1-11 Corrected adsorption coefficients (K_{oc}) of fenoxaprop-P-ethyl (AE F046360) on basis of extractable amounts in soil - RMS AT assessment

Substance	Soil	Conc. in solution (mg/L)[(a)]	Total conc. in soil (mg/kg)[(a)]	Extractable conc. in soil (mg/kg)[(b)]	K_d (L/kg)	OC %	K_{oc} (L/kg)
Fenoxaprop-P-ethyl (AE F046360)	Clay	0.0533	0.6699	0.6505	12.2	0.23	**5306**
	Silty clay loam	0.0013	0.2678	0.2525	194	0.81	**23982**
	Sandy loam	0.0007	0.2933	0.2654	379	2.55	**14870**
	Clay loam	0.0011	0.1890	0.1682	153	2.65	**5770**

(a) Raw data from the report (used by the study author to calculate the sorption coefficient)
(b) Corrected by the RMS AT to account for non-extractable residues

B.8.1.3.1.2. Adsorption and desorption of metabolites, breakdown and reaction products

Studies submitted for first Annex I inclusion:

- **Goerlitz & Rutz (1988)**, investigating adsorption/desorption of fenoxaprop-P-ethyl (AE F046360) and fenoxaprop-P-acid (AE F088406) in four soils
- **Reynolds (1992)**, investigating adsorption/desorption of fenoxaprop-P-ethyl (AE F046360), fenoxaprop-P-acid (AE F088406) and chlorobenzoxazolone (AE F054014) in four soils
- **Rupprecht (1999)**, investigating adsorption/desorption of fenoxaprop-P-acid (AE F088406) in six soils and one sediment
- **Allan (2004)**, investigating adsorption/desorption of chlorobenzoxazolone (AE F054014) in nine soils and one sediment

New studies submitted by the Fenoxaprop-P-ethyl Task Force:

- **Voelkel (2008a)**, investigating adsorption/desorption of fenoxaprop-P-acid (AE F088406) in three soils
- **Voelkel (2008b)**, investigating adsorption/desorption of chlorobenzoxazolone (AE F054014) in three soils
- **Mills (2010)**, investigating adsorption/desorption of HOPP-acid (AE F096918) in three soils

Goerlitz & Rutz (1988) and Reynolds (1992), including results on fenoxaprop-P-acid (AE F088406) and chlorobenzoxazolone (AE F054014), were already discussed in Section B.8.1.3.1.1 (Adsorption of the active substance).

Reference:	**The adsorption/desorption of [^{14}C]-AE F088406 on six soils and one sediment**
Author(s), year:	Rupprecht, J.K. (1999)
Report/Doc. Number:	C000921, M-181475-01-1
Guideline(s):	OECD 106 (1997), US EPA § 163-1 (1982)
GLP:	Yes
Validity:	Partly (refer to comment section)
Status:	**Previously submitted**

[The following study report is a copy/paste of the original text in the DAR for Annex I inclusion slightly amended in order to meet editorial settings and to improve readability]

Material and methods:

The objective of this study was to investigate the adsorption/desorption behaviour of [UL-^{14}C-chlorophenyl]-fenoxaprop-P-acid (AE F088406) in a batch equilibrium study. Preliminary investigations showed that the test substance is soluble and stable in 0.01 M $CaCl_2$ in treatment solutions up to 5 µg/ml. fenoxaprop-P-acid (AE F088406) did not adhere to the test vessels, and there was not a significant change in soil solution pH upon treatment. It was further determined that a soil/solution ratio of 1:3 is appropriate. Analysis of the solution and soil extracts showed good stability in the neutral and slightly alkaline soils, but up to 25 % degradation over 24 hours in the acidic soils. Five soils were chosen for the Freundlich isotherm determinations, based on their soil characteristics and adequate stability of the test substance in that soil. For the adsorption period and the two desorption steps 24 hours each were found to be appropriate, in order to achieve equilibrium but also minimise degradation, even in one of the acidic soils.

The nominal test concentrations were 0.01, 0.1, 1.0 and 5.0 µg/mL. Samples were kept at 25 °C in the dark.

The quantity of radioactivity in extracts and solutions was determined by LSC. Radioactivity in solid residue was determined by combustion. Radiochemical purity and samples analysis was determined using TLC and reverse phase HPLC with flow-through radiochemical detection. A gradient elution program was applied. Solution concentrations were expressed in µg/g.

At a specific activity of 35.964 dpm/µg (16.2 µCi/mg) the LSC limit of quantitation is equivalent to 0.83 ng and the HPLC/TLC limit is 8.3 ng. No corrections of the concentrations, calculated from the total radioactivity, were performed since the stability of fenoxaprop-P-acid (AE F088406) was adequate in all five test soils.

Table B.8.1.3.1.2-1 Soil characteristics

Soil(BBA classification)	% Sand	% Silt	% Clay	% OM	% OC	*p*H ($CaCl_2$)	CEC (meq/100 g)	% WHC at 1/3 bar
Sandy loam, EFS-6, IL, USA	58.5	25.0	16.4	4.54	2.64	7.3	14.98	19.66
Sand, EFS-8, NC USA	88.8	4.4	6.8	0.92	0.53	4.7	1.66	4.47
Silty clay loam, EFS-16, IA, USA	10.4	60.8	28.8	2.88	1.67	7.1	15.64	28.02
Sand, EFS-24, England	92.2	1.8	6.0	1.40	0.81	6.4	3.67	4.45
Loam, EFS-29, England[(a)]	42.9	34.3	22.8	2.46	1.43	7.5	9.67	25.03
Clay loam, EFS-38, France	29.8	38.0	32.2	3.43	1.99	7.4	7.99	24.53
Sandy loam sediment, EFS-54, NC USA[(b)]	48.4	31.7	19.8	3.56	2.07	4.5	10.61	26.71

(a) Not selected for Freundlich isotherm as soil properties were not significantly different from other soils
(b) Not selected for Freundlich isotherm due to instability of the test substance in the soil

Findings:

Mass balances ranged from 85.1 % to 113.3 %.

It was stated that the sorption behaviour appeared to be related to soil *p*H in the acidic North Carolina sand (EFS-8, Kf_{oc} = 568). This was supported from results of the other low *p*H soil, North Carolina sediment (EFS-54), examined during the preliminary K_d experiments conducted with 5.0 µg/mL solution (soil/solution ratio 1:2). In this preliminary experiment K_{oc} values of 500 and 1117 were determined for soils EFS-8 and EFS-54, respectively.

A summary of the results from the Freundlich isotherms is given in the table below:

Table B.8.1.3.1.2-2 Adsorption/desorption characteristics for ^{14}C-fenoxaprop-P-acid (AE F088406)

Soil	% OC	*p*H	Isotherm	K_f (L/kg)	K_{foc} (L/kg)	1/*n* (-)	r^2
Sandy loam, EFS-6, IL USA	2.64	7.3	Adsorption	8.76	332	0.733	0.999
			Desorption step 1	11.97	454	0.730	0.999
			Desorption step 2	16.15	612	0.760	0.999
Sand, EFS-8, NC USA	0.53	4.7	Adsorption	3.01	568	0.782	1.000
			Desorption step 1	3.86	729	0.755	1.000
			Desorption step 2	5.37	1013	0.770	0.999
Silty clay loam, EFS-16, IA USA	1.67	7.1	Adsorption	3.05	182	0.823	1.000
			Desorption step 1	3.71	222	0.690	0.972
			Desorption step 2	5.75	344	0.744	0.997
Sand, EFS-24, England	0.81	6.4	Adsorption	1.17	145	0.880	1.000
			Desorption step 1	1.98	244	0.863	0.997
			Desorption step 2	3.75	463	0.860	0.989
Clay loam, EFS-38, France	1.99	7.4	Adsorption	3.67	184	0.719	0.987
			Desorption step 1	5.43	273	0.723	0.969
			Desorption step 2	7.00	352	0.713	0.977

Conclusions:

For fenoxaprop-P-acid (AE F088406) K_{foc} values between 145 and 332 L/kg were derived in acidic to slightly alkaline soils indicating high to medium mobility. The substance appears to be less mobile in acidic soils. In one acidic soil (*p*H 4.7) a K_{foc} of 568 L/kg was calculated. Considering the K_{foc} values derived from the other four soils, this *p*H dependence is not that clear (*p*H 6.4 – K_{foc} 145 L/kg; *p*H 7.1– K_{foc} 182 L/kg; *p*H 7.4 – K_{foc} 184 L/kg; *p*H 7.3 – K_{foc} 332 L/kg).

Comments RMS AT:

- The study broadly follow OECD guideline 106 with some deviations:
    - The range of concentration for determination of Freundlich adsorption isotherms does not cover 3 orders of magnitude (0.01 - 5.0 mg/L only) with only 4 instead of 5 different concentrations investigated. However, Freundlich isotherms obtained in this study are not considered reliable by the RMS AT for other reasons (see comment below).
    - The soils investigated do not always fulfil soil selection criteria in relation to *p*H, organic carbon content, clay content and soil texture as given in OECD guideline 106

  On overall the RMS AT is of the opinion that these deviations are minor and do on overall not invalidate the study.

- The test item mass balance in the preliminary adsorption experiments calculated on basis of Eq. 10 in the OECD guideline 106 (accounting for degradation and NER) was only 57.1 to 84.5 % for all 7 soils (see tables below). In case of a test item mass balance below 90 % OECD guideline 106 recommends applying the *direct* method for the advanced Freundlich isotherm experiments as well. As this is not the case (instead the *indirect* method was used), obtained **Freundlich isotherms are considered non-reliable** (also refer to more general RMS AT comments in Reynolds, 1992).

  In contrast to the advanced test (Freundlich isotherm experiment), the RMS AT considers results from the preliminary experiment (24 hrs adsorption, 5 mg/l test concentration) adequate to calculate robust distribution coefficients (K_d/K_{oc}) on basis of the test item recovered (liquid phase and extractable amounts in soil). As the preliminary experiment was performed only at the highest concentration no Freundlich isotherms can be deduced. Instead a linear sorption is assumed ($1/n = 1$). The RMS AT calculation is given in the tables below.

  As this calculation is based on the test item recovered from both phases (liquid and extract), it is also justified to include the acidic soils which have been excluded by the study authors from the advanced test (*indirect* method) owing to distinct instability of the test item observed there.

Table B.8.1.3.1.2-3 Recovery of radioactivity (% AR) in the preliminary experiment (24 hrs adsorption, 5 mg/l test concentration) and stability (%) of the test item - <u>raw data from the study report</u>

Soil	pH ($CaCl_2$)	---------- Recovery of total radioactivity (%) ----------					Stability of fenoxaprop-P-acid (AE F088406) (%)	
		Aqueous phase	Soil extract (extr. 1)	Soil extract (extr. 2)	Soil residues	Total	Aqueous phase	Soil extracts
EFS-6	7.3	13.8	44.1	1.7	32.7	92.3	97	100
EFS-8	4.7	35.6	40.7	3.4	11.5	91.2	95	89
EFS-16	7.1	31.7	38.7	1.7	18.6	90.8	99	100
EFS-24	6.4	52.4	29.7	1.6	9.3	93.0	100	100
EFS-29	75	23.6	44.5	1.6	21.5	91.1	100	100
EFS-38	7.4	27.9	41.9	1.8	20.2	91.8	99	100
EFS-54	4.5	5.5	57.0	13.7	16.9	93.1	87	74

Table B.8.1.3.1.2-4 Mass balance of fenoxaprop-P-acid (AE F088406) in the preliminary experiment (24 hrs adsorption experiment, 5 mg/l test concentration) on basis of <u>extractable amounts</u> in soil - <u>RMS AT assessment</u> based on raw data

Soil	Test substance applied (µg)	Test substance in aqueous phase[(a)] (µg)	Test substance in soil extract (extr. 1 & 2)[(a)] (µg)	Total test substance recovered (µg)	Mass balance (%)
EFS-6	101	13.5	46.3	59.8	59.2
EFS-8	101	34.2	39.6	73.8	73.1
EFS-16	101	31.7	40.8	72.5	71.8
EFS-24	101	52.9	31.6	84.5	83.7

EFS-29	101	23.8	46.6	70.4	69.7
EFS-38	101	27.9	44.1	72.0	71.3
EFS-54	101	4.8	52.8	57.7	57.1

(a) Considering stability of the test compound

Table B.8.1.3.1.2-5 Distribution coefficients (K_{oc}) of fenoxaprop-P-acid (AE F088406) in the preliminary experiment (24 hrs adsorption, 5 mg/l test concentration) on basis of extractable amounts in soil - RMS AT assessment based on raw data

Soil	Aqueous solution (ml)	Soil mass (g)	Test substance in aqueous phase (µg/ml)[(a)]	Test substance in soil extract (extr. 1 & 2) (µg/g)[(a)]	K_d (ml/g)	OC (%)	K_{oc} (ml/g)
EFS-6	20.1	10.0	0.67	4.63	6.91	2.64	**262**
EFS-8	20.0	10.0	1.71	3.96	2.32	0.53	**438**
EFS-16	20.1	10.0	1.58	4.08	2.58	1.67	**154**
EFS-24	20.0	10.0	2.64	3.16	1.20	0.81	**148**
EFS-29	20.1	10.0	1.18	4.66	3.95	1.43	**276**
EFS-38	20.1	10.1	1.39	4.36	3.14	1.99	**158**
EFS-54	20.1	10.0	0.24	5.25	21.9	2.07	**1058**

(a) Considering stability of the test compound

- Fenoxaprop-P-acid (AE F088406) appears to be less stable under more acidic soil conditions.

Reference:	**The adsorption/desorption of [^{14}C]-AE F054014 on nine soils and one sediment**
Author(s), year:	Allan, J.G. (2004)
Report/Doc. Number:	B004850, M-181470-02-1
Guideline(s):	OECD 106 (1981), US EPA § 163-1 (1982)
GLP:	Yes
Validity:	Yes
Status:	**Previously submitted**

[The following study report is a copy/paste of the original text in the DAR for Annex I inclusion slightly amended in order to meet editorial settings and to improve readability]

Material and methods:

The objective of this study was to investigate the adsorption/desorption behaviour of [UL-^{14}C-chlorophenyl]-chlorobenzoxazolone (AE F054014), a metabolite of fenoxaprop-P-ethyl (AE F046360), in a batch equilibrium study. Preliminary studies showed that the test substance is soluble and stable in 0.01 M $CaCl_2$ in treatment solutions up to 5 µg/ml. Chlorobenzoxazolone (AE F054014) did not adhere to the test vessels. It was further determined that a soil/solution ratio of 1:5 is appropriate. Analysis of the solution and soil extracts showed sufficient stability in four acidic soils and the acidic sediment but poor stability in the remaining five neutral to alkaline soils over the timeframe of the experiment.

Freundlich isotherms were conducted in the four acidic soils and one acidic sediment where stability had been confirmed for an adsorption period of 10 hours followed by two desorption steps of 5 hours each, which were shown to be adequate for the achievement of equilibrium with no degradation of the test substance. The nominal test concentrations were 0.01, 0.1, 1.0 and 5.0 µg/mL. Samples were kept at 25 °C in the dark.

The quantity of radioactivity in extracts and solutions was determined by LSC. Radioactivity in solid residue was determined by combustion. Radiochemical purity and samples analysis was determined using TLC and reverse phase HPLC with flow-through radiochemical detection and, when necessary, fraction collection. A gradient elution program was applied. Solution concentrations were expressed in µg/g.

The LOQ for TLC and HPLC was determined using the highest specific activity of 127.9 µCi/mg to be in the range of 0.35 to 1.1 ng.

No corrections of the concentrations, calculated from the total radioactivity, were performed since the stability of chlorobenzoxazolone (AE F054014) was adequate in all five test soils.

Table B.8.1.3.1.2-6 Soil characteristics

Soil (USDA classification)	% Sand	% Silt	% Clay	% OM	% OC	*p*H ($CaCl_2$)	CEC (meq /100 g)	% WHC at 1/3 bar
Sandy loam, EFS-6, IL, USA	58.6	25.0	16.4	4.54	2.54	7.3	14.96	19.66
Silty clay loam, EFS-16, IA, USA	10.4	60.8	28.8	2.88	1.67	7.1	15.64	28.02
Sand, EFS-24, UK	92.2	1.8	6.0	1.4	0.81	6.4	3.67	4.45
Loam, EFS-29, UK	42.9	34.3	22.8	2.46	1.43	7.5	9.67	25.03
Clay loam, EFS-38, France	29.8	38.0	32.2	3.43	1.99	7.4	7.99	24.53
Sand, EFS-8, NC, USA[(a)]	88.8	4.4	6.8	0.92	0.53	4.7	1.66	4.47
Clay, EFS-25, France[(a)]	22.1	38.0	40.0	3.16	1.84	5.4	9.98	30.34
Loam, EFS-35, Idaho[(a)]	35.3	45.4	19.2	2.62	1.52	5.4	12.13	19.4
Loam, EFS-54, NC, USA[(a)]	48.4	31.7	19.8	3.56	2.07	4.5	10.61	26.71
Loamy sand, EFS-66, Germany[(a)]	79.3	11.2	9.4	3.35	1.95	6.0	7.9	29.4

(a) Acidic soils and sediment used for determination of Freundlich isotherms

Findings:

Mass balances were quantitative, ranging from 88.9 % to 104.7 %.

A summary of the results from the Freundlich isotherms is given in the table below:

Table B.8.1.3.1.2-7 Adsorption/desorption characteristics for ^{14}C-chlorobenzoxazolone (AE F054014)

Soil	% OC	*p*H	Isotherm	K_f (L/kg)	K_{foc} (L/kg)	1/*n*	r^2
Sand, EFS-8, NC, USA	0.53	4.7	Adsorption	2.85	537	0.765	0.999
			Desorption step 1	5.41	1022	0.814	0.999
			Desorption step 2	9.47	1786	0.862	1.000
Clay, EFS-25, France	1.84	5.4	Adsorption	5.45	296	0.826	0.999
			Desorption step 1	11.58	629	0.834	0.997
			Desorption step 2	28.14	1529	0.882	0.996
Loam, EFS-35, Idaho	1.52	5.4	Adsorption	6.51	429	0.816	0.998
			Desorption step 1	11.28	742	0.826	0.997
			Desorption step 2	19.70	1296	0.852	0.996
Loam, EFS-54, NC, USA	2.07	4.5	Adsorption	6.47	312	0.859	1.000
			Desorption step 1	8.80	425	0.852	1.000
			Desorption step 2	11.27	545	0.850	1.000
Loamy sand, EFS-66, Germany	1.95	6.0	Adsorption	7.02	360	0.826	0.999
			Desorption step 1	16.85	864	0.842	0.996
			Desorption step 2	51.70	2651	0.897	0.995

Desorption K_f values increased with each step indicating some hysteresis.

No predictions of the sorption behaviour in neutral or slightly alkaline soils can be done since chlorobenzoxazolone (AE F054014) is not stable under these conditions.

Conclusions:

^{14}C-chlorobenzoxazolone (AE F054014), a metabolite of fenoxaprop-P-ethyl (AE F046360), is not stable in neutral or alkaline soil. In acidic soil K_{foc} values between 296 and 537 L/kg were derived, indicating medium mobility in soil.

Comments RMS AT:

- The study broadly follow OECD guideline 106 with some deviations:

- The range of concentration for determination of Freundlich adsorption isotherms does not cover 3 orders of magnitude (0.01 - 5.0 mg/L only) with only 4 instead of 5 different concentrations investigated. However, Freundlich isotherms obtained in this study are not considered reliable by the RMS AT for other reasons (see comment below).
- The soils investigated do not always fulfil soil selection criteria related to *p*H, organic carbon content, clay content and soil texture as given in OECD guideline 106

On overall the RMS AT is of the opinion that these deviations are minor and do on overall not invalidate the study.

- The test item mass balance calculated on basis of Eq. 10 in the OECD guideline 106 in the preliminary adsorption experiments (accounting for degradation and NER) was only 70.6 to 89.3 % for 5 of the 10 soils (no complete mass balance is available for the other 5 soils, see tables below). In case of a test item mass balance below 90 % OECD guideline 106 recommends applying the *direct* method for the advanced Freundlich isotheres experiment as well. As this is not the case (instead the *indirect* method was applied), obtained **Freundlich isotherms are considered non-reliable** (also refer to more general RMS AT comments in Reynolds, 1992).

  In contrast to the advanced test (Freundlich isotherm experiment), the RMS AT considers results from the preliminary experiment (22 hrs adsorption, 5 mg/l test concentration) adequate to calculate robust distribution coefficients (K_d/K_{oc}) on basis of the test item recovered (liquid phase and extractable amounts in soil). This additional calculation is given in the tables below. Notice that a complete mass balance (including stability measurements in the liquid phase and in the extract) is only available for 5 of the 10 soils investigated (see tables below). Thus, reliable distribution coefficients could only be calculated for these 5 soils.

Table B.8.1.3.1.2-8 Recovery of radioactivity (% AR) in the preliminary experiment (22 hrs adsorption, 5 mg/l test concentration) and stability (%) of the test item - raw data from the study report (all soils)

Soil	*p*H ($CaCl_2$)	---------- Recovery of total radioactivity ---------- (%)				Stability of chlorobenzoxazolone (AE F054014) (%)	
		Aqueous phase	Soil extract	Soil residues	Total	Aqueous phase	Soil extract
EFS-6	7.3	1.5	7.2	na	na	na	na
EFS-16	7.1	3.4	24.0	na	na	na	na
EFS-29	7.5	3.8	27.3	na	na	na	na
EFS-38	7.4	3.2	38.2	na	na	na	na
EFS-24	6.4	34.6	30.3	27.6	92.6	na	na
EFS-8	4.7	60.1	29.2	7.1	96.4	100.0	100.0
EFS-54	4.5	35.0	46.8	7.8	89.9	97.8	100.0
EFS-25	5.4	33.7	39.4	19.2	92.4	94.2	98.6
EFS-35	5.4	37.2	48.6	15.4	101.2	98.1	100.0
EFS-66	6.0	32.8	42.1	23.4	98.3	98.0	100.0

na denotes not analysed

Table B.8.1.3.1.2-9 Mass balance of chlorobenzoxazolone (AE F054014) in the preliminary experiment (22 hrs adsorption, 5 mg/l test concentration) on basis of extractable amounts in soil - RMS AT assessment based on raw data

Soil/sediment	Test substance applied (µg)	Test substance in aqueous phase[(a)] (µg)	Test substance in soil extract[(a)] (µg)	Total test substance recovered (µg)	Mass balance (%)
EFS-8	205	123	59.9	183	89.3
EFS-54	205	70.2	95.9	166	81.0
EFS-25	205	65.1	79.6	145	70.6
EFS-35	205	74.8	99.6	174	85.1
EFS-66	205	65.9	86.3	152	74.2

(a) Considering stability of the test compound

Table B.8.1.3.1.2-10 Distribution coefficients (K_{oc}) of chlorobenzoxazolone (AE F054014) in the preliminary experiment (22 hrs adsorption, 5 mg/l test concentration) on basis of extractable amounts in soil - RMS AT assessment based on raw data

Soil/sediment	Aqueous solution (ml)	Soil mass (g)	Test substance in aqueous phase[(a)] (µg/ml)	Test substance in soil extract[(a)] (µg/g)	K_d (ml/g)	OC (%)	K_{oc} (ml/g)
EFS-8	50	10	2.46	5.99	2.43	0.53	**458**
EFS-54	50	10	1.40	9.59	6.84	2.07	**330**
EFS-25	50	10	1.30	7.96	6.12	1.84	**333**
EFS-35	50	10	1.50	9.96	6.66	1.52	**438**
EFS-66	50	10	1.32	8.63	6.55	1.95	**336**

(a) Considering stability of the test compound

- Similar to observations made in Voelkel (2008b) chlorobenzoxazolone (AE F054014) appears to be much less stable under more alkaline soil conditions.

Reference:	**^{14}C-Fenoxaprop-P - Adsorption/desorption on soil**
Author(s), year:	Voelkel, W. (2008a)
Report/Doc. Number:	251 FPE, M-548178-01-1
Guideline(s):	OECD 106 (2000)
GLP:	Yes
Validity:	Partly (refer to comment section)
Status:	**New submission**

Executive Summary:

The adsorption/desorption characteristics of [UL-phenoxy-^{14}C]-fenoxaprop-P-acid (AE F088406) were determined by batch equilibrium tests for three EU soils at a concentration range covering two orders of magnitude.

In the definitive test the overall mean values of recoveries were found to range from 96 to 100 % AR for all soils.

Values for the Freundlich adsorption coefficients (K_f) in soils ranged from 1.36 to 5.39 mL/g with corresponding values referenced to organic carbon (K_{foc}) to range from 124 to 228 mL/g. Values for the Freundlich coefficient of adsorption 1/n ranged from 0.86 to 0.99.

Material and methods:

Test Material [UL-phenoxy-^{14}C]-fenoxaprop-P-acid (AE F088406)
Specific radioactivity: 5.51 MBq/mg (149.0 µCi/mg)
Radiochemical purity: 98.6 % (HPLC)
Sample ID: 2527GAR005-1

Soils
Sorption tests were performed with three soils covering a range of *p*H, organic carbon content and texture. The characteristics of soils originating from France and Germany are summarised in the table below.

Table B.8.1.3.1.2-11 Characteristics of test soils

Soil	Attenschwiller	Speyer 6S	Speyer 2.2
Geographic location (City/State/Country)	Haut-Rhin, France	Rhineland-Palatinate, Germany	Rhineland-Palatinate, Germany
GPS coordinates	N 47°34'/ E 07°27'	N 49°12'/ E 08°03'	N 49°19'/ E 08°20'
Soil preparation		Air-dried and sieved to 2 mm	

Textural class (USDA)	Silt loam	Clay	Loamy sand
Sand (%)	23.0	22.0	79.1
Silt (%)	54.0	36.1	13.5
Clay (%)	23.0	42.0	7.9
*p*H (0.01 M $CaCl_2$)	7.4	6.9	5.6
Org. matter[(a)] (%)	1.90	3.28	4.07
Org. carbon (%)	1.10	1.90	2.36
CEC (meq / 100 g)	10.5	18.0	11.0

(a) % Organic matter = % organic carbon × 1.724
CEC = Cation exchange capacity

Experimental conditions
For the definitive test samples of 10 g dry weight of soil were weighed each into centrifuge tubes to which 9 mL of 0.01 M aqueous calcium chloride solution was added. Following pre-equilibration, 1 mL of a test item solution (prepared in 0.01 M aqueous calcium chloride) was added. Within pre-tests controls containing no soil were prepared for determination of stability of the test item in calcium chloride solution and adsorption tests to the walls of the test vessels.

Initial nominal concentrations of the ^{14}C-test substance in the aqueous phase were 0.939, 0.380, 0.094, 0.037 and 0.009 mg/L thus covering two orders of magnitude.

The maximum amount of organic co-solvent present in samples during the tests was 0.1 % acetone (by vol.) for the highest test concentration. Each determination was performed in duplicate by shaking with an overhead shaker in the dark at 20 ± 2 °C.

Preliminary tests included the determination of the adequate soil-to-solution ratio (1/25, 1/5, 1/1) and the corresponding adequate times needed to reach adsorption equilibrium (total shaking time of 48 hours) for all soils accompanied by the test for stability of the test item in the presence of soil.

For the definitive test an adsorption step of 24 hours at a soil-to-solution-ratio of 1/1 was performed for all soils followed by one desorption step for 24 hours.

For work-up the aqueous supernatant was separated from soil by decantation and centrifugation. Radioactivity in water and soil extracts was determined by liquid scintillation counting (LSC). Non-extractable radioactivity in soil was determined by combustion followed by LSC to establish a full material balance.

Finally, the adsorption and desorption parameters were calculated using the Freundlich adsorption and desorption isotherm.

Analytical procedures
In the definite test, the supernatant was removed and the soil was extracted three times using acetonitrile/water (4:1, by vol.). Radioactivity in the aqueous phase and soil extracts were determined by liquid scintillation counting (LSC). The extracts resulting from the same tube were combined and concentrated. Supernatants and concentrated extracts were analysed by reversed phase radio-HPLC analysis using ^{14}C-flow-through detection techniques. The determination of non-extractable residues (NER) was performed by combustion/LSC of aliquots of the air-dried extracted soil. The purity and stability of the test item was investigated by radio-HPLC and the identity of the test item was confirmed by co-chromatography with reference items.

Results and discussion:

Mass balance and results of preliminary tests
Pre-tests on adsorption to the walls of test vessels by shaking an aqueous solution of the test substance in the absence of soil showed no adsorption. The tests also confirmed the solubility and stability of the test item in aqueous calcium chloride solution. The test item was found to be degraded in the presence of soil to form non-extractable residues thus taken into account within the evaluation of results.

The overall mass balance for individual samples was established for all soils in the preliminary test and ranged from 96.0 to 95.5 % AR.

Table B.8.1.3.1.2-12 Preliminary phase: Total recovery of [UL-phenoxy-^{14}C]-fenoxaprop-P-acid

(AE F088406) in samples following adsorption and desorption

Soil	Ratio	Rep. No.	Mass applied [µg]	Ads_{aq} (%)	Des_{aq} (%)	$Ads_{extract}$ (%)	$Ads_{residue}$ (%)	Recovery (%)
		1	9.1	32.0	0.7	24.1	39.6	96.4
Attenschwiller	1/1	2	9.1	32.0	0.8	23.4	39.3	95.6
		mean	**9.1**	**32.0**	**0.8**	**23.8**	**39.5**	**96.0**
		1	9.1	31.8	8.4	35.7	24.1	100.0
Speyer 6S	1/1	2	9.1	33.2	8.9	28.8	28.1	99.0
		mean	**9.1**	**32.5**	**8.6**	**32.3**	**26.1**	**99.5**
		1	9.1	12.3	4.4	48.4	29.8	94.9
Speyer 2.2	1/1	2	9.1	12.7	3.9	50.5	32.4	99.5
		mean	**9.1**	**12.5**	**4.1**	**49.4**	**31.1**	**97.2**

Ads_{aq} % of the amount applied remaining in the aqueous phase after the adsorption step
Des_{aq} % of the amount applied remaining in the aqueous phase after the desorption step
$Ads_{extract}$ % of the amount applied extracted by acetonitrile/water after adsorption
$Ads_{residue}$ % of the amount applied remaining non-extractable in soil

Transformation of test substance
The test item showed limited stability in some supernatants and soil extracts throughout the 24-hour agitation period of the definite test. Anyway, this was taken into account by correction factors upon calculation of sorption values.

Findings
The definitive test was performed at a soil-to-solution ratio of 1/1 for all soils. An adsorption time of 24 hours was chosen for the definitive test followed by a desorption step.

Within definitive tests, the portion of ^{14}C-fenoxaprop-P-acid (AE F088406) adsorbed to soil after 24 hours ranged from 54.9 to 68.8 % AR for soil Attenschwiller, 71.2 to 75.9 % AR for soil Speyer 6S and 79.2 to 82.6 % AR for soil Speyer 2.2.

The sorption behaviour of ^{14}C-fenoxaprop-P-acid (AE F088406) could be described within a range of test concentrations of 0.009 mg/L to 0.093 mg/L by the Freundlich equation for all soils. The corresponding correlation coefficients of adsorption isotherms ranged from 0.9956 to 0.9995 indicating an excellent fit to the measured data.

The adsorption constants K_f from Freundlich isotherms ranged from 1.362 to 5.385 mL/g. Freundlich adsorption coefficients normalised for organic carbon content of soil (K_{foc}) ranged from 124 mL/g (soil Attenschwiller) to 228 mL/g in maximum (soil Speyer 2.2). The corresponding Freundlich exponents 1/*n* ranged from 0.86 to 0.99.

Table B.8.1.3.1.2-13 Definitive test: Concentration of [UL-phenoxy-^{14}C]-fenoxaprop-P-acid (AE F088406) in aqueous and solid phase following 24 hours of adsorption and 24 hours of desorption (mean values of two replicates)

Nominal concentration (mg/L)	Soil (mg/kg)	Solution (mg/L)	Adsorbed (%)
	Attenschwiller		
0.093	0.515	0.348	54.9
0.380	0.228	0.118	60.1
0.094	0.062	0.024	65.3
0.037	0.024	0.010	64.9
0.009	0.006	0.002	68.8
	Speyer 6S		
0.093	0.669	0.245	71.2
0.380	0.279	0.090	73.5
0.094	0.070	0.021	74.6
0.037	0.028	0.008	75.9
0.009	0.007	0.002	75.8
	Speyer 2.2		
0.093	0.744	0.158	79.2
0.380	0.312	0.051	82.3
0.094	0.078	0.012	82.6

Nominal concentration (mg/L)	Soil (mg/kg)	Solution (mg/L)	Adsorbed (%)
	Attenschwiller		
0.037	0.031	0.005	81.6
0.009	0.007	0.001	80.0

Table B.8.1.3.1.2-14 Adsorption constants of fenoxaprop-P-acid (AE F088406) in soil (soil-to-solution ratio 1/1 and an agitation time of 24 hrs)

Soil	Soil type	*p*H[(a)]	OC (%)	----------Adsorption ----------			
				K_f (mL/g)	1/*n*	R^2	K_{foc} (mL/g)
Attenschwiller	Silt loam	7.4	1.10	1.362	0.86	0.9983	124
Speyer 6S	Clay	6.9	1.90	2.673	0.95	0.9995	140
Speyer 2.2	Loamy sand	5.6	2.36	5.385	0.99	0.9956	228

(a) *p*H: 0.01 M calcium chloride solution
K_f: Freundlich coefficient of adsorption
K_{foc}: Organic carbon normalised Freundlich coefficient of adsorption
1/*n* : Slope of the Freundlich adsorption/desorption isotherm
R^2: Regression coefficient of Freundlich equation

Conclusions:

For metabolite fenoxaprop-P-acid (AE F088406) adsorption to soil was medium to range from 1.362 to 5.385 mL/g for Freundlich adsorption constants K_f. Freundlich adsorption coefficients normalised for organic carbon content of soil (K_{foc}) ranged from 124 mL/g (soil Attenschwiller) to 228 mL/g in maximum (soil Speyer 2.2). The corresponding Freundlich exponents 1/*n* ranged from 0.86 to 0.99.

Comments RMS AT:

- The study follow OECD guideline 106 with some deviations:
  - The soils investigated do not always fulfil all four soil selection criteria related to *p*H, organic carbon content, clay content and soil texture as given in OECD guideline 106.

  On overall the RMS AT is of the opinion that deviations observed are minor and do in principal not invalidate the study.

- The test item mass balance in the preliminary 48 hrs adsorption experiments calculated on basis of Eq. 10 in the OECD guideline 106 (accounting for NER only) was only 56.6 - 73.4 % for all 3 soils (see table below). In case of a test item mass balance below 90 % OECD guideline 106 recommends applying the *direct* method for the advanced Freundlich isotheres experiment as well. As this is not the case (instead the *indirect* method was applied), obtained **Freundlich isotherms are considered non-reliable** (also refer to more general RMS AT comments in Reynolds, 1992).

  In contrast to the advanced test (Freundlich isotherm experiment), the RMS AT considers results from the preliminary experiment (48 hrs adsorption, 0.91 mg/l test concentration) in principal adequate to calculate robust distribution coefficients (K_d/K_{oc}) on basis of the test item recovered (liquid phase and extractable amounts in soil). However, as no data on the stability of fenoxaprop-P-acid (AE F088406) in the liquid as well as in the soil extract are available for the 48 hrs adsorption phase (stability data are available only for 24 hrs), no reliable distribution coefficient can be calculated from the dataset available.

Table B.8.1.3.1.2-15 Recovery of radioactivity (% AR, mean of two replicates) in the preliminary experiment (48 hrs adsorption phase, 0.91 mg/l test concentration) and stability (%) of the test item following 24 hrs adsorption phase- raw data from the study report

Soil	*p*H ($CaCl_2$)	---------- Recovery of total radioactivity ---------- (%)	Stability of fenoxaprop-P-acid

							(AE F088406)[a] (%)	
		Aqueous phase (ads)	Aqueous phase (des)[b]	Soil extract (ads)	Soil residues	Total recovery	Aqueous phase	Soil extract
Attenschwiller	7.4	32.0	0.8	23.8	39.5	96.0	98.6	87.2
Speyer 6S	6.9	32.5	8.6	32.3	26.1	99.5	95.6	96.4
Speyer 2.2	5.6	12.5	4.1	49.4	31.1	97.2	90.8	95.2

(a) 24 hrs of adsorption (no data available for 48 hrs adsorption period)
(b) Considered to be part of the test compound sorbed to the soil following adsorption phase

Reference:	**^{14}C-6-Chloro-2,3-dihydrobenzoxazol-2-one (metabolite of fenoxaprop-P-ethyl) - adsorption/desorption on soil**
Author(s), year:	Voelkel, W. (2008b)
Report/Doc. Number:	250 FPE, M-548174-01-1
Guideline(s):	OECD 106 (2000)
GLP:	Yes
Validity:	Yes
Status:	**New submission**

Executive Summary:

The adsorption/desorption characteristics of [UL-^{14}C-chlorophenyl]-chlorobenzoxazolone (AE F054014) were determined by batch equilibrium tests for three sterilised EU soils at a concentration range covering two orders of magnitude.

In the definitive test the overall mean values of recoveries were found to range from 95.2 to 99.5 % AR for all soils. Degradation of the test substance was observed in contact with soil. Definitive adsorption tests were therefore performed at a single test concentration.

Values of adsorption coefficients (K_d) in soil based on single test concentrations ranged from 3.26 to 10.78 mL/g with corresponding values referenced to organic carbon (K_{oc}) to range from 296 to 457 mL/g.

Material and methods:

Test Material	[UL-phenyl-^{14}C]-6-chloro-2,3-dihydrobenzoxazol-2-one (chlorobenzoxazolone, AE F054014)
Specific radioactivity:	11.78 MBq/mg (318.3 µCi/mg)
Radiochemical purity:	100 % (HPLC)
Sample ID:	2525MFO007-6

Soils
Sorption tests were performed with three soils covering a range of *p*H, organic carbon content and texture.

Table B.8.1.3.1.2-16 Characteristics of test soils

Soil	Attenschwiller	Speyer 6S	Speyer 2.2
Geographic Location (City/State/Country)	Haut-Rhin, France	Rhineland-Palatinate, Germany	Rhineland-Palatinate, Germany
GPS coordinates	N 47°34’ / E 07°27’	N 49°12’ / E 08°03’	N 49°19’ / E 08°20’
Soil preparation		Air-dried and sieved to 2 mm	
Textural class (USDA)	Silt loam	Clay	Loamy sand
Sand (%)	23.0	22.0	79.1
Silt (%)	54.0	36.1	13.5
Clay (%)	23.0	42.0	7.9
*p*H (0.01 M $CaCl_2$)	7.4	6.9	5.6
Org. matter[a] (%)	1.90	3.28	4.07
Org. carbon (%)	1.10	1.90	2.36
CEC (meq/100 g)	10.5	18.0	11.0

(a) % Organic matter = % organic carbon × 1.724
CEC = Cation exchange capacity

Experimental conditions
For the definitive (i.e. reported as screening) test, samples of 1 g dry weight of sterilised (gamma irradiation) soil were weighed each into centrifuge tubes to which 22.5 mL of 0.01 M aqueous calcium chloride solution was added. Following pre-equilibration, 2.5 mL of a test item solution (prepared in 0.01 M aqueous calcium chloride) was added to result in a water-to-soil ratio of 1 to 25. Within pre-tests, controls containing no soil were prepared for determination of stability of the test item in calcium chloride solution and adsorption tests to the walls of the test vessels.

The initial nominal concentration of the ^{14}C-test substance in the aqueous phase was 0.20 mg/L.

The maximum amount of organic co-solvent present in samples during the tests was < 0.1 % acetonitrile (by vol.) for the test concentration. Each determination was performed in duplicate by shaking with an overhead shaker in the dark at 20 ± 2 °C.

For the definitive test on adsorption, duplicate tubes were sampled after 2, 4, 24 and 48 hours of shaking.

For work-up, the aqueous supernatant was separated from soil by decantation and centrifugation. Radioactivity in water and soil extracts was determined by liquid scintillation counting (LSC). Non-extractable radioactivity in soil after the 48-hour adsorption step was determined by combustion followed by LSC to establish a full material balance.

Finally, the distribution coefficients K_d and K_{oc} were determined for the test concentration. Consequently, no Freundlich adsorption isotherms were calculated since test concentrations did not include two orders of magnitude.

Analytical procedures
After sampling in the definite test, the supernatant was removed and the soil equilibrated for 48 hours was extracted three times using acetonitrile/water (4:1, by vol.). Radioactivity in the aqueous phase and soil extracts were determined by liquid scintillation counting (LSC). The extracts resulting from the same tube were combined and concentrated. The concentrated extracts and the aqueous phases were analysed by reversed phase radio-HPLC analysis using ^{14}C-flow-through detection techniques or by normal phase radio-TLC. The determination of non-extractable residues (NER) was performed by combustion/LSC of aliquots of the air-dried extracted soil. The purity and stability of the test item was investigated by radio-HPLC and the identity of the test item was confirmed by co-chromatography with reference items.

Results and discussion:

Mass balance and results of preliminary and screening tests
Pre-tests on adsorption to the walls of test vessels by shaking an aqueous solution of the test substance in the absence of soil showed no adsorption. The tests also confirmed the solubility and stability of the test item in aqueous calcium chloride solution.

The overall mass balance for individual samples was established for all soils in the definitive test and ranged from 91.5 to 101.9 % AR. Mean recoveries ranged from 95.2 to 99.5 % AR. The test item was found to degrade in the presence of soil with soils therefore sterilised for the screening test (definitive phase).

Table B.8.1.3.1.2-17 Preliminary test: Total recovery of [UL-phenyl-^{14}C]-chlorobenzoxazolone (AE F054014) in samples after adsorption phase of 48 hours

Soil	Ratio	Rep. No.	Mass applied [µg]	Ads_{aq} [%]	$Ads_{extract}$ [%]	$Ads_{residue}$ [%]	Recovery [%]
Attenschwiller	1/25	1	4.8	40.1	8.3	43.9	92.3
		2	4.8	42.1	9.3	48.8	100.2
		Mean	**4.8**	**41.1**	**8.8**	**46.3**	**96.2**
Speyer 6S	1/25	1	4.9	73.1	13.6	4.9	91.5
		2	4.9	74.3	18.2	6.4	98.9
		Mean	**4.9**	**73.7**	**15.9**	**5.6**	**95.2**

Soil	Ratio	Rep. No.	Mass applied [µg]	Ads_{aq} [%]	$Ads_{extract}$ [%]	$Ads_{residue}$ [%]	Recovery [%]
Speyer 2.2	1/25	1	4.9	69.6	29.0	3.3	101.9
		2	4.9	65.6	28.3	3.2	97.1
		Mean	**4.9**	**67.6**	**28.6**	**3.3**	**99.5**

Ads_{aq} % of the amount applied remaining in the aqueous phase after the adsorption step
$Ads_{extract}$ % of the amount applied extracted by acetonitrile/water after adsorption
$Ads_{residue}$ % of the amount applied remaining non-extractable in soil

Transformation of test substance
Analysis showed that the test item was stable in the aqueous phase of the control samples (i.e. in the absence of soil) after 48 hours of agitation in the definite test. No degradation was observed for soils Speyer 6S and Speyer 2.2. However, degradation of the ^{14}C-test item was observed in aqueous phases of soil Attenschwiller, possibly resulting in formation of non-extractable residues. Consequently, extractable portions of radioactivity from soil only were taken into account for calculation of values of K_d and K_{oc} for all soils.

Findings
For all soils the definitive test was performed at a soil-to-solution ratio of 1/25 and at adsorption times of 2, 4, 24 and 48 hours.

Adsorption equilibrium was reached in soil Speyer 2.2 after 48 hours to result in 32.4 % AR adsorbed to soil. For soils Attenschwiller and Speyer 6S, no adsorption equilibrium was found since the adsorbed test item continually increased from 11.9 % and 14.9 % after 2 hours to 58.9 % and 26.3 % AR after 48 hours, respectively.

The resulting K_d values after 24 hours were 3.26 mL/g, 6.59 mL/g and 10.78 mL/g for soils Attenschwiller, Speyer 6S and Speyer 2.2, respectively associated with values of the K_{oc} of 296 mL/g, 347 mL/g and 457 mL/g.

As a conservative approach the calculation considered the extent of degradation of the test item in supernatant and soil extracts of soil Attenschwiller.

Table B.8.1.3.1.2-18 Definite test: Adsorption kinetics of [UL-chlorophenyl-^{14}C]-chlorobenzoxazolone (AE F054014) in soil (% of applied radioactivity)

Ratio	Replicate No.	----------Adsorption time (hours) ---------- 2	4	24	48
		Attenschwiller			
1/25	A	12.8	12.7	45.0	59.9
	B	10.9	13.3	40.4	57.9
	mean	**11.9**	**13.0**	**42.7**	**58.9**
		Speyer 6S			
1/25	A	16.8	15.0	20.0	26.9
	B	13.0	13.9	20.2	25.7
	mean	**14.9**	**14.5**	**20.1**	**26.3**
		Speyer 2.2			
1/25	A	23.3	25.2	31.1	30.4
	B	22.2	24.1	28.6	34.4
	mean	**22.7**	**24.6**	**29.8**	**32.4**
		Controls			
1/25	A	99.9	99.7	101.0	100.6
	B	100.5	100.4	102.4	101.7
	mean	**100.2**	**100.0**	**101.7**	**101.1**

Table B.8.1.3.1.2-19 Adsorption coefficients of chlorobenzoxazolone (AE F054014) in soil (soil-to-solution ratio 1/25 and an agitation time of 48 hrs)

Soil	Soil type	*p*H ($CaCl_2$)	OC (%)	---------- Adsorption ---------- K_d (mL/g)	K_{oc} (mL/g)	1/*n*	R^2
Attenschwiller	Silt loam	7.4	1.10	3.26	296	n.a.	n.a.
Speyer 6S	Clay	6.9	1.90	6.59	347	n.a.	n.a.
Speyer 2.2	Loamy sand	5.6	2.36	10.78	457	n.a.	n.a.

n.a. = not applicable

Conclusions:

Degradation was observed for chlorobenzoxazolone (AE F054014) in contact with soil. Definitive adsorption tests were therefore performed at a single test concentration.

Values of adsorption coefficients (K_d) in soil based on single test concentrations ranged from 3.26 to 10.78 mL/g with corresponding values referenced to organic carbon (K_{oc}) to range from 296 to 457 mL/g.

Comments RMS AT:

- The study follows OECD guideline 106 and is considered reliable.
- Similar to what was observed in other adsorption studies in this dossier, formation of non-extractable residues (NER) was partly significant in this study as well (NER from 3.3 - 46.3 % after 48 hrs adsorption phase), leading to a test item mass balance of 32.2 - 96.2 % only. However, in contrast to all other studies authors in this dossier the study author actually excluded NER from the calculation of the K_d/K_{oc} values (as proposed by the RMS AT for all other adsorption studies in this dossier as well). As necessary, the study author also corrected for degradation of the test item observed in the more alkaline Attenschwiller soil.

  The RMS AT checked the calculations done by the study author (based on the raw data given in the study report, see tables below) obtaining almost the same results for Attenschwiller and Speyer 2.2 soil. However, results for the Speyer 6S soil were significantly lower in comparison to results obtained by the study author. It appears that the study author may not have adequately corrected for NER in case of this soil.

Table B.8.1.3.1.2-20 Recovery of radioactivity (% AR, mean of two replicates) in the screening test (48 hrs adsorption phase, 0.2 mg/l test concentration) and stability (%) of the test item - raw data from the study report

Soil	*p*H ($CaCl_2$)	-------- Recovery of total radioactivity -------- (%)				Stability of chlorobenzoxazolone (AE F054014) (%)	
		Aqueous phase	Soil extract	Soil residues	Total	Aqueous phase	Soil extract
Attenschwiller	7.4	41.1	8.8	46.3	96.2	69.6[(a)]	40.8[(b)]
Speyer 6S	6.9	73.7	15.9	5.6	95.2	100	100
Speyer 2.2	5.6	67.6	28.6	3.3	99.5	100	100

(a) Arithmetic mean of the two replicates as stated in the bottom of the HPLC chromatograms (Fig. 5 of the study report)
(b) As stated in the bottom of the HPLC chromatogram (Fig. 7 of the study report)

Table B.8.1.3.1.2-21 Mass balance of chlorobenzoxazolone (AE F054014) in the screening test (48 hrs adsorption phase, 0.2 mg/l test concentration) on basis of extractable amounts in soil - RMS AT assessment based on raw data

Soil	Test substance applied (µg)	Test substance in aqueous phase[(a)] (µg)	Test substance in soil extract[(a)] (µg)	Total test substance recovered (µg)	Mass balance (%)
Attenschwiller	4.80	1.37	0.17	1.55	32.2
Speyer 6S	4.90	3.61	0.78	4.39	89.6
Speyer 2.2	4.90	3.31	1.40	4.71	96.2

(a) Considering stability of the test compound

Table B.8.1.3.1.2-22 Re-calculated distribution coefficients (K_{oc}) of chlorobenzoxazolone (AE F054014) in the screening test (48 hrs adsorption phase, 0.2 mg/l test concentration) on basis

of extractable amounts in soil - RMS AT assessment based on raw data							
Soil	**Aqueous solution (ml)**	**Soil mass (g)**	**Test substance in aqueous phase[(a)] (µg/ml)**	**Test substance in soil extract[(a)] (µg/g)**	**K_d (ml/g)**	**OC (%)**	**K_{oc} (ml/g)**
Attenschwiller	25	1	0.055	0.17	3.14	1.1	**285**
Speyer 6S	25	1	0.14	0.78	5.39	1.9	**284**
Speyer 2.2	25	1	0.13	1.40	10.6	2.36	**448**

(a) Considering stability of the test compound

- As observed in Allan (2004) chlorobenzoxazolone (AE F054014) appears to be much less stable under more alkaline soil conditions.

Reference:	**[^{14}C]-HPPA: Adsorption to and desorption from three soils**
Author(s), year:	Mills, E.A.M. (2010)
Report/Doc. Number:	316 FPE, M-548276-01-1
Guideline(s):	OECD 106 (2000)
GLP:	Yes
Validity:	Yes
Status:	**New submission**

Executive Summary:

The adsorption/desorption characteristics of [UL-phenoxy-^{14}C]-hydroxyphenoxy propanoic acid (HOPP-acid, AE F096918) was determined by batch equilibrium tests for three soils.

Results of the preliminary adsorption tests revealed that HOPP-acid (AE F096918) was very unstable in contact with non-sterilised and sterilised soil. Adsorption or desorption parameters to soil could thus not be determined for HOPP acid (AE F096918) by the batch equilibrium method.

Material and methods:

Test Material	[Phenoxy-UL-^{14}C]-(R)-2-(4-hydroxyphenoxy)-propanoic acid (HOPP acid, AE F096918)
Specific radioactivity:	5.43 MBq/mg (146.8 µCi/mg)
Radiochemical purity:	98.8 % (HPLC)
Sample ID:	3420FDG008-4

Soils
Sorption tests were performed with three soils covering a range of *p*H, organic carbon content and texture.

Table B.8.1.3.1.2-23 Characteristics of test soils

Soil Batch ID	**Farditch (09/044)**	**Longwoods (09/045)**	**Lockington (09/047)**
Geographic location (City/State/Country)	Longwoods / Derbyshire / United Kingdom	Longwoods Quarry / Lincolnshire / United Kingdom	Lockington Grounds farm / Leicestershire / United Kingdom
GPS coordinates	N 53°13’8.6’’ W 01°50’39.4’’	N 53°7’6.6’’ W 00°25’26.7’’	N 52°52.132’ W 01°16.447’
Soil preparation		Air-dried and sieved to 2 mm	
Textural class (USDA)	loam	sandy loam	sandy clay loam
Sand (%)	36	72	52
Silt (%)	49	12	18
Clay (%)	15	16	30
*p*H (deionised water)	6.1	7.7	5.9
*p*H (0.01 M $CaCl_2$)	5.5	7.2	5.2
*p*H (0.01 M $CaCl_2$)[(a)]	5.6	7.2	5.6
*p*H (1 M KCl)	5.8	7.4	5.7
Org. matter (%)	6.2	2.4	5.8

Org. carbon[(b)] (%)	3.6	1.4	3.4
CEC (meq/100 g)	12.5	12.3	21.1

(a) Measured after a longer equilibration (24 hours) in the background control test
(b) % Organic carbon = % organic matter / 1.724
CEC = Cation exchange capacity

Experimental conditions
A preliminary test was performed to determine an adequate soil-to-solution ratio by weighing of 1, 2, 4 and 8 g of non-sterilised soil each into centrifuge tubes. There was added 39 mL (less the soil moisture) of 0.01 M aqueous calcium chloride solution to result in water-to-soil ratios of 1:40, 1:20, 1:10 and 1:5. Following pre-equilibration, 1 mL of 0.01 M aqueous calcium chloride solution was added containing the test item to result in a final concentration of 0.2 mg test item/L. The stability of the test item in calcium chloride solution and adsorption to the walls of the test vessels was also tested by controls containing no soil.

The maximum amount of organic co-solvent present in samples during the tests was < 0.1 % acetonitrile (by vol.) for the test concentration. Each determination was performed in single by shaking with an overhead shaker in the dark at 20 ± 2 °C for 24 hours.

For work-up, the aqueous supernatant was separated from soil by decantation and centrifugation. Radioactivity in water and soil extracts was determined by liquid scintillation counting (LSC).

In addition, stability tests were performed with sterilised soils at a soil-to-solution ratio of 1:5 and 1:40. The applied test item concentration and pre-equilibration time was similar to the preliminary test. Following removal of samples at various time points up to 24 hours and centrifugation, aliquots of the aqueous supernatants were analysed by LSC and HPLC.

Analysis of supernatants indicated that the test substance was not stable following contact with non-sterilised and sterilised soil. No definite test was therefore performed.

Analytical procedures
At the end of the preliminary test and following removal of the supernatant the soil was extracted three times. The first step was performed using acetonitrile/1-%-aqueous EDTA (1:1, by vol.) at ambient temperature while the second and third step used acetonitrile/water/formic acid (50:50:5, by vol.) as solvent mixture. The third extraction was performed at a temperature of 70 °C supported by ultra-sonication. Radioactivity in the aqueous phase and soil extracts were determined by liquid scintillation counting (LSC). The aqueous phases and the soil extracts were analysed by reversed phase radio-HPLC analysis using ^{14}C-flow-through detection techniques. In addition, the identity of the test item was confirmed by liquid chromatography/mass spectroscopic analysis (LC-MS).

Results and discussion:

Mass balance and results of preliminary test
Preliminary tests showed no adsorption to the walls of test vessels. The test item was sufficiently soluble and stable in aqueous calcium chloride solution. The test item was found to be extensively degraded in the presence of sterilised or non-sterilised soil. Consequently, no full mass balance was established since no definitive phase was performed.

Transformation of test substance
Analysis showed stability of the test item in aqueous solution of control samples, i.e. in the absence of soil. The test item was extensively degraded in the presence of soil irrespective of their sterilised or non-sterilised character. No degradation products were identified. The study was abandoned prior to the definitive phase.

Findings
The preliminary test performed with non-sterilised soils showed HOPP-acid (AE F096918) to represent less than 12 % of the supernatant in HPLC analysis. LSC analysis of soil extracts at the same soil-to-solution ratio of 1:40 showed that 23.0 % of AR (soil Farditch), 64.5 % (Longwoods) and 21.1 % (Lockington) were recovered. This indicated strong binding of either HOPP-acid (AE F096918) or of its breakdown product(s) to soil. It was concluded from the results that a 90 % recovery for HOPP-acid (AE F096918) from soil would not be obtainable in samples with viable soils. However, considerable breakdown of the test item was also observed in the supernatant of sterilised soils up to 7 hours (soil-to-solution ratios of 1 to 5 and 1 to 40) as indicated by HPLC

analysis.

Stability of HOPP-acid (AE F096918) was thus not given for a determination adsorption even for an adsorption time of one hour. Consequently, no definite phase was performed.

Table B.8.1.3.1.2-24 Preliminary test: Stability of [UL-phenyl-^{14}C]-HOPP-acid (AE F096918) in non-sterilised soils

Soil ID	Farditch		Longwoods		Lockington	
	% AR in sample	% test item (ROI in HPLC)	% AR in sample	% test item (ROI in HPLC)	% AR in sample	% test item (ROI in HPLC)
Ratio determination 1:40						
Supernatant	9.04	9.93	52.7	11.15	9.39	5.52
Solvent Extract 1	8.76	n.a.	6.66	n.a.	7.86	n.a.
Solvent Extract 2	2.64	n.a.	1.93	n.a.	2.07	n.a.
Solvent Extract 3	2.51	n.a.	3.21	n.a.	1.81	n.a.
Total extractable radioactivity (% AR)						
	23.0	0.90	64.5	5.87	21.1	0.52
Ratio determination 1:5						
Supernatant	3.11	0.0	20.7	11.33	5.02	0.0
Total extractable radioactivity (% AR)						
	3.11	0.0	20.70	2.35	5.02	0.0

AR = applied radioactivity
n.a. = not analysed
ROI = region of interest

Table B.8.1.3.1.2-25 Preliminary test: Stability of [UL-phenoxy-^{14}C]-HOPP-acid (AE F096918) in sterilised soils

---------- Soil-to-solution ratio 1:5 ----------					---------- Soil-to-solution ratio 1:40 ----------				
Equilibration time (hours)	Time to analysis (hours)	% ROI as HOPP acid (AE F096918)	% AR in supernatant	% AR as HOPP acid (AE F096918)	Equilibration time (hours)	Time to analysis (hours)	% ROI as HOPP acid (AE F096918)	% AR in supernatant	% AR as HOPP acid (AE F096918)
Control (without soil)									
0.0	7.09[(a)]	97.1	100.4	97.4	0.0	0.13[(a)]	97.1	100.4	97.5
1.2	7.60	96.1	99.9	96.0	0.9	3.52	98.2	99.6	97.8
2.5	9.63	96.8	99.3	96.2	1.9	4.16	98.4	100.3	98.7
4.4	12.15	96.3	100.0	96.3	3.9	6.61	98.2	99.5	97.7
6.7	14.19	96.7	100.8	97.5	5.4	8.25	97.2	99.4	96.6
Farditch soil									
0.0	7.09[(a)]	97.1	100.4	97.4	0.0	0.13[(a)]	97.1	100.4	97.5
1.2	8.11	40.2	60.0	24.1	0.9	1.24	84.9	96.3	81.7
2.5	10.14	20.8	32.5	6.8	1.9	2.93	72.9	92.7	67.6
4.4	12.66	1.4	18.2	0.3	3.9	5.38	68.9	82.0	56.5
6.7	14.69	0.8	15.0	0.1	5.4	7.02	58.3	73.0	42.6
Longwoods soil									
0.0	7.09[(a)]	97.1	100.4	97.4	0.0	0.13[(a)]	97.1	100.4	97.5
1.2	8.61	69.1	78.7	54.4	0.9	1.24	95.1	98.3	93.5
2.5	10.65	52.1	59.6	31.1	1.9	2.93	90.6	96.4	87.4
4.4	13.17	33.9	43.5	14.7	3.9	5.38	83.0	93.6	77.7
6.7	15.20	19.7	35.0	6.9	5.4	7.02	81.9	93.1	76.2
Lockington soil									
0.0	7.09[(a)]	97.1	100.4	97.4	0.0	0.13[(a)]	97.1	100.4	97.5
1.2	9.12	27.4	42.9	11.8	0.9	1.65	59.6	93.1	55.5
2.5	11.16	2.7	24.5	0.7	1.9	3.34	42.9	85.4	36.7
4.4	13.68	0.5	22.5	0.1	3.9	5.79	27.7	65.4	18.1
6.7	15.71	0.0	22.2	0.0	5.4	7.43	15.8	55.2	8.7

ROI = region of interest
AR = applied radioactivity
(a) Absence of soil, hence no degradation

Conclusions:

HOPP-acid (AE F096918) was found to degrade very fast in contact with non-sterilised and sterilised soils thus not enabling the determination of adsorption or desorption characteristics to soil by the batch equilibrium method.

Comments RMS AT:

- The study follows OECD guideline 106 and is considered reliable. The instability of HOPP-acid (AE F096918) observed in these studies closely follows observations made in soil degradation experiments with this substance (see Fitzmaurice, 2010, and Stroech & Junge, 2014).

B.8.1.3.2. Aged sorption

No studies provided.

B.8.1.4. Mobility in soil

B.8.1.4.1. Column leaching studies

B.8.1.4.1.1. Column leaching of the active substance

Studies submitted for first Annex I inclusion:

- **Gildemeister & von Fleischbein (1988)**, investigating aged fenoxaprop-P-ethyl (AE F046360) in three soils
- **Buhl et al. (1993)**, investigating fresh and aged fenoxaprop-P-ethyl (AE F046360) with and without the safener fenchlorazole-ethyl (AE F070542) in three soils
- **Tarara (2003)**, discussing the influence of safeners on the leaching behaviour and soil degradation of fenoxaprop-P-ethyl (AE F046360)

No new studies were submitted by the Fenoxaprop-P-ethyl Task Force.

Reference:	**Hoe 046360 – Examination of the leaching behaviour in accordance with BBA Guideline IV, 4-2**
Author(s), year:	Gildemeister, H., von Fleischbein, I. (1988)
Report/Doc. Number:	A43632, M-119529-01-2
Guideline(s):	BBA Guideline IV, 4-2
GLP:	Yes
Validity:	Supplemental information (refer to comment section)
Status:	**Previously submitted**

[The following study report is a copy/paste of the original text in the DAR for Annex I inclusion slightly amended in order to meet editorial settings and to improve readability]

Material and methods:

In this study the leaching behaviour of fenoxaprop-P-ethyl (AE F046360, called Hoe 046360 in the report) and its residues aged in the soil were examined. The UL-chlorophenyl-^{14}C-labelled active substance was supplied in the form of a 7 % oil-in-water emulsion. The blank formulation 'Hoe 046360 OH EW00 A101' was used for the production of the formulated product with a radioactive active ingredient (code 'Hoe 046360 OH ZE98 0001') content of 7.22 % (w/w).

The air dried soils were sieved through a 1 mm sieve and filled into columns up to a height of 30 cm (inner diameter 5 cm) by shaking with a vibrator. After soils were saturated with water the test substance was applied at a rate equivalent to 100 g a.i./ha. Subsequently sprinkler irrigation was conducted with distilled water. 200 mm were dropped slowly and evenly during 48 hours.

For the aged leaching study the soil was passed through a 2 mm sieve. Soil was kept at 40 % of the MWHC at 20 °C in the dark for 4, 8, 16 and 30 days. After 16 and 30 days aged soil samples were applied onto the soil columns and treated as described above.

In case of the fresh column study, aliquots of the leachates were examined for its content of radioactivity by LSC. Aged soil samples were extracted exhaustively with acetonitrile/water (80/20, v/v) after 4, 8, 16 and 30 days. Radioactivity was analysed by HPLC with gradient elution technique. The leachates of the soil columns treated with aged residues were examined for their content of radioactivity by LSC. Since radioactivity was observed they were also examined by radio HPLC. The leachates were first extracted three times with ethyl acetate, then adjusted to *p*H 2 and extracted again three times with ethyl acetate. Representative samples were concentrated and then examined by HPLC.

Table B.8.1.4.1.1-1 Soil characteristics

Soil (BBA classification)	Used in columns	% Silt + clay	% OC	*p*H	CEC (meq/100 g)	% MWHC
Sand, Standard soil 2.1	Fresh and aged	8.1	0.69	6.0	5.0	21.0

Loamy sand, Standard soil 2.2	Fresh	9.5	2.13	6.2	8.0	41.0
Sandy loam, Standard soil 2.3	Fresh	24.3	0.96	5.2	6.0	20.4

Findings:

The volumes of leachates collected were between 360 and 395 ml.

Fresh soil columns
No radioactivity could be observed in any leachate (< 0.1 dpm/ml, < 0.01 % AR).

Aged soil columns

Table B.8.1.4.1.1-2 Metabolite spectrum in the aged soil samples (Sand, Standard soil 2.1, HPLC) – in % AR (values in brackets % of extractable radioactivity)

Ageing period	Extractable	Fenoxaprop-P-ethyl (AE F046360)	Fenoxaprop-P-acid (AE F088406)	Chloro-benzoxazolone (AE F054014)	Unknown metabolite
4 days	87.3	not given	78.8 (90.3)	8.5 (9.7)	not given
8 days	66.5	not given	62.9 (94.6)	3.6 (5.4)	not given
16 days[(a)]	50.7	not given	44.2 (87.1)	4.5 (8.9)	2.0 (4.0)
30 days[(a)]	26.7	2.4 (9.0)	20.3 (76.1)	4.0 (15.0)	not given

(a) Used for leaching study

The soil samples used for leaching differed with regard to the amount of the extractable radioactivity and also with regard to the composition of these extracts.

Table B.8.1.4.1.1-3 Distribution of radioactivity of the leachates from aged soil columns (% AR)

Ageing period	Leachate prior to extraction	Org. extract (neutral)	Org. extract (*p*H 2)	Extracted aqueous phase
16 days	3.62	1.29	1.11	0.90
30 days - I	2.32	0.03	1.22[(a)]	1.07[(a)]
30 days - II	2.18	0.02	0.92	1.15

(a) Samples for HPLC examinations

3.6 % of the initially applied radioactivity was found in the leachate of the soil column filled with residues aged for 16 days. 2.3 % and 2.2 % were found in the column filled with residues aged for 30 days. Both fractions of the samples of day 30 were concentrated and applied to HPLC. No defined signal could be registered beside the normal background noise. Thus, no assignment of the applied radioactivity to one of the known metabolites or the active substance was possible.

Conclusions:

In a column leaching study with three different, fresh soils, where formulated fenoxaprop-P-ethyl (AE F0462360) was applied at a rate equivalent to 100 g a.i./ha, no radioactivity was found in the leachates.

Tests with aged soil residues showed 3.6 % AR (ageing period 16 days) and 2.3 % of applied radioactivity (ageing period 30 days) in the leachates. Fenoxaprop-P-ethyl (AE F046360) and its metabolites (fenoxaprop-P-acid (AE F088406) and chlorobenzoxazolone (AE F054014)) could not be detected in the leachate. The chosen ageing period was probably too long to catch the maximum concentration of fenoxaprop-P-acid (AE F088406). It is assumed that the leaching behaviour of fenoxaprop-P-acid (AE F088406) is included in the study part with fresh soil.

According to the results of the column leaching studies fenoxaprop-P-ethyl (AE F040630) and its two metabolites are of low mobility.

Comments RMS AT:

- Data resulting from these soil column leaching studies are regarded as qualitative information on

mobility in soil only, broadly reflecting the behaviour of fenoxaprop-P-ethyl (AE F046360) and its metabolites observed in dedicated soil degradation and batch sorption experiments.

Reference:	**Hoe 046360-^{14}C: Leaching behaviour of the formulated non-aged active ingredient in the presence of Hoe 070542 (Hoe 046360 01 EW11 A2) in the LUFA standard soil 2.1, 2.2 and 2.3 and leaching behaviour of the aged active ingredient in the LUFA standard soil 2.1**
Author(s), year:	Buhl, H. J., Schwab, W., Mueller, A. (1993)
Report/Doc. Number:	C003248, M-132667-01-2
Guideline(s):	BBA Guideline IV, 4-1
GLP:	Yes
Validity:	Supplemental information (refer to comment section)
Status:	**Previously submitted**

[The following study report is a copy/paste of the original text in the DAR for Annex I inclusion slightly amended in order to meet editorial settings and to improve readability]

Material and methods:

The objective of this study was to examine i) the leaching tendency of ^{14}C-fenoxaprop-P-ethyl (AE F046360) formulated with the safener fenchlorazole-ethyl (AE F070542, called Hoe 070542 in the study report) in soil columns with fresh standard soils and ii) of aged residues of pure ^{14}C-fenoxaprop-P-ethyl (AE F046360) in one standard soil.

For experiment i) a blank formulation was prepared containing the safener fenchlorazole-ethyl (AE F070542) in the non-labelled form, but no active ingredient. In order to prepare the final formulation ('Hoe 046360 01 EW 11 A2') used in the study, the active substance was added in the form of UL-chlorophenyl-^{14}C labelled fenoxaprop-P-ethyl (AE F046360). The formulation was applied to the soils at a rate of 16.51 µg a.i./soil column (equivalent to 82.6 g a.i./ha).

For experiment ii) 17.81 µg a.i./soil columns were applied (equivalent to 89.1 g a.i./ha).

Soils were passed through a 1 mm sieve and filled into glass columns (inner diameter 5 cm), while shaking with a vibrator until a height of 30 cm (28 cm aged column study) was reached, and thereafter soils were saturated with water.

Ageing of soil samples was carried out at room temperature in the dark for 2 days. Samples were kept at 40 % of MWHC. After this incubation two of the four soil samples were extracted with acetonitrile/water (4:1, v/v) until < 2 % AR was found in the extract. The radioactivity of all extracts was measured. The first extracts were concentrated and the identity of the extracted substances was investigated by HPLC. The radioactivity remaining in the soil was determined after combustion of the soil and measurement of the $^{14}CO_2$ thus formed.

Soil columns were irrigated with completely desalted water in an amount of 200 mm over 2 days.

Table B.8.1.4.1.1-4 Soil characteristics

Soil (BBA classification)	Used in columns	% Sand	% Silt	% Clay	% OC	*p*H	CEC (meq/100 g)	% MWHC
Sand, Standard soil 2.1[(a)]	Fresh and aged	87.3	9.5	3.3	0.98	5.5	3.8	21.0
Loamy sand, Standard soil 2.2	Fresh	86.6	9.2	4.3	2.5	5.5	10.3	41.3
Sandy loam, Standard soil 2.3	Fresh	62.8	27.8	9.4	1.11	6.4	9.5	31.4

(a) At the beginning of ageing: 22.7 mg C/100 g microbial biomass

Findings:

The volumes of leachates collected were between 379 ml and 390 ml. In the test with formulated fenoxaprop-P-ethyl (AE F046360) and fresh soil 0.29 % of applied radioactivity, 0.08 % AR and 0.12 % AR were found in the

leachates of soils 2.1, 2.2 and 2.3, respectively.

In the test with pure fenoxaprop-P-ethyl (AE F046360) and aged soil 1.91 % of applied radioactivity was found in the leachate (equivalent to 0.34 µg/total leachate or 0.87 µg/l). Values are given as mean of two replicates. In the extracts of soil samples, which were aged for 2 days 79.7 and 83.7 % AR were found. Non-extractable residues amounted for 16.7 % and 14.8 % AR. Thus the recovery was between 96.4 and 98.5 %. In the soil extracts parent compound and three polar metabolites were detected: Fenoxaprop-P-acid (AE F088406) as the major compound, chlorobenzoxazolone (AE F054014) and the phenolic metabolite (AE F040356).

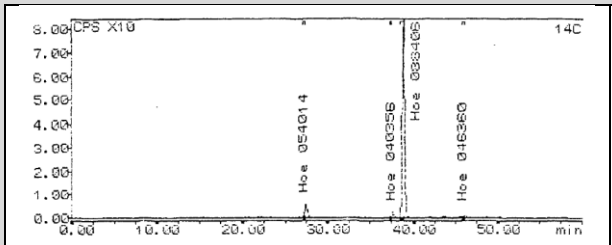
Conclusions:

In a column leaching study with three different, fresh soils, where formulated fenoxaprop-P-ethyl (AE F046360 with safener fenchlorazole-ethyl, AE F070542) was applied at a rate equivalent to 82.6 g a.i./ha, 0.29 % of applied radioactivity, 0.08 % AR and 0.12 % AR were found in the leachates of soils 2.1, 2.2 and 2.3, respectively.

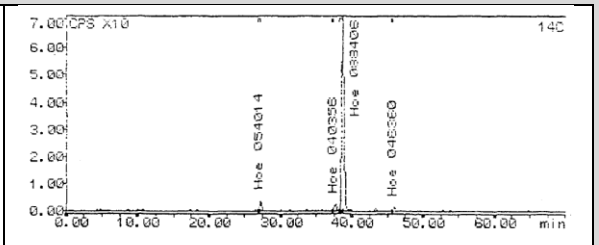
Tests with aged soil residues of fenoxaprop-P-ethyl (AE F046360, ageing period 2 days, one soil) showed 1.91 % of applied radioactivity in the leachate. Due to the very low amounts of radioactivity in the leachates, no further examinations were conducted. According to the results of the column leaching studies fenoxaprop-P-ethyl (AE F046360) and its metabolites are of low mobility.

Comments RMS AT:

- No quantitative data on amounts of fenoxaprop-P-acid (AE F088406) in the aged soil extracts (2 day aging period) are given in the report. However, HPLC chromatograms (radio detection) demonstrate that fenoxaprop-P-acid (AE F088406) was by far the dominating substance in these extracts with almost no fenoxaprop-P-ethyl (AE F046360) present any more.



2 day aging period - replicate I



2 day aging period - replicate II

- Data resulting from these soil column leaching studies are regarded as qualitative information on mobility in soil only, broadly reflecting the behaviour of fenoxaprop-P-ethyl (AE F046360) and its metabolites observed in dedicated soil degradation and batch sorption experiments.

Reference:	**The influence of the addition of a safener on the leaching behaviour and soil degradation of the active ingredient**
Author(s), year:	Tarara, G. (2003)
Report/Doc. Number:	C038236, M-224570-01-1
Guideline(s):	Not applicable
GLP:	Not applicable
Validity:	Supplemental information (refer to comment section)
Status:	**Previously submitted**

[The following study report is a copy/paste of the original text in the DAR for Annex I inclusion slightly amended in order to meet editorial settings and to improve readability]

In Buhl et al. (1993) the mobility of the aged and non-aged active ingredient fenoxaprop-P-ethyl (AE F046360) was investigated with the formulate product 'Hoe 046360 01 EW11 A2'. In this product fenoxaprop-P-ethyl (AE

F046360) has been co-formulated with the safener fenchlorazole-ethyl (AE F070542). The safener fenchlorazole-ethyl (AE F070542) was the predecessor of the safener actually in use, e.g. mefenpyr-diethyl (AE F107892) as used in the representative formulation evaluated in the dossier. The study was not repeated with the safener mefenpyr-diethyl (AE F0107892) as the existing study is still able to describe adequately the leaching behaviour of the active ingredient. It is stated that in contrast to detergents which act by their bipolar character as wetting agents, the safener is a neutral organic molecule with no functional groups that could interfere in such a way. With the close and direct contact of the spray mixture to soil particles the leaching behaviour of all components is mainly influenced by the intrinsic properties of the individual molecule itself. These basic properties are water solubility and adsorption behaviour to soil particles. There can no longer be assumed a homogenous distribution and a direct contact of the components to each other after spraying onto soil. As a consequence the adsorption to soil of each individual component of the formulation becomes the predominant intrinsic property and this effect overrules the potential influences on the leaching behaviour in column leaching studies. Due to this behaviour the adsorption to soil was determined with the non-formulated active ingredient separately as described in the batch-equilibrium studies. Further it is stated that, apart from the difference in safener, the compositions of both formulations (the one tested and the one used as representative) are basically the same. It was concluded that there is a very low probability and there was no sign for a significant influence of the safener to actively contribute to the behaviour of the active ingredient in column leaching. The same was concluded for the dissipation behaviour of fenoxaprop-P-ethyl (AE F046360) in the field. In the field, any effect on degradation imaginable and coming from the safener would be overruled by the more predominant climatic factors such as soil moisture and temperature.

Comments RMS AT:

- The RMS AT agrees with the applicant that the impact of the safener fenchlorazole-ethyl (AE F070542) on the leaching behaviour of fenoxaprop-P-ethyl (AE F046360) is considered insignificant.

B.8.1.4.1.2. Column leaching of metabolites, breakdown and reaction products

Column leaching studies with soil metabolites of fenoxaprop-P-ethyl (AE F046360) have not been performed and are regarded as not necessary.

B.8.1.4.2. Lysimeter studies

No lysimeter studies had been performed with the active substance fenoxaprop-P-ethyl (AE F046360).

B.8.1.4.3. Field leaching studies

No field leaching studies had been performed with the active substance fenoxaprop-P-ethyl (AE F046360).

B.8.1.4.4. Summary on adsorption and mobility in soil

The adsorption of fenoxaprop-P-ethyl (AE F046360), fenoxaprop-P-acid (AE F088406) and chlorobenzoxazolone (AE F054014) in soil has been assessed in OECD guideline 106 batch studies and is summarised in the tables below. Batch sorption studies with HOPP-acid (AE F096918) failed due to the instability of HOPP-acid (AE F096918) observed in these test systems.

Due to the instability of the test items as well as significant formation of non-extractable residues (NER) observed in batch sorption studies conducted with fenoxaprop-P-ethyl (AE F046360), fenoxaprop-P-acid (AE F088406) and chlorobenzoxazolone (AE F054014) parental mass balances were in most cases below 90 % recommended by OECD guideline 106 in order to allow the *indirect* method to be applied for the determination of Freundlich isotherm constants. Despite of the low mass balance, advanced Freundlich isotherm experiments were conducted by the study authors applying the *indirect* method throughout, thus calculating the mass of test item adsorbed on basis of the test item in the liquid phase only. In view of insufficient test item mass balance the RMS AT considers the obtained results on Freundlich isotherms obtained in these experiments non-reliable.

It may be noted that formation of NER in OECD 106 batch experiments with fenoxaprop-P-ethyl (AE F046360) and its main metabolites is not unexpected to occur, as NER in soil degradation experiments conducted with fenoxaprop-P-ethyl (AE F046360) were generally high accounting for up to 17.3 % AR already one day after application. Applying the *indirect* method, NER are implicitly assumed to equally contribute to the equilibrium sorption, which is not defendable from a scientific point of view.

In contrast to the advanced tests (Freundlich isotherm experiments), the RMS AT considers results from the preliminary experiments (usually conducted at the highest test concentration, only) applying the *direct* method adequate to calculate distribution coefficients (K_d/K_{oc}) on basis of the test item recovered (i.e. in the liquid phase and in the soil extract). As these results are based on one concertation only, linear sorption ($1/n$ = 1) is assumed by default.

In Reynolds (1993), investigating fenoxaprop-P-ethyl (AE F046360), fenoxaprop-P-acid (AE F088406) and chlorobenzoxazolone (AE F054014), no pre-equilibrium phase (i.e. shaking of soil with pure $CaCl_2$ solution overnight) was accounted for. In principle this invalidates this study with respect to recommendations given in OECD guideline 106. However, soil adsorption tests according to OECD guideline 106 with fenoxaprop-P-ethyl (AE F046360) will always be somehow limited due to the instability of fenoxaprop-P-ethyl (AE F046360) in these test systems. In this respect, the RMS AT considers results obtained in Reynolds (1993) sufficiently robust to at least give an estimate of the sorption coefficient of fenoxaprop-P-ethyl (AE F046360) in soils even without pre-equilibrium phase. However, results of Reynolds (1993) are not considered further in case of fenoxaprop-P-acid (AE F088406) and chlorobenzoxazolone (AE F054014) as dedicated batch sorption studies with an adequate pre-equilibration phase are available for these two metabolites. It may be added, that despite missing pre-equilibrium phase, results from Reynolds (1993) are nevertheless well in line with results from valid soil sorption studies.

Table B.8.1.4.4-1: Summary on soil adsorption of <u>fenoxaprop-P-ethyl (AE F046360)</u>

Soil name	Soil type (USDA)	OC (%)	*p*H[(a)]	K_d (L/kg)	K_{oc} (L/kg)	K_f (L/kg)	K_{foc} (L/kg)	1/*n* (-)	Reference
Arizona	Clay	0.23	7.6	12.8	5419	na	na	1.0[(b)]	Reynolds (1993)[(c)]
Mississippi	Silty clay loam	0.81	6.5	212	26207	na	na	1.0[(b)]	
Maryland	Sandy loam	2.55	6.4	443	17352	na	na	1.0[(b)]	
Michigan	Clay loam	2.65	6.8	176	6667	na	na	1.0[(b)]	
		Arithmetic mean (n = 4)		-	-	-	-	**1.0**	
		Geometric mean (n = 4)		**121**	**11322**	-	-	-	
		pH-dependency: y/n		n					

na denotes not applicable (one test concentration only); note that results on Freundlich isotherms are not considered reliable by the RMS AT
(a) Matrix not specified
(b) Default assuming linear adsorption (one test concentration only)
(c) This sorption study was conducted without a pre-equilibration phase thus leaving some uncertainty regarding the reliability of the obtained K_d/K_{oc} values

Table B.8.1.4.4-2: Summary on soil adsorption of fenoxaprop-P-acid (AE F088406)

Soil name	Soil type (USDA)	OC (%)	*p*H ($CaCl_2$)	K_d (L/kg)	K_{oc} (L/kg)	K_f (L/kg)	K_{foc} (L/kg)	1/*n* (-)	Reference
EFS-6	Sandy loam	2.64	7.3	6.91	262	na	na	1.0[(a)]	Rupprecht (1999)
EFS-8	Sand	0.53	4.7	2.32	438	na	na	1.0[(a)]	
EFS-16	Silty clay loam	1.67	7.1	2.58	154	na	na	1.0[(a)]	
EFS-24	Sand	0.81	6.4	1.20	148	na	na	1.0[(a)]	
EFS-29	Loam	1.43	7.5	3.95	276	na	na	1.0[(a)]	
EFS-38	Clay loam	1.99	7.4	3.14	158	na	na	1.0[(a)]	
EFS-54[(b)]	Sandy loam	2.07	4.5	21.9	1058	na	na	1.0[(a)]	
	Arithmetic mean (all soil, n = 7)			**-**	**-**	**-**	**-**	**1.0**	
	Geometric mean (all soil, n = 7)			**3.89**	**276**	**-**	**-**	**-**	
Geometric mean (neutral and alkaline soils, n = 5)				**3.05**	**192**				
	pH-dependency: y/n			y[(c)]					

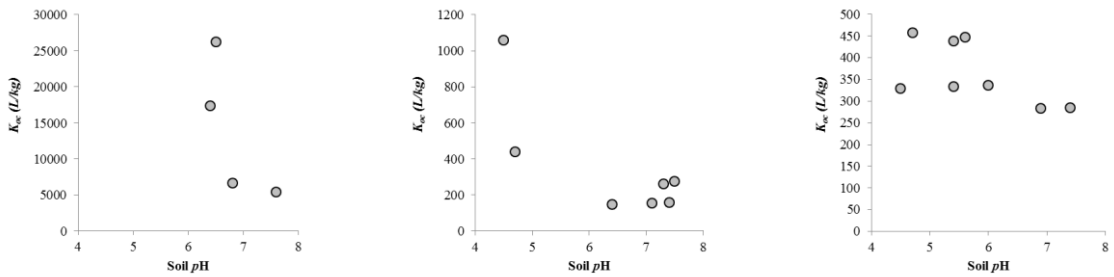
na denotes not applicable (one test concentration only); note that results on Freundlich isotherms are not considered reliable by the RMS AT
(a) Default assuming linear adsorption (one test concentration only)
(b) Sediment
(c) Refer to text below

Table B.8.1.4.4-3: Summary on soil adsorption of chlorobenzoxazolone (AE F054014)

Soil name	Soil type (USDA)	OC (%)	*p*H ($CaCl_2$)	K_d (L/kg)	K_{oc} (L/kg)	K_f (L/kg)	K_{foc} (L/kg)	1/*n* (-)	Reference
EFS-8	Loamy sand	0.53	4.7	2.43	458	na	na	1.0[(a)]	Allan (2004)
EFS-25	Sandy loam	1.84	5.4	6.12	333	na	na	1.0[(a)]	
EFS-35	Silty loam	1.52	5.4	6.66	438	na	na	1.0[(a)]	
EFS-54[(b)]	Sandy loam	2.07	4.5	6.84	330	na	na	1.0[(a)]	
EFS-66	Loamy sand	1.95	6.0	6.55	336	na	na	1.0[(a)]	
Attenschwiller	Silt loam	1.10	7.4	3.26	285	na	na	1.0[(a)]	Voelkel (2008b)
Speyer 6S	Clay	1.90	6.9	6.59	284	na	na	1.0[(a)]	
Speyer 2.2	Loamy sand	2.36	5.6	10.8	448	na	na	1.0[(a)]	
	Arithmetic mean (n = 8)			**-**	**-**	**-**		**1.0**	
	Geometric mean (n = 8)			**5.64**	**358**	**-**	**-**	**-**	
	pH-dependency: y/n				n				

na denotes not applicable (one test concentration only), note that results on Freundlich isotherms are not considered reliable by the RMS AT
(a) Default assuming linear adsorption (one test concentration only)
(b) Sediment

The RMS AT investigated a possible relationship between sorption coefficient (K_{oc}) and soil *p*H for fenoxaprop-P-ethyl (AE F046360), fenoxaprop-P-acid (AE F088406) and chlorobenzoxazolone (AE F054014) more in detail (Figure B.8.1.4.4-1). No such relationship was observed for fenoxaprop-P-ethyl (AE F046360) and chlorobenzoxazolone (AE F054014). In case of fenoxaprop-P-acid (AE F088406), sorption in the two fairly acidic soils (*p*H ≤ 4.7) was higher in comparison to the more neutral and alkaline soils. In view of fenoxaprop-P-acid (AE F088406), being an organic acid, *p*H-dependent sorption may *a priori* be expected (depending on the protonation status). For reasons of conservativeness, the RMS AT therefore recommends omitting sorption results of the two rather acidic soils for calculating the average K_{oc} of fenoxaprop-P-acid (AE F088406) to be used in the exposure assessment.



Fenoxaprop-P-ethyl (AE F046360) **Fenoxaprop-P-acid (AE F088406)** **Chlorobenzoxazolone (AE F054014)**

Figure B.8.1.4.4-1: Soil sorption (K_{oc}) *vs* soil *p*H for fenoxaprop-P-ethyl (AE F046360) and metabolites

Data resulting from two soil column leaching studies are regarded as qualitative information on mobility in soil only, broadly reflecting the behaviour of fenoxaprop-P-ethyl (AE F046360) and its metabolites observed in dedicated soil degradation and batch sorption experiments.

B.8.2. FATE AND BEHAVIOUR IN WATER AND SEDIMENT

B.8.2.1. Route and rate of degradation in aquatic systems (chemical and photochemical degradation)

B.8.2.1.1. Hydrolytic degradation

Studies submitted for first Annex I inclusion:

- **Van der Gaauw (2002**), investigating chlorophenyl-labelled fenoxaprop-P-ethyl (AE F046360)
- **Schollmeier & Eyrich (1993)**, investigating unlabelled fenoxaprop-P-acid (AE F088406)
- **Burgener (1999)**, investigating chlorobenzoxazolone (AE F054014)

New studies submitted by the Fenoxaprop-P-ethyl Task Force:

- **Fitzmaurice (2008)**, investigating phenoxy-labelled fenoxaprop-P-ethyl (AE 046360)
- **Adam (2008)**, investigating chlorophenyl-labelled fenoxaprop-P-ethyl (AE F046360)
- **Adam (2007)**, investigating chlorobenzoxazolone (AE F054014)

Reference:	**[^{14}C]-fenoxaprop-ethyl: Hydrolysis at 5 different pH values**
Author(s), year:	Van der Gaauw, A. (2002)
Report/Doc. Number:	C028353, M-215094-01-1
Guideline(s):	OECD 111 (1981); EPA Guideline OPPTS 835.2110
GLP:	Yes
Validity:	Yes
Status:	**Previously submitted**

[The following study report is a copy/paste of the original text in the DAR for Annex I inclusion slightly amended in order to meet editorial settings and to improve readability]

Material and methods:

The rate of hydrolysis of UL-chlorophenyl-^{14}C-labelled fenoxaprop-P-ethyl (AE F046360, test concentration ~ 0.34 mg/L) was investigated in sterile aqueous buffer solutions at four *p*H levels (*p*H 4, 5, 7, 9) at 25 °C and 40 °C. Initially, a pre-test was done at five *p*H levels (*p*H 1.2, 4, 5, 7 and 9) at 50 °C (37 °C for *p*H 1.2). In addition, the formation of possible hydrolysis products was investigated.

All test samples were maintained in the dark at required temperatures in a thermo-regulated oven or water bath under constant stirring or shaking for up to 5 (pre-test) and 30 days (main test).

During the incubation time repeatedly, the *p*H of each buffer solution was recorded and test samples were taken and analysed by LSC (determination of total radioactivity) and HPLC (determination of amounts of ^{14}C-Fenoxaprop-ethyl and hydrolysis products).

Findings:

All solutions in the pre- and main test remained sterile and the *p*H value was constant during the incubation time. Recovery rates ranged from 97.7 ± 3.6 % to 106.2 ± 4.8 % of applied radioactivity in the pre-test at 50 °C and from 95.0 ± 3.3 % to 103.4 ± 2.5 % of applied radioactivity in main test for both temperatures.

In the pre-test at *p*H 1.2 and 37 °C fenoxaprop-P-ethyl was instantly hydrolysed. At 50 °C and pH 4 and 9, the active substance was nearly completely hydrolysed after five days, whereas at *p*H 5 and 7, 19 % and 14 % of the initial concentration were found as parent after five days, respectively.

Table B.8.2.1.1-1 Distribution of [UL-chlorophenyl-^{14}C]-fenoxaprop-P-ethyl (AE F046360) and metabolites under conditions of abiotic hydrolysis at 25 and 40 °C (% AR, numbers shaded in grey indicate exceedance of 10 % AR)

*p*H	Temp. (°C)	DAT	Fenoxaprop-P-ethyl (AE F046360)	Fenoxaprop-P-acid (AE F088406)	Chlorobenzoxazolone (AE F054014)
4	25	**0**	93.4	nd	2.1
		0.17	89.0	0.2	4.7
		1	70.0	nd	21.0
		2	50.6	nd	40.7
		4	34.3	nd	60.5
		7	19.9	nd	77.0
		11	10.0	nd	92.5
		30	nd	nd	101.6
	40	**0**	93.4	nd	2.1
		30	nd	nd	103.1
5	25	**0**	93.1	1.0	1.6
		0.17	91.2	1.1	1.4
		1	88.6	nd	5.3
		2	80.5	nd	11.3
		3.5	79.6	0.9	12.4
		17	48.3	nd	43.7
		30	32.3	0.7	63.9
	40	**0**	93.1	1.0	1.6
		30	3.2	nd	96.9
7	25	**0**	95.9	1.0	1.0
		1	92.6	3.3	4.1
		2	89.1	4.9	3.9
		3.5	84.6	7.8	5.1
		6	79.1	11.8	6.6
		15	57.6	23.1	12.9
		30	41.3	31.7	23.4
	40	**0**	95.9	1.0	1.0
		30	nd	43.0	63.1
9	25	**0**	91.6	4.8	1.4
		0.08	85.4	10.1	1.9
		0.17	70.1	19.9	2.0
		1	27.4	69.1	2.6
		2	12.9	87.3	3.7
		3	5.7	90.4	4.7
		6	nd	95.9	6.1
		15	nd	93.0	11.1
		20	nd	91.2	13.6
		30	nd	84.3	20.4
	40	**0**	93.7	4.9	1.4
		30	nd	15.6	79.6

nd denotes not detected or below the detection limit

Degradation products:

Up to eleven radioactive fractions were formed, whereas three were identified as fenoxaprop-P-acid (AE F088406, max.: 95.6 % after 6 d, at *p*H 9, 25 °C), chlorobenzoxazolone (AE F054014, max.: 103.1 % after 30 d, at *p*H 4, 40 °C) and 5-hydroxy-6-chloro-2,3-dihydrobenzoxazol-2-one (AE F064124, observed at max. 1.0 % after 1 d at *p*H 4, 40 °C, only). The other non-identified fractions reached maximal levels of ≤ 5.0 (25 °C) and ≤ 8.7 % (40 °C).

Under acidic conditions (*p*H 4 and 5) only chlorobenzoxazolone (AE F054014) was found and under neutral (*p*H 7) and more alkaline conditions (*p*H 9) additionally fenoxaprop-P-acid (AE F088406) was detected which was further transformed to chlorobenzoxazolone (AE F054014). Chlorobenzoxazolone (AE F054014) was not further degraded under these test conditions.

Assuming first order reaction kinetic half-lives for fenoxaprop-P-ethyl (AE F046360) were calculated using the computer program MicroCal.

Table B.8.2.1.1-2 Calculated *DT50* and *DT90* values for fenoxaprop-P-ethyl (AE F046360) using the program MicroCal Origin (non-linear curve fitting)

	*p*H 4		*p*H 5		*p*H 7		*p*H 9	
	25 °C	40 °C	25 °C	40 °C	25 °C	40 °C	25 °C	40 °C
***DT50* [d]**	2.8	0.8	19.2	6.6	23.2	5.1	0.6	0.2
***DT90* [d]**	9.4	2.7	63.8	21.8	77.1	16.9	2.0	0.5

Conclusion:

At *p*H values of 4, 5, 7 and 9 (test temperature 25 °C) fenoxaprop-P-ethyl (AE F046360) was hydrolytically instable with the rate of hydrolysis at *p*H 4 and 9 being faster than at *p*H 5 and 7. The estimated *DT50* values are 2.8 d (*p*H 4), 19.2 d (*p*H 5), 23.2 d (*p*H 7) and 0.6 d (*p*H 9).

The major hydrolysis degradation product under acid conditions (*p*H 4, 5) was chlorobenzoxazolone (AE F054014) and under more alkaline conditions (*p*H 7, 9) additionally fenoxaprop-P-acid (AE F088406) was detected, which was further transformed to chlorobenzoxazolone (AE F054014).

Comments RMS AT:

- The study follows OECD guideline 111 and is still considered reliable.
- Hydrolysis rates of fenoxaprop-P-ethyl (AE F046360) and fenoxaprop-P-acid (AE F088406) where re-assessed by the RMS AT in line with pertinent guidance (applying CAKE 3.3).

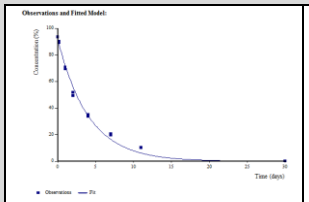
Table B.8.2.1.1-3 Re-calculated hydrolysis *DT50* and *DT90* values for fenoxaprop-P-ethyl (AE F046360) at 25 °C - RMS AT assessment

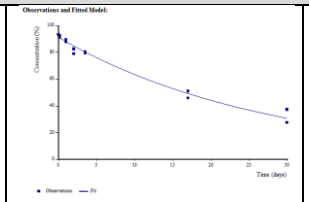
Matrix	Substance	Kinetics	*DT50* (d)	*DT90* (d)	χ^2 error (%)
***p*H 4**	Fenoxaprop-P-ethyl (AE F046360)	SFO	2.8	9.4	5.0
***p*H 5**	Fenoxaprop-P-ethyl (AE F046360)	SFO	19.1	63.5	2.1
***p*H 7**	Fenoxaprop-P-ethyl (AE F046360)	SFO	23.8	79.1	1.7
***p*H 9**	Fenoxaprop-P-ethyl (AE F046360)	SFO	0.58	1.9	6.1

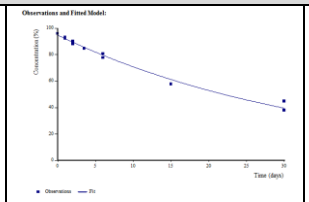
Table B.8.2.1.1-4 Re-calculated hydrolysis *DT50* and *DT90* values for fenoxaprop-P-ethyl (AE F046360) and fenoxaprop-P-acid (AE F088406) at 40 °C - RMS AT assessment

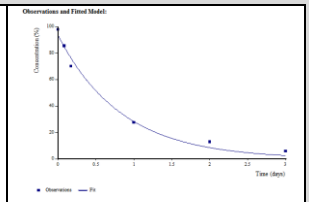
Matrix	Substance	Kinetics	*DT50* (d)	*DT90* (d)	χ^2 error (%)
***p*H 4**	Fenoxaprop-P-ethyl (AE F046360)	SFO	0.80	2.7	2.7
***p*H 5**	Fenoxaprop-P-ethyl (AE F046360)	SFO	6.6	21.8	3.2
***p*H 7**	Fenoxaprop-P-ethyl (AE F046360)	$P_{SFO} \rightarrow M_{SFO}$	5.1	16.8	2.3
	Fenoxaprop-P-acid (AE F088406)	$P_{SFO} \rightarrow M_{SFO}$	24.7	82.1	4.1
***p*H 9**	Fenoxaprop-P-ethyl (AE F046360)	$P_{SFO} \rightarrow M_{SFO}$	0.16	0.52	2.2
	Fenoxaprop-P-acid (AE F088406)	$P_{SFO} \rightarrow M_{SFO}$	12.3	40.8	8.8

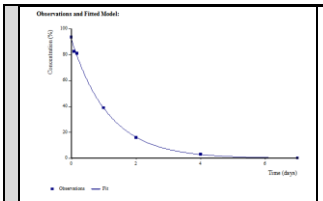
Table B.8.2.1.1-5 Fits on re-calculated hydrolysis *DT50* and *DT90* values for fenoxaprop-P-ethyl (AE F046360) and fenoxaprop-P-acid (AE F088406) at 25 °C (top) and 40 °C (bottom) - RMS AT assessment


25 °C - *p*H 4

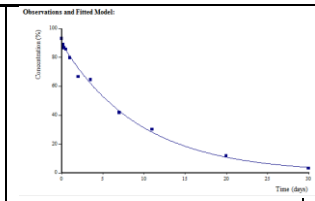

25 °C - *p*H 5


25 °C - *p*H 7

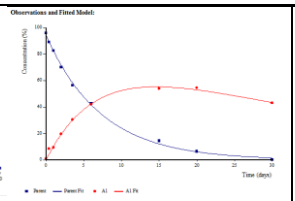

25 °C - *p*H 9



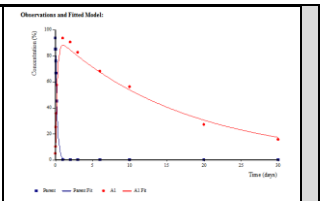
40 °C - *p*H 4



40 °C - *p*H 5



40 °C - *p*H 7



40 °C - *p*H 9

- Note that hydrolysis of fenoxaprop-P-ethyl (AE F046360) was also investigated in Fitzmaurice (2008) and Adam (2008). Despite the high standardisation of hydrolysis studies, results, particular at *p*H 7, are quite different (even between different labels used). On request by the RMS AT, the applicant could not give a sound explanation for these discrepancies.

Reference:	**Hoe 088406 (Fenoxaprop-P) [Metabolite of Hoe 046360 (Fenoxaprop-P-ethyl)]: Determination of the abiotic hydrolysis as a function of pH according to OECD Guideline #111 and EEC Guideline C.7.**
Author(s), year:	Schollmeier, M., Eyrich, U. (1993)
Report/Doc. Number:	A51145, M-132116-01-1
Guideline(s):	OECD 111 (1981)
GLP:	Yes
Validity:	Yes
Status:	**Previously submitted**

[The following study report is a copy/paste of the original text in the DAR for Annex I inclusion slightly amended in order to meet editorial settings and to improve readability]

Material and methods:

The abiotic hydrolysis of unlabelled fenoxaprop-P-acid (AE F088406, called Hoe 088406 in the study report, test concentration ~ 100 mg/L) was studied in sterile aqueous buffer solutions at *p*H 5, 7 and 9 at 50, 55 and 60 °C. The test samples were incubated in a water bath in the dark for up to 9 days. During the incubation time periodically, the *p*H of each buffer solution was recorded and test samples were taken and analysed by HPLC. Metabolites were identified by co-chromatography with authentic reference material. The rate of hydrolysis at more environmentally relevant temperatures (20 and 25 °C) and corresponding *DT50* values were estimated by the Arrhenius Equation.

Findings:

All test solutions remained sterile and the *p*H value of each buffer solution was constant during the test period. Mean recoveries ranged from 86.2 % (*p*H 9), 97.9 % (*p*H 7) to 103.7 % (*p*H 5) of initial concentration. For lower recoveries at *p*H 9 the following explanation was provided: the polarity of one degradation product (2-amino-5-chlorophenol) increased due to the acidification during the extraction step. This compound was no longer extractable and therefore could not be analysed by HPLC.

At all *p*H-values the formation of HOPP-acid (AE F096918, < 10 %) and chlorobenzoxazolone (AE F054014, max 37.7 %) was observed.

The rate of hydrolysis of fenoxaprop-P-acid (AE F088406) could be described by first-order reaction kinetics for all *p*H values and temperatures. From measurements at tested temperatures (50, 55 and 60 °C), the *DT50* values were extrapolated to 20 °C and 25 °C, respectively, by the Arrhenius equation.

Table B.8.2.1.1-6 Calculated *DT50* values for fenoxaprop-P-acid (AE F088406) assuming a first-order reaction kinetic and using the Arrhenius Equation

	***p*H 5**		***p*H 7**		***p*H 9**	
	20 °C	**25 °C**	**20 °C**	**25 °C**	**20 °C**	**25 °C**
***DT50* (d)**	43.1	26.8	319.6	182.7	66.2	33.5

Conclusion:

At *p*H 7 (temperature 20, 25 °C) the metabolite fenoxaprop-P-acid (AE F088406) is hydrolytically stable. The estimated *DT50* values are 319.6 d and 182.7 d. Under more acid (*p*H 5) and alkaline (*p*H 9) conditions, more rapid hydrolytic degradation was observed: *DT50* values of 43.1 d (*p*H 5) and 66.2 d (*p*H 9) were extrapolated at 20 °C. Identified degradation products were: chlorobenzoxazolone (AE F054014, max 37.7 %) and HOPP-acid (AE F096918, < 10 %).

Comments RMS AT:

- The study broadly follows OECD guideline 111 and is still considered reliable. However, in case of experiments conducted at 55 and 65 °C only three sampling points are available (with the exception of the 65 °C experiment at *p*H 9).

- The RMS AT re-calculated degradation half-lives at 50, 55 and 65 °C according to pertinent guidance applying SFO kinetics (CAKE 3.3, perfect fit in any case). Degradation rates at 25 and 40 °C were extrapolated applying the Arrhenius equation in line with OECD guideline 111. Results obtained are close to results given in the study report.

Table B.8.2.1.1-7 Re-calculated hydrolysis *DT50* and *DT90* values for fenoxaprop-P-acid (AE F088406) at 50, 55 and 65 °C and, following interpolation, at 25 and 40 °C - RMS AT assessment

Matrix	T (°C)	Kinetics	*DT50* (d)	*DT90* (d)	χ^2 error (%)
*p*H 5	50	SFO	2.9	9.7	3.6
	55	SFO	2.0	6.5	0.6
	65	SFO	0.9	3.1	3.9
	40[(a)]	SFO	6.9	22.7	na
	25[(a)]	**SFO**	**27.4**	**90.8**	**na**
*p*H 7	50	SFO	13.8	45.8	1.9
	55	SFO	9.9	32.9	1.9
	65	SFO	3.7	12.3	1.8
	40[(a)]	SFO	38.1	127	na
	25[(a)]	**SFO**	**189**	**627**	**na**
*p*H 7	50	SFO	1.7	5.5	3.4
	55	SFO	0.9	3.0	0.6
	65	SFO	0.3	1.1	2.3
	40[(a)]	SFO	5.2	17.4	na
	25[(a)]	**SFO**	**35.0**	**116**	**na**

(a) Interpolated applying the Arrhenius equation

- The study authors also investigated enantiomer composition (R/S ratio) of fenoxaprop-acid during hydrolysis, which was not reported in the study summary above. The enantiomeric composition (R/S ratio approx. 95/5, R = AE F088406, S = AE F088405) of the test substance was not altered during abiotic hydrolysis.

- Hydrolysis experiments conducted at 50 °C with varying buffer concentrations revealed the occurrence of slight buffer catalysis.

Reference:	**Hydrolysis of ^{14}C-AE F054014 at different pH values**
Author(s), year:	Burgener, A. (1999a)
Report/Doc. Number:	C003621, M-186478-01-1
Guideline(s):	OECD 111, 1981; EPA Guidelines OPPTS 835.2110 & 835.2130
GLP:	Yes
Validity:	Yes

Status:	**Previously submitted**

[The following study report is a copy/paste of the original text in the DAR for Annex I inclusion slightly amended in order to meet editorial settings and to improve readability]

Material and methods:

The abiotic hydrolysis of UL-chlorophenyl-^{14}C-labelled chlorobenzoxazolone (AE F054014, test concentration ~ 2 mg/L) was investigated in sterile aqueous buffer solutions at *p*H 4, 7, 9 at 50 °C and at *p*H 5, 7, 9 at 25 °C. The test samples were incubated in the dark in a water bath for up to 5 days (50 °C) and 30 days (25 °C). During the incubation time the *p*H of each buffer solution was recorded periodically and test samples were taken and analysed by LSC (determination of total radioactivity) and HPLC (determination of amounts of ^{14}C-chlorobenzoxazolone (AE F054014) and hydrolysis products).

Findings:

The *p*H values of buffer solutions were constant and all samples were sterile during the incubation. Mean recovery for each sampling time ranged from 99.1 % to 105.6 % of initial radioactivity. No degradation of chlorobenzoxazolone (AE F054014) was observed at 50 °C at *p*H 4, 7 and 9 and at 25 °C at *p*H 5, 7 and 9. Therefore the test substance was hydrolytically stable under test conditions.

Conclusion:

At a *p*H range from 4 - 9 (test temperature 25 and 50 °C) chlorobenzoxazolone (AE F054014) is hydrolytically stable. The extrapolated half-lives resulted in *DT50* values > 1 year.

Comments RMS AT:

- The study follows OECD guideline 111and is still considered reliable.

Reference:	**[^{14}C]-Fenoxaprop-P-ethyl: Hydrolytic degradation at pH 4, 7 and 9**
Author(s), year:	Fitzmaurice, M. (2008a)
Report/Doc. Number:	CX/05/001, M-344546-01-1
Guideline(s):	OECD 111, 2004; US EPA, Subdivision N 161-1, 1982; Japan MAFF 12 Nousan 8147, 2001
GLP:	Yes
Validity:	Yes
Status:	**New submission**

Executive Summary:

The hydrolysis of [UL-phenoxy-^{14}C]-fenoxaprop-P-ethyl (AE F046360) was investigated at a test concentration of 0.3 mg/L in sterile buffer solution of *p*H 4, 7 and 9 and at 25 °C and 40 °C for 30 days in maximum.

At the test temperature of 25 °C, hydrolysis of fenoxaprop-P-ethyl (AE F046360) resulted in half-lives of 4.3 days (*p*H 4), 110.7 days (*p*H 7) and 0.85 days (*p*H 9).

At this temperature, fenoxaprop-P-acid (AE F088406), the hydroxyphenoxy propanoic acid ethyl ester (AE F029062) and its successor following ester hydrolysis, HOPP-acid (AE F096918), were observed as major transformation products. Metabolite AE F029062 was observed under the abiotic conditions of the test only supporting the formation of this compound in its ester form. In contrast and as the result of investigations in microbiological active natural water, spontaneous ester hydrolysis was observed thus to form HOPP-acid (AE F096918). Considering this fact, AE F029062 is extremely unlikely to occur in a natural aquatic environment.

Based on the results of the study, abiotic hydrolysis may contribute to a limited extent the overall elimination of

fenoxaprop-P-ethyl from the aquatic environment.

Material and Methods:

Test Material: [UL-phenoxy-^{14}C]-fenoxaprop-P-ethyl (AE F046360)
Specific radioactivity: 5.84 MBq/mg (157.84 µCi/mg)
Radiochemical purity: > 98 %
Sample ID: BECH 1641

Aqueous buffer
The investigations were performed at three *p*H values using sterile aqueous buffer solutions of *p*H 4 (acetate), 7 (tris hydroxymethyl aminomethane) and 9 (borate) each at a concentration of 0.05 mol/L.

Experimental conditions
The test was performed at an initial concentration of 0.3 mg active substance/L thus corresponding to less than half the water solubility in sterile aqueous buffers. The final content of the co-solvent acetonitrile was < 0.9 %. The test vessels were incubated in the dark at 50 °C (pre-test) for five days and 25 °C or 40 °C for 30 days in maximum. The *p*H and sterility of the test solutions was determined at selected time points.

Sampling
Duplicate samples were removed for analysis at various sampling intervals.

Table B.8.2.1.1-8 Sampling intervals

Temperature	*p*H	Sampling Intervals (days)
25 °C	4	0, 0.2, 1, 2, 3, 7, 15, 25, 30
	7	0, 1, 5, 13, 23, 30
	9	0, 0.1, 0.2, 0.3, 1, 2, 3, 10, 16, 21, 29
40 °C	4	0, 1, 2, 7, 11, 15, 22, 30
	7	0, 9, 15, 21, 26, 30
	9	0, 0.06, 0.12, 0.18, 0.8, 1.85, 4, 14, 22, 30

Analytical procedures
The total radioactivity was determined by liquid scintillation counting (LSC) followed by reversed-phase HPLC and ^{14}C-flow-through detection techniques as primary analytical method for separation and quantitation of transformation products. HPLC-MS/MS was performed as confirmatory method for selected samples.

Kinetic evaluation
The rate of degradation was calculated for fenoxaprop-P-ethyl using the software KinGUI/MatLab Version 7.0.4.365.

Results and Discussion:

Determinations confirmed the stability of *p*H in buffer solutions and their sterility throughout the incubation.

At 25 °C, the material balance in terms of mean values of two replicates was 96.4 to 106.7 % AR at *p*H 4, 100.0 to 107.9 % at *p*H 7 and 100.0 to 105.0 % at *p*H 9. At 40 °C, the material balance was 99.9 to 109.5 % AR at *p*H 4, 100.0 to 108.0 % at *p*H 7 and 96.9 to 107.6 % at *p*H 9.

Transformation of the test substance at 25 °C
At a *p*H of 4, the test substance declined from 98.5 % at day zero to 1.3 % after 30 days of incubation. At a *p*H of 7, the decline of the test substance was from 98.8 % at day zero to 80.4 % after 30 days of incubation. For a *p*H of 9, the decline was from 98.3 % at day zero to below the LOD after 30 days of incubation.

At a *p*H of 4, the hydroxyphenoxy propanoic acid ethyl ester AE F029062 was observed as the only major hydrolysis product at 101.2 % in maximum after 30 days triggering formally further assessment in environmental exposure assessment. However, the abiotic conditions of the test should be considered supporting the formation of this compound in its ester form. In contrast and as the result of investigations in microbiological active natural water, rapid ester hydrolysis was always observed to occur spontaneously and thus to form HOPP-

acid (AE F096918). Considering this fact, AE F029062 is extremely unlikely to occur in a natural aquatic environment.

At a *p*H of 7, fenoxaprop-P-acid (AE F088406) was observed as the only major transformation product at 12.6 % in maximum after 30 days.

At a *p*H of 9, fenoxaprop-P-acid (AE F088406) and HOPP-acid (AE F096918) were observed as major transformation products at 95.6 % and 14.2 % after 10 days and 30 days of incubation, respectively.

Transformation of the test substance at 40 °C
At a *p*H of 4, the test substance declined from 98.9 % at day zero to below the LOD after 15 days of incubation. At a *p*H of 7, the decline of the test substance was from 99.3 % at day zero to 58.1 % after 30 days of incubation. For a *p*H of 9, the decline was from 99.4 % at day zero to below the LOD after 1.85 days of incubation.

At a *p*H of 4, the hydroxyphenoxy propanoic acid ethyl ester AE F029062 was observed as the only major hydrolysis product at 98.6 % in maximum after 15 days triggering formally further assessment in environmental exposure assessment with arguments for non-inclusion given under the results reported for 25°C.

At a *p*H of 7, fenoxaprop-P-acid (AE F088406) and AE F029062 were observed as major transformation products at 24.1 % and 11.9 % AR in maximum each after 30 days.

At a *p*H of 9, fenoxaprop-P-acid (AE F088406) and HOPP-acid (AE F096918) were observed as major transformation products at 89.1 % (day 0.83/0.94) and 46.8 % after 30 days of incubation. In addition, a 'dimer' compound of HOPP-acid was formed lately in the tests at 10.6 % in maximum after 30 days of incubation.

All other fractions at the three *p*H values detected were minor, none individually exceeding 5 % AR for an individual component.

Table B.8.2.1.1-9 Transformation of [UL-phenoxy-^{14}C]-fenoxaprop-P-ethyl (AE F046360) in sterile aqueous buffer of *p*H 4 at 25 °C

Component	Rep. No.	Sampling interval (days) 0	0.21	1	2	3	7	15	25	30
Fenoxaprop-P-ethyl (AE F046360)	1	97.7	96.3	85.9	71.2	60.2	33.0	10.5	2.4	1.4
	2	99.3	97.2	86.9	70.5	56.6	33.0	10.6	3.3	1.2
	mean	**98.5**	**96.8**	**86.4**	**70.9**	**58.4**	**33.0**	**10.5**	**2.8**	**1.3**
Fenoxaprop-P-acid (AE F088406)	1	n.d.	n.d.	n.d.	n.d.	0.0	0.5	0.0	n.d.	n.d.
	2	n.d.	n.d.	n.d.	n.d.	0.5	0.3	0.2	n.d.	n.d.
	mean	**n.a.**	**n.a.**	**n.a.**	**n.a.**	**0.2**	**0.4**	**0.1**	**n.a.**	**n.a.**
AE F029062	1	1.3	2.8	12.8	26.4	35.8	66.9	90.5	97.9	101.4
	2	1.3	2.9	13.6	26.9	39.7	64.7	88.2	98.7	101.1
	mean	**1.3**	**2.9**	**13.2**	**26.7**	**37.8**	**65.8**	**89.3**	**98.3**	**101.2**
HOPP-acid (AE F096918)	1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.2	0.5	1.2
	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.5	1.7	1.5
	mean	**n.a.**	**n.a.**	**n.a.**	**n.a.**	**n.a.**	**n.a.**	**1.3**	**1.1**	**1.4**
Unknown[(a)]	1	0.5	1.4	3.3	4.4	5.0	4.3	1.7	1.0	n.d.
	2	0.2	1.0	3.3	4.8	5.3	4.3	1.5	0.4	n.d.
	mean	**0.4**	**1.2**	**3.3**	**4.6**	**5.1**	**4.3**	**1.6**	**0.7**	**n.a.**
Total radioactivity	1	99.4	100.5	102.0	102.0	101.1	104.7	103.9	101.7	104.0
	2	100.8	101.2	103.8	102.2	102.1	102.3	101.9	104.1	103.8
	mean	**100.1**	**100.9**	**102.9**	**102.1**	**101.6**	**103.5**	**102.9**	**102.9**	**103.9**

n.a. = not applicable
n.d. = not detected
(a) Reported as 'Unidentified 7'
Values expressed as percentage of total applied radioactivity (AR)

Table B.8.2.1.1-10 Transformation of [UL-phenoxy-^{14}C]-fenoxaprop-P-ethyl (AE F046360) in sterile aqueous buffer of *p*H 4 at 40 °C

Component	Rep. No.	Sampling interval (days) 0	1	2	7	11	15	22	30
Fenoxaprop-P-ethyl	1	98.7	50.5	34.1	3.0	n.d.	n.d.	n.d.	n.d.

(AE F046360)	2	99.0	52.2	35.6	2.9	0.6	n.d.	n.d.	n.d.
	mean	**98.9**	**51.4**	**34.9**	**2.9**	**0.3**	**n.a.**	**n.a.**	**n.a.**
Fenoxaprop-P-acid (AE F088406)	1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	2.6	n.d.
	2	n.d.	n.d.	n.d.	n.d.	n.d.	1.6	2.6	n.d.
	mean	**n.a.**	**n.a.**	**n.a.**	**n.a.**	**n.a.**	**0.8**	**2.5**	**n.a.**
AE F029062	1	1.4	43.5	63.0	94.7	96.9	97.3	95.0	91.5
	2	1.3	43.4	61.0	98.1	98.2	99.8	94.2	89.3
	mean	**1.3**	**43.5**	**62.0**	**96.4**	**97.5**	**98.6**	**94.6**	**90.4**
HOPP-acid (AE F096918)	1	n.d.	n.d.	n.d.	n.d.	0.0	1.0	0.8	0.7
	2	n.d.	n.d.	n.d.	n.d.	0.6	0.9	1.4	0.5
	mean	**n.a.**	**n.a.**	**n.a.**	**n.a.**	**0.3**	**0.9**	**1.1**	**0.6**
Unknown[(a)]	1	n.d.	2.3	1.9	1.2	2.4	1.5	2.0	6.0
	2	n.d.	2.8	1.4	1.0	2.5	1.4	1.3	9.3[(b)]
	mean	**n.a.**	**2.6**	**1.6**	**1.1**	**2.4**	**1.5**	**1.7**	**7.7[(b)]**
Total radioactivity	1	100.1	96.3	99.0	99.0	99.3	99.8	100.3	98.3
	2	100.3	98.4	98.0	102.0	101.8	103.7	99.6	99.0
	mean	**100.2**	**97.4**	**98.5**	**100.5**	**100.5**	**101.8**	**99.9**	**98.7**

n.a. = not applicable
n.d. = not detected
(a) Includes unknowns reported as 'Unidentified 1, 3 and 7' and the phenol metabolite (AE F040356), all at a maximum at or below 3.9 % AR in the course of the study
(b) Corrected by RMS AT
Values expressed as percentage of total applied radioactivity (AR)

Table B.8.2.1.1-11 Transformation of [UL-phenoxy-^{14}C]-fenoxaprop-P-ethyl (AE F046360) in sterile aqueous buffer of *p*H 7 at 25 °C

Component	Rep. No.	Sampling interval (days) 0	1	5	13	23	30
Fenoxaprop-P-ethyl (AE F046360)	1	98.1	92.9	94.6	88.7	84.4	79.9
	2	99.5	94.1	94.8	90.7	82.6	80.8
	mean	**98.8**	**93.5**	**94.7**	**89.7**	**83.5**	**80.4**
Fenoxaprop-P-acid (AE F088406)	1	n.d.	0.6	2.2	6.1	9.5	13.7
	2	n.d.	0.9	1.9	5.2	11.6	11.5
	mean	**n.a.**	**0.7**	**2.0**	**5.6**	**10.6**	**12.6**
AE F029062	1	1.7	1.3	1.9	2.4	3.0	3.1
	2	1.7	1.7	2.4	2.2	3.0	3.3
	mean	**1.7**	**1.5**	**2.1**	**2.3**	**3.0**	**3.2**
HOPP-acid (AE F096918)	1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	mean	**n.a.**	**n.a.**	**n.a.**	**n.a.**	**n.a.**	**n.a.**
Unknown[(a)]	1	0.5[(b)]	0.9[(b)]	0.8[(b)]	1.2[(b)]	1.2[(b)]	1.7[(b)]
	2	0.0[(b)]	0.7[(b)]	1.1[(b)]	1.4[(b)]	1.4[(b)]	1.8[(b)]
	mean	**0.2[(b)]**	**0.8[(b)]**	**0.9[(b)]**	**1.3[(b)]**	**1.3[(b)]**	**1.8[(b)]**
Total radioactivity	1	100.2	95.7	99.4	98.5	98.2	98.5
	2	101.2	97.4	100.2	99.5	98.6	97.4
	mean	**100.7**	**96.5**	**99.8**	**99.0**	**98.4**	**97.9**

n.a. = not applicable
n.d. = not detected
(a) Includes unknowns reported as 'Unidentified 7, 8 and 9', all at a maximum at or below 1.8 % AR in the course of the study
(b) Corrected by the RMS AT
Values expressed as percentage of total applied radioactivity (AR)

Table B.8.2.1.1-12 Transformation of [UL-phenoxy-^{14}C]-fenoxaprop-P-ethyl (AE F046360) in sterile aqueous buffer of *p*H 7 at 40 °C

Component	Rep. No.	Sampling interval (days) 0	9	15	21	26	30
Fenoxaprop-P-ethyl (AE F046360)	1	98.4	80.6	75.0	64.7	58.4	54.8
	2	100.1	80.2	72.0	64.9	60.7	61.3
	mean	**99.3**	**80.4**	**73.5**	**64.8**	**59.6**	**58.1**
Fenoxaprop-P-acid (AE F088406)	1	n.d.	8.7	13.6	19.7	21.5	25.6
	2	n.d.	9.2	13.6	18.1	22.4	22.5
	mean	**n.a.**	**9.0**	**13.6**	**18.9**	**22.0**	**24.1**
AE F029062	1	0.9	4.8	6.8	8.7	11.7	12.6
	2	0.8	4.8	7.9	8.4	10.1	11.1

	mean	**0.9**	**4.8**	**7.3**	**8.5**	**10.9**	**11.9**
HOPP-acid (AE F096918)	1	n.d.	n.d.	0.9	1.9	2.6	3.7
	2	n.d.	n.d.	1.0	2.4	2.7	3.0
	mean	**n.a.**	**n.a.**	**1.0**	**2.1**	**2.7**	**3.4**
Unknown[(a)]	1	n.d.	0.9	1.4	2.1	3.4[(b)]	2.8
	2	n.d.	1.6	1.2	2.1	2.4	2.4
	mean	**n.a.**	**1.2**	**1.3**	**2.1**	**2.9[(b)]**	**2.6**
Total radioactivity	1	99.4	95.0	97.6	97.2	97.7	99.5
	2	100.9	95.8	95.8	95.8	98.3	100.3
	mean	**100.2**	**95.4**	**96.7**	**96.5**	**98.0**	**99.9**

n.a. = not applicable
n.d. = not detected
(a) Includes unknowns reported as 'Unidentified 7, 8 and 9', all at maximum at or below 2.6 % AR in the course of the study
(b) Corrected by the RMS AT
Values expressed as percentage of total applied radioactivity (AR)

Table B.8.2.1.1-13 Transformation of [UL-phenoxy-^{14}C]-fenoxaprop-P-ethyl (AE F046360) in sterile aqueous buffer of *p*H 9 at 25 °C

Component	Rep. No.	Sampling interval (days) 0	0.11	0.21	0.32	1	2	3	10	16	21	29
Fenoxaprop-P-ethyl (AE F046360)	1	100.8	88.3	85.4	79.5	43.9	17.1	10.5	n.d.	n.d.	n.d.	n.d.
	2	95.7	85.0	84.4	76.3	44.9	13.4	12.4	n.d.	n.d.	n.d.	n.d.
	mean	**98.3**	**86.7**	**84.9**	**77.9**	**44.4**	**15.2**	**11.4**	**n.a.**	**n.a.**	**n.a.**	**n.a.**
Fenoxaprop-P-acid (AE F088406)	1	0.0	8.5	12.5	18.8	56.6	80.4	84.9	95.3	92.4	85.0	85.2
	2	2.1	9.3	14.5	20.2	53.1	83.2	85.3	95.9	90.3	85.6	85.5
	mean	**1.0**	**8.9**	**13.5**	**19.5**	**54.9**	**81.8**	**85.1**	**95.6**	**91.3**	**85.3**	**85.3**
AE F029062	1	1.4	1.4	1.0	0.0	0.5	0.0	1.2	0.2	n.d.	n.d.	n.d.
	2	2.7	1.3	0.4	1.1	1.1	0.7	0.0	0.3	n.d.	n.d.	n.d.
	mean	**2.1**	**1.3**	**0.7**	**0.5**	**0.8**	**0.3**	**0.6**	**0.3**	**n.a.**	**n.a.**	**n.a.**
HOPP-acid (AE F096918)	1	n.d.	n.d.	n.d.	n.d.	n.d.	1.1	2.2	6.5	8.2	11.3	14.5
	2	n.d.	n.d.	n.d.	n.d.	n.d.	2.4	1.3	5.1	9.2	11.2	13.8
	mean	**n.a.**	**n.a.**	**n.a.**	**n.a.**	**n.a.**	**1.7**	**1.7**	**5.8**	**8.7**	**11.3**	**14.2**
Unknown[(a)]	1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	2	1.2[(b)]	0.9[(b)]	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	mean	**0.6[(b)]**	**0.5[(b)]**	**n.a.**	**n.a.**	**n.a.**	**n.a.**	**n.a.**	**n.a.**	**n.a.**	**n.a.**	**n.a.**
Total radioactivity	1	102.3	98.2	98.9	98.3	101.0	98.6	98.7	102.0	100.6	96.3	99.7
	2	101.6	96.5	99.3	97.6	99.1	99.6	99.0	101.3	99.4	96.9	99.3
	mean	**101.9**	**97.3**	**99.6**	**98.0**	**100.1**	**99.1**	**98.9**	**101.7**	**100.0**	**96.6**	**99.5**

n.a. = not applicable
n.d. = not detected
(a) Includes unknown reported as 'Unidentified 8' at a maximum at or below 0.6 % AR in the course of the study
(b) Corrected by the RMS AT
Values expressed as percentage of total applied radioactivity (AR)

Table B.8.2.1.1-14 Transformation of [UL-phenoxy-^{14}C]-fenoxaprop-P-ethyl (AE F046360) in sterile aqueous buffer of *p*H 9 at 40 °C

Component	Rep. No.	Sampling interval (days) 0	0.06	0.12/ 0.13	0.18/ 0.19	0.83/ 0.94	1.85	4	14	22	30
Fenoxaprop-P-ethyl (AE F046360)	1	99.0	75.5	63.9	48.8	6.2	n.d.	n.d.	n.d.	n.d.	n.d.
	2	99.9	76.2	62.4	51.0	4.6	0.6	n.d.	n.d.	n.d.	n.d.
	mean	**99.4**	**75.8**	**63.1**	**49.9**	**5.4**	**0.3**	**n.a.**	**n.a.**	**n.a.**	**n.a.**
Fenoxaprop-P-acid (AE F088406)	1	n.d.	19.5	33.4	46.5	90.1	89.8	82.9	57.1	37.5	27.4
	2	n.d.	18.7	33.2	45.2	88.1	87.6	83.3	54.7	38.4	28.5
	mean	**n.a.**	**19.1**	**33.3**	**45.8**	**89.1**	**88.7**	**83.1**	**55.9**	**38.0**	**27.9**
AE F029062	1	n.d.	0.6	1.4	1.5	0.8	n.d.	n.d.	n.d.	n.d.	n.d.
	2	n.d.	1.1	1.5	2.0	0.0	n.d.	n.d.	n.d.	n.d.	n.d.
	mean	**n.a.**	**0.9**	**1.4**	**1.7**	**0.4**	**n.a.**	**n.a.**	**n.a.**	**n.a.**	**n.a.**
AE F096918-dimer	1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	3.4	8.6	10.8
	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	3.6	7.6	10.4
	mean	**n.a.**	**n.a.**	**n.a.**	**n.a.**	**n.a.**	**n.a.**	**n.a.**	**3.5**	**8.1**	**10.6**
HOPP-acid (AE F096918)	1	n.d.	n.d.	n.d.	0.0	4.4	9.3	16.0	36.9	45.9	45.7
	2	n.d.	n.d.	n.d.	0.8	5.0	9.3	15.7	38.9	45.4	47.8

	mean	**n.a.**	**n.a.**	**n.a.**	**0.4**	**4.7**	**9.2**	**15.9**	**37.9**	**45.6**	**46.8**
Unknown[(a)]	1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.8	7.7	10.7
	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.7	7.0	10.3
	mean	**n.a.**	**n.a.**	**n.a.**	**n.a.**	**n.a.**	**n.a.**	**n.a.**	**1.7**	**7.3**	**10.4**
Total radioactivity	1	99.0	95.6	98.6	96.8	101.5	99.1	99.0	99.2	99.7	94.6
	2	99.9	95.9	97.1	98.9	97.6	97.2	99.0	98.9	98.3	96.9
	mean	**99.4**	**95.8**	**97.9**	**97.8**	**99.6**	**98.1**	**99.0**	**99.1**	**99.0**	**95.8**

n.a. = not applicable
n.d. = not detected
(a) Includes unknowns reported as 'Unidentified 1, 2, 5 and 6', all at a maximum at or below 5.0 % AR in the course of the study
Values expressed as percentage of total applied radioactivity (AR)

Table B.8.2.1.1-15 Transformation products of ^{14}C-fenoxaprop-P-ethyl (AE F046360) following incubation in sterile aqueous buffer solution of *p*H 4, 7 and 9 at 25 °C

Label position	Component	*p*H	Maximum fraction (% AR)	Maximum occurrence by day[(a)]
UL-phenoxy	Fenoxaprop-P-acid (AE F088406)	4	0.4	7
		7	12.6	30
		9	95.6	10
	AE F029062	4	101.2	30
		7	3.2	30
		9	2.1	0
	HOPP-acid (AE F096918)	4	1.3	15
		7	-	-
		9	14.2	29
	AE F096918-dimer	4	-	-
		7	-	-
		9	-	-

(a) Total duration was 30 days

Table B.8.2.1.1-16 Transformation products of ^{14}C-fenoxaprop-P-ethyl (AE F046360) following incubation in sterile aqueous buffer solution of *p*H 4, 7 and 9 at 40 °C

Label position	Component	*p*H	Maximum fraction (% AR)	Maximum occurrence after days[(a)]
UL-phenoxy	Fenoxaprop-P-acid (AE F088406)	4	2.5	22
		7	24.1	30
		9	89.1	0.83/0.94
	AE F029062	4	98.6	15
		7	11.9	30
		9	1.7	0.18/0.19
	HOPP-acid (AE F096918)	4	1.1	22
		7	3.4	30
		9	46.8	30
	AE F096918-dimer	4	-	-
		7	-	-
		9	10.6	30

(a) Total duration was 30 days

Hydrolysis rates were calculated for fenoxaprop-P-ethyl (AE F046360) by applying simple first-order as kinetic model.

Table B.8.2.1.1-17 Single first-order kinetics of hydrolytic degradation of fenoxaprop-P-ethyl (AE F046360) in sterile buffer solutions of *p*H 4, 7 and 9 at 25 °C

Compound		*p*H 4	*p*H 7	*p*H 9
Fenoxaprop-P-ethyl	*DT50* (days)	4.31	110.7	0.85
(AE F046360)	*DT90* (days)	14.32	367.6	2.83

Table B.8.2.1.1-18 Single first-order kinetics of hydrolytic degradation of fenoxaprop-P-ethyl (AE F046360) in sterile buffer solutions of *p*H 4, 7 and 9 at 40 °C

Compound		*p*H 4	*p*H 7	*p*H 9
Fenoxaprop-P-ethyl	*DT50* (days)	1.22	37.0	0.19
(AE F046360)	*DT90* (days)	4.07	122.8	0.62

Conclusion:

At the environmentally relevant test temperature of 25 °C, fenoxaprop-P-ethyl (AE F046360) was hydrolysed in sterile aqueous buffer solution of *p*H 4, 7 and 9 to result in half-lives of 4.3 days (*p*H 4), 110.7 days (*p*H 7) and 0.85 days (*p*H 9).

At the same temperature, fenoxaprop-P-acid (AE F088406), the hydroxyphenoxy propanoic acid ethyl ester AE F029062 and its successor following ester hydrolysis, HOPP-acid (AE F096918), were observed as major transformation products.

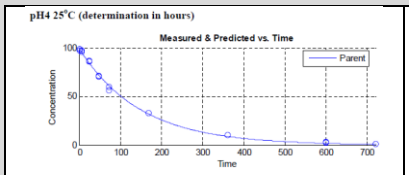
AE F029062 was observed under the abiotic conditions of the test only supporting the formation of this compound in its ester form. In contrast and as the result of investigations in microbiological active natural water, spontaneous ester hydrolysis was observed thus to form HOPP-acid (AE F096918). Considering this fact, AE F029062 is extremely unlikely to occur in a natural aquatic environment.

Based on the results of the study, abiotic hydrolysis may contribute to a limited extent the overall elimination of fenoxaprop-P-ethyl from the aquatic environment.

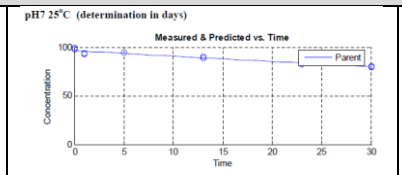
Comments RMS AT:

- The study follows OECD guideline 111 and is considered reliable.
- Dissipation fits are not included in the applicant summary. Therefore this information is provided here:

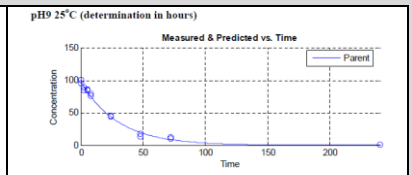
Table B.8.2.1.1-19 Dissipation fits for fenoxaprop-P-ethyl (AE F046360) at 25 and 40 °C obtained by the applicant and agreed by the RMS AT



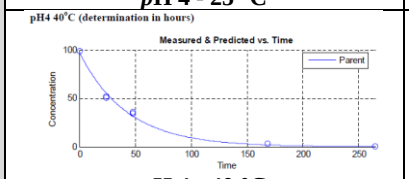
***p*H 4 - 25 °C**



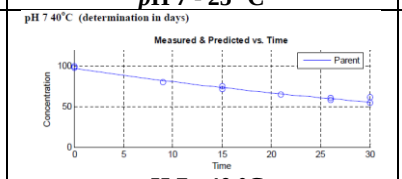
***p*H 7 - 25 °C**



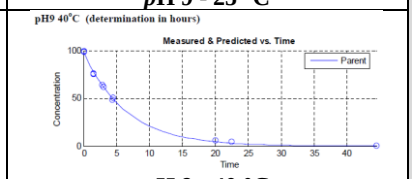
***p*H 9 - 25 °C**



***p*H 4 - 40 °C**



***p*H 7 - 40 °C**



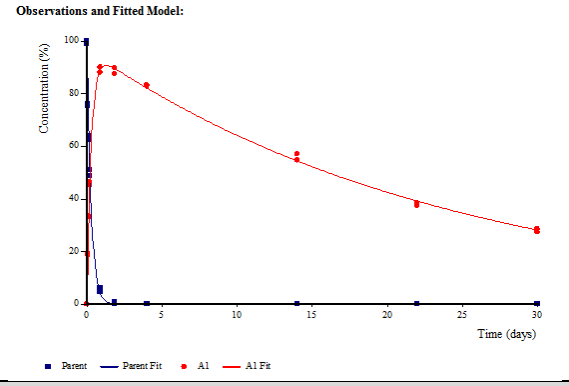
***p*H 9 - 40 °C**

- Residue data at *p*H 9 and 40 °C allow for hydrolysis rates to be calculated for fenoxaprop-P-acid (AE F088406) as well. Thus these data where re-assessed by the RMS AT applying a $P_{SFO} \rightarrow M_{SFO}$ degradation pathway fit in line with pertinent guidance (applying CAKE 3.3).

Table B.8.2.1.1-20 Re-calculated hydrolysis *DT50* and *DT90* values for fenoxaprop-P-ethyl (AE F046360) and fenoxaprop-P-acid (AE F088406) at *p*H 9 and 40 °C - RMS AT assessment

Matrix	Substance	Kinetics	*DT50* (d)	*DT90* (d)	χ^2 error (%)
***p*H 9, 40 °C**	Fenoxaprop-P-ethyl (AE F046360)	$P_{SFO} \rightarrow M_{SFO}$	0.2	0.6	3.3
	Fenoxaprop-P-acid (AE F088406)	$P_{SFO} \rightarrow M_{SFO}$	16.9	56.0	1.3

Table B.8.2.1.1-21 Dissipation fits for fenoxaprop-P-ethyl (AE 046360) and fenoxaprop-P-acid (AE F088406) at pH 9 at 40 °C - RMS AT assessment



- As already indicated in Van der Gaauw (2002) results on hydrolysis of fenoxaprop-P-ethyl (AE F046360) investigated in Van der Gaauw (2002), Adam (2008) and in this study are somehow deviating for unknown reasons.

Reference:	**[^{14}C]-fenoxaprop-P-ethyl - Hydrolysis at three different pH values**
Author(s), year:	Adam, D. (2008)
Report/Doc. Number:	244 FPE, M-548135-01-1
Guideline(s):	OECD Guideline 111, 2004; Directive 92/69/EEC Part C.7; EPA Guideline OPPTS 835.2110
GLP:	Yes
Validity:	Yes
Status:	**New submission**

Executive Summary:

The hydrolysis of [UL-chlorophenyl-^{14}C]-fenoxaprop-P-ethyl (AE F046360) was investigated at a test concentration of 0.22 mg/L in sterile buffer solution of *p*H 4, 7 and 9 and at 25 °C and 40 °C for 30 days in maximum.

At the test temperature of 25 °C, fenoxaprop-P-ethyl (AE F046360) was hydrolysed in sterile aqueous buffer solution of *p*H 4, 7 and 9 to result in half-lives of 2.1 days (*p*H 4), 8.6 days (*p*H 7) and 0.7 days (*p*H 9).

At the same temperature, fenoxaprop-P-acid (AE F088406) and chlorobenzoxazolone (AE F054014) were observed as major transformation products.

Fenoxaprop-P-acid (AE F088406) was hydrolysed in sterile aqueous buffer solution of *p*H 4 and 9 to result in half-lives of 2.5 days at *p*H 4 and 12.7 days at *p*H 9. No half-lives were calculated at *p*H 7 for fenoxaprop-P-acid (AE F088406) since the compound was hydrolytically stable at this *p*H.

Chlorobenzoxazolone (AE F054014) was stable to abiotic hydrolysis at all *p*H.

Based on the results of the study, abiotic hydrolysis may contribute to a limited extent the overall elimination of fenoxaprop-P-ethyl (AE F046360) from the aquatic environment.

Material and Methods:

Test Material:	[UL-chlorophenyl-^{14}C]-fenoxaprop-P-ethyl (AE F046360)
Specific radioactivity:	6.96 MBq/mg (188.11 µCi/mg)
Radiochemical purity:	95.9 % (HPLC)

Sample ID: 2382MFO014-3

Aqueous buffer
Investigations were performed in sterile aqueous buffer solutions of *p*H 4 (citrate), 7 (phosphate) and 9 (borate) at a concentration of buffer solutions of 0.05 mol/L.

Experimental conditions
The test was performed at an initial concentration of 0.22 mg active substance/L thus corresponding to less than half the water solubility in sterile aqueous buffers. The final content of the co-solvent acetonitrile was 1.0 %. The test vessels containing 10 mL buffer solution each were incubated in the dark at 50 °C (pretest) for five days and 25 °C or 40 °C for 30 days in maximum. The *p*H and sterility of the test solutions was determined each at the start and at the end of the incubation period.

Sampling
Duplicate samples were removed for analysis at various sampling intervals.

Table B.8.2.1.1-22 Sampling dates

Temperature	pH	Intervals (days)
25 °C	4	0, 0.33, 1, 2, 7, 15, 30
	7	0, 2, 4, 8, 24, 30
	9	0, 0.25, 1, 2, 4, 15, 30
40 °C	4	0, 0.16, 1, 2, 15, 30
	7	0, 1, 2, 4, 15, 30
	9	0, 0.04, 0.08, 1, 7, 30

Analytical procedures
The total radioactivity was determined by liquid scintillation counting (LSC) followed by reversed-phase HPLC and ^{14}C-flow-through detection techniques as primary analytical method for separation and quantitation of transformation products. Thin-layer chromatography (TLC) was performed as confirmatory method for selected samples. The limit of detection (LOD) was 0.4 % AR.

Kinetic evaluation
The rate of degradation was calculated for fenoxaprop-P-ethyl (AE F046360) and its major transformation product fenoxaprop-P-acid (AE F088406) by non-linear curve fitting using the software MicroCal Origin (version 6.1, MicroCal Software Inc./USA).

Results and Discussion:

Determinations confirmed the stability of *p*H in buffer solutions and their sterility throughout the incubation.

At 25 °C, the material balance in terms of mean values of two replicates was 96.4 to 106.7 % AR at *p*H 4, 100.0 to 107.9 % at *p*H 7 and 100.0 to 105.0 % at *p*H 9. At 40 °C, the material balance was 99.9 to 109.5 % AR at *p*H 4, 100.0 to 108.0 % at *p*H 7 and 96.9 to 107.6 % at *p*H 9.

Transformation of the test substance at 25 °C
At a *p*H of 4, the test substance declined from 96.2 % at day zero to below the LOD after 30 days of incubation. At a *p*H of 7, the decline of the test substance was from 95.7 % at day zero to below the LOD after 24 days of incubation. For a *p*H of 9, the decline was from 95.3 % at day zero to below the LOD after 15 days of incubation.

At a *p*H of 4, fenoxaprop-P-acid (AE F088406) and chlorobenzoxazolone (AE F054014) were observed as major hydrolysis products at 22.2 % (day 1) and at 102.4 % (day 15) in maximum.

At a *p*H of 7, fenoxaprop-P-acid (AE F088406) and chlorobenzoxazolone (AE F054014) were observed as major hydrolysis products at 84.4 % (day 24) and at 27.9 % (day 30) in maximum.

At a *p*H of 9, fenoxaprop-P-acid (AE F088406) and chlorobenzoxazolone (AE F054014) were observed as major hydrolysis products at 89.4 % (day 4) and at 24.5 % (day 30) in maximum.

Transformation of the test substance at 40 °C

At a *p*H of 4, the test substance declined from 96.2 % at day zero to below the LOD after 15 days of incubation. At a *p*H of 7, the decline of the test substance was from 95.7 % at day zero to 1.9 % after 30 days of incubation. For a *p*H of 9, the decline was from 95.3 % at day zero to below the LOD after 7 days of incubation.

At a *p*H of 4, fenoxaprop-P-acid (AE F088406) and chlorobenzoxazolone (AE F054014) were observed as major hydrolysis products at 32.8 % (day 0.16) and at 109.5 % (day 15) in maximum.

At a *p*H of 7, fenoxaprop-P-acid (AE F088406) and chlorobenzoxazolone (AE F054014) were observed as major hydrolysis products at 61.3 % (day 15) and at 54.0 % (day 30) in maximum.

At a *p*H of 9, fenoxaprop-P-acid (AE F088406) and chlorobenzoxazolone (AE F054014) were observed as major hydrolysis products at 87.0 % (day 1) and at 78.3 % (day 30) in maximum.

For the two temperatures tested all other fractions at the three *p*H values detected were minor, none individually exceeding 8.9 % AR for an individual component.

Table B.8.2.1.1-23 Transformation of [UL-chlorophenyl-^{14}C]-fenoxaprop-P-ethyl (AE F046360) in sterile aqueous buffer of *p*H 4 at 25 °C

Component	Rep. No.	Sampling interval (days) 0	0.33	1	2	7	15	30
Fenoxaprop-P-ethyl (AE F046360)	1	96.9	73.8	46.6	45.5	16.1	4.1	n.d.
	2	95.5	68.8	59.0	45.6	18.6	4.5	n.d.
	mean	**96.2**	**71.3**	**52.8**	**45.5**	**17.4**	**4.3**	**n.a.**
Chlorobenzoxazolone (AE F054014)	1	3.8	10.5	26.3	41.5	81.5	102.6	95.8
	2	3.8	13.3	25.4	41.8	81.3	102.3	96.9
	mean	**3.8**	**11.9**	**25.8**	**41.7**	**81.4**	**102.4**	**96.3**
Fenoxaprop-P-acid (AE F088406)	1	n.d.	16.9	29.3	15.1	4.7	n.d.	n.d.
	2	n.d.	18.6	15.2	17.3	4.7	n.d.	n.d.
	mean	**n.a.**	**17.7**	**22.2**	**16.2**	**4.7**	**n.a.**	**n.a.**
Unknown[(a)]	1	n.d.	1.3	n.d.	n.d.	n.d.	n.d.	n.d.
	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	mean	**n.a.**	**0.7**	**n.a.**	**n.a.**	**n.a.**	**n.a.**	**n.a.**
Total radioactivity in solution	1	100.7	102.6	102.2	102.1	102.3	106.7	95.8
	2	99.3	100.7	99.5	104.7	104.6	106.7	96.9
	mean	**100.0**	**101.7**	**100.9**	**103.4**	**103.5**	**106.7**	**96.4**

n.a. = not applicable
n.d. = not detected
(a) Reported as 'M4'
All values expressed as percentage of total applied radioactivity (AR)

Table B.8.2.1.1-24 Transformation of [UL-chlorophenyl-^{14}C]-fenoxaprop-P-ethyl (AE F046360) in sterile aqueous buffer of *p*H 4 at 40 °C

Component	Rep. No.	Sampling interval (days) 0	0.16	1	2	15	30
Fenoxaprop-P-ethyl (AE F046360)	1	96.9	45.9	33.6	14.2	n.d.	n.d.
	2	95.5	45.9	36.3	15.7	n.d.	n.d.
	mean	**96.2**	**45.9**	**35.0**	**14.9**	**n.a.**	**n.a.**
Chlorobenzoxazolone (AE F054014)	1	3.8	21.7	63.2	82.4	110.2	101.4
	2	3.8	20.6	63.6	81.3	108.8	100.5
	mean	**3.8**	**21.1**	**63.4**	**81.8**	**109.5**	**100.9**
Fenoxaprop-P-acid (AE F088406)	1	n.d.	30.9	10.2	5.2	n.d.	n.d.
	2	n.d.	34.8	8.5	4.9	n.d.	n.d.
	mean	**n.a.**	**32.8**	**9.4**	**5.0**	**n.a.**	**n.a.**
Total radioactivity in solution	1	100.7	98.5	107.0	101.8	110.2	101.4
	2	99.3	101.3	108.4	101.8	108.8	100.5
	mean	**100.0**	**99.9**	**107.7**	**101.8**	**109.5**	**101.0**

n.a. = not applicable
n.d. = not detected
All values expressed as percentage of total applied radioactivity (AR)

Table B.8.2.1.1-25 Transformation of [UL-chlorophenyl-^{14}C]-fenoxaprop-P-ethyl (AE F046360) in sterile aqueous buffer of *pH* 7 at 25 °C

Component	Rep. No.	Sampling interval (days) 0	2	4	8	24	30
Fenoxaprop-P-ethyl (AE F046360)	1	95.1	91.4	74.2	52.2	n.d.	n.d.
	2	96.2	89.0	79.3	58.4	n.d.	n.d.
	mean	**95.7**	**90.2**	**76.7**	**55.3**	**n.a.**	**n.a.**
Chlorobenzoxazolone (AE F054014)	1	4.0	6.9	8.4	27.1	24.1	33.5
	2	4.7	7.0	8.7	18.0	22.7	22.4
	mean	**4.3**	**6.9**	**8.6**	**22.5**	**23.4**	**27.9**
Fenoxaprop-P-acid (AE F088406)	1	n.d.	4.9	17.9	27.1	84.1	66.6
	2	n.d.	4.5	13.8	28.6	84.8	77.7
	mean	**n.a.**	**4.7**	**15.8**	**27.9**	**84.4**	**72.2**
Unknown[(a)]	1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	2	n.d.	n.d.	n.d.	1.9	n.d.	n.d.
	mean	**n.a.**	**n.a.**	**n.a.**	**0.9**	**n.a.**	**n.a.**
Total radioactivity in solution	1	99.1	103.2	100.5	106.4	108.2	100.1
	2	100.9	100.5	101.7	107.0	107.5	100.1
	mean	**100.0**	**101.9**	**101.1**	**106.7**	**107.9**	**100.1**

n.a. = not applicable
n.d. = not detected
(a) Reported as 'M4'
Values expressed as percentage of total applied radioactivity (AR)

Table B.8.2.1.1-26 Transformation of [UL-chlorophenyl-^{14}C]-fenoxaprop-P-ethyl (AE F046360) in sterile aqueous buffer of *pH* 7 at 40 °C

Component	Rep. No.	Sampling interval (days) 0	1	2	4	15	30
Fenoxaprop-P-ethyl (AE F046360)	1	95.1	84.9	74.5	63.9	n.d.	3.8
	2	96.2	80.5	74.5	61.6	19.2	n.d.
	mean	**95.7**	**82.7**	**74.5**	**62.7**	**9.6**	**1.9**
Chlorobenzoxazolone (AE F054014)	1	4.0	8.9	11.4	15.0	35.7	53.1
	2	4.7	9.1	10.5	15.6	37.1	54.9
	mean	**4.3**	**9.0**	**11.0**	**15.3**	**36.4**	**54.0**
Fenoxaprop-P-acid (AE F088406)	1	n.d.	8.5	16.6	25.2	73.4	46.9
	2	n.d.	9.5	17.3	24.8	49.3	49.6
	mean	**n.a.**	**9.0**	**16.9**	**25.0**	**61.3**	**48.2**
Unknown[(a)]	1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	2	n.d.	n.d.	n.d.	n.d.	1.3	n.d.
	mean	**n.a.**	**n.a.**	**n.a.**	**n.a.**	**0.7**	**n.a.**
Total radioactivity in solution	1	99.1	102.3	102.5	104.0	109.1	103.7
	2	100.9	99.1	102.3	102.0	106.9	104.4
	mean	**100.0**	**100.7**	**102.4**	**103.0**	**108.0**	**104.1**

n.a. = not applicable
n.d. = not detected
(a) Reported as 'M4'
Values expressed as percentage of total applied radioactivity (AR)

Table B.8.2.1.1-27 Transformation of [UL-chlorophenyl-^{14}C]-fenoxaprop-P-ethyl (AE F046360) in sterile aqueous buffer of *pH* 9 at 25 °C

Component	Rep. No.	Sampling interval (days) 0	0.25	1	2	4	15	30
Fenoxaprop-P-ethyl (AE F046360)	1	95.7	75.6	30.0	17.4	6.5	n.d.	n.d.
	2	94.8	74.2	25.6	17.4	4.2	n.d.	n.d.
	mean	**95.3**	**74.9**	**27.8**	**17.4**	**5.4**	**n.a.**	**n.a.**
Chlorobenzoxazolone (AE F054014)	1	4.1	6.2	14.0	11.3	10.0	15.0	24.6
	2	5.4	6.2	22.5	11.3	9.7	13.4	24.3
	mean	**4.7**	**6.2**	**18.3**	**11.3**	**9.9**	**14.2**	**24.5**
Fenoxaprop-P-acid (AE F088406)	1	n.d.	15.6	58.0	76.4	88.2	87.0	78.7
	2	n.d.	13.9	50.9	76.2	90.7	90.1	79.2
	mean	**n.a.**	**14.8**	**54.5**	**76.3**	**89.4**	**88.5**	**78.9**

Unknowns[(a)]	1	n.d.	n.d.	1.2	n.d.	n.d.	1.4	n.d.
	2	n.d.	n.d.	3.5	n.d.	n.d.	n.d.	n.d.
	mean	**n.a.**	**n.a.**	**2.4**	**n.a.**	**n.a.**	**0.7**	**n.a.**
Total radioactivity in solution	1	99.8	97.3	103.3	105.1	104.7	103.3	103.3
	2	100.2	94.3	102.6	104.9	104.6	103.5	103.5
	mean	**100.0**	**95.8**	**103.0**	**105.0**	**104.7**	**103.4**	**103.4**

n.a. = not applicable
n.d. = not detected
(a) Reported as 'M3, M4 and M10', each to occur at 1.6 % AR or less in course of incubation
Values expressed as percentage of total applied radioactivity (AR)

Table B.8.2.1.1-28 Transformation of [UL-chlorophenyl-^{14}C]-fenoxaprop-P-ethyl (AE F046360) in sterile aqueous buffer of *pH* 9 at 40 °C

Component	Rep. No.	Sampling interval (days) 0	0.04	0.08	1	7	30
Fenoxaprop-P-ethyl (AE F046360)	1	95.7	69.7	57.1	1.6	n.d.	n.d.
	2	94.8	70.5	59.2	1.7	n.d.	n.d.
	mean	**95.3**	**70.1**	**58.1**	**1.6**	**n.a.**	**n.a.**
Chlorobenzoxazolone (AE F054014)	1	4.1	6.4	7.8	20.2	42.1	76.4
	2	5.4	6.2	7.6	14.3	43.0	80.1
	mean	**4.7**	**6.3**	**7.7**	**17.2**	**42.5**	**78.3**
Fenoxaprop-P-acid (AE F088406)	1	n.d.	19.4	35.3	82.4	63.4	18.8
	2	n.d.	18.6	35.8	91.6	63.3	16.4
	mean	**n.a.**	**19.0**	**35.6**	**87.0**	**63.4**	**17.6**
Unknowns[(a)]	1	n.d.	1.6	1.4	3.4	n.d.	9.1
	2	n.d.	1.4	n.d.	n.d.	n.d.	10.2
	mean	**n.a.**	**1.5**	**0.7**	**1.7**	**n.a.**	**9.7**
Total radioactivity in solution	1	99.8	97.1	101.6	107.6	105.4	104.4
	2	100.2	96.7	102.6	107.6	106.3	106.7
	mean	**100.0**	**96.9**	**102.1**	**107.6**	**105.9**	**105.6**

n.a. = not applicable
n.d. = not detected
(a) Reported as 'M3, M4, M10 and M12', each to occur at 8.9 % AR or less in course of incubation
All values expressed as percentage of total applied radioactivity (AR)

Table B.8.2.1.1-29 Transformation products of ^{14}C-fenoxaprop-P-ethyl (AE F046360) following incubation in sterile aqueous buffer solution of *p*H 4, 7 and 9 at 25 °C

Label position	Component	*p*H	Maximum fraction (% AR)	Maximum occurrence by day [A)]
UL-chlorophenyl	Fenoxaprop-P-acid (AE F088406)	4	22.2	1
		7	84.4	24
		9	89.4	4
	Chlorobenzoxazolone (AE F054014)	4	102.4	15
		7	27.9	30
		9	24.5	30

[A)] Total duration was 30 days

Table B.8.2.1.1-30 Transformation products of ^{14}C-fenoxaprop-P-ethyl (AE F046360) following incubation in sterile aqueous buffer solution of *p*H 4, 7 and 9 at 40 °C

Label position	Component	*p*H	Maximum fraction (% AR)	Maximum occurrence by day [A)]
UL-chlorophenyl	Fenoxaprop-P-acid (AE F088406)	4	32.8	0.16
		7	61.3	15
		9	87.0	1
	Chlorobenzoxazolone (AE F054014)	4	109.5	15
		7	54.0	30
		9	78.3	30

[A)] Total duration was 30 days

For the two test temperatures, hydrolysis rates were calculated for fenoxaprop-P-ethyl (AE F046360) and fenoxaprop-P-acid (AE F088406) by applying simple first-order each as kinetic model. No hydrolysis rates were

determined for chlorobenzoxazolone (AE F054014) since the compound was hydrolytically stable under the conditions of the test at both test temperatures.

Table B.8.2.1.1-31 Single first-order kinetics of hydrolytic degradation of fenoxaprop-P-ethyl (AE F046360) and fenoxaprop-P-acid (AE F088406) in sterile buffer solutions of *p*H 4, 7 and 9 at 25 °C

Compound		*p*H 4	*p*H 7	*p*H 9
Fenoxaprop-P-ethyl	*DT50* (days)	2.1	8.6	0.7
(AE F046360)	*DT90* (days)	6.8	28.6	2.2
Fenoxaprop-P-acid	*DT50* (days)	2.5	-[(a)]	143
(AE F088406)	*DT90* (days)	8.2	-[(a)]	474

(a) No value calculated due to insufficient data points/degradation

Table B.8.2.1.1-32 Single first-order kinetics of hydrolytic degradation of fenoxaprop-P-ethyl (AE F046360) and fenoxaprop-P-acid (AE F088406) in sterile buffer solutions of *p*H 4, 7 and 9 at 40 °C

Compound		*p*H 4	*p*H 7	*p*H 9
Fenoxaprop-P-ethyl	*DT50* (days)	0.7	6.5	0.1
(AE F046360)	*DT90* (days)	2.3	21.7	0.4
Fenoxaprop-P-acid	*DT50* (days)	0.5	-[(a)]	12.7
(AE F088406)	*DT90* (days)	1.7	-[(a)]	42.1

(a) No value calculated due to insufficient data points/degradation

Conclusion:

At the environmentally relevant test temperature of 25 °C, UL-chlorophenyl-labelled fenoxaprop-P-ethyl (AE F046360) was hydrolysed in sterile aqueous buffer solution of *p*H 4, 7 and 9 to result in half-lives of 2.1 days (pH 4), 8.6 days (pH 7) and 0.7 days (pH 9).

At the same temperature, fenoxaprop-P-acid (AE F088406) and chlorobenzoxazolone (AE F054014) were observed as major transformation products.

Fenoxaprop-P-acid (AE F088406) was hydrolysed in sterile aqueous buffer solution of *p*H 4 and 9 to result in half-lives of 2.5 days at *p*H 4 and 12.7 days at *p*H 9. No half-lives were calculated at *p*H 7 for fenoxaprop-P-acid (AE F088406) since the compound was hydrolytically stable at this *p*H.

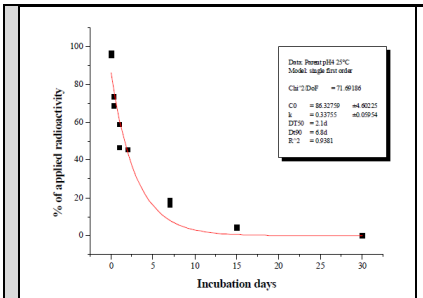
Chlorobenzoxazolone (AE F054014) was stable to abiotic hydrolysis at all *p*H.

Based on the results of the study, abiotic hydrolysis may contribute to a limited extent the overall elimination of fenoxaprop-P-ethyl (AE F046360) from the aquatic environment.

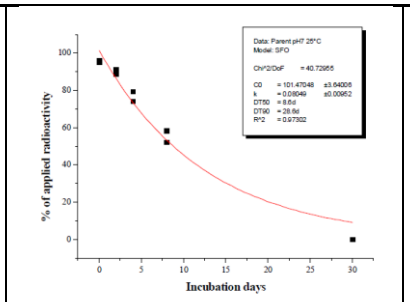
Comments RMS AT:

- The study follows OECD guideline 111 and is considered reliable.
- Dissipation fits are not included in the applicant summary. Therefore this information is provided here:

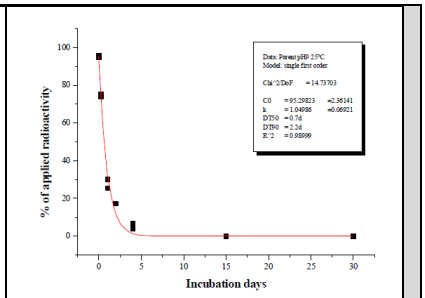
Table B.8.2.1.1-33 Dissipation fits for fenoxaprop-P-ethyl (AE F046360) at 25 and 40 °C obtained by the applicant and agreed by the RMS AT



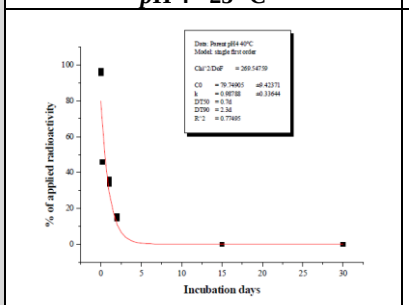
*p*H 4 - 25 °C



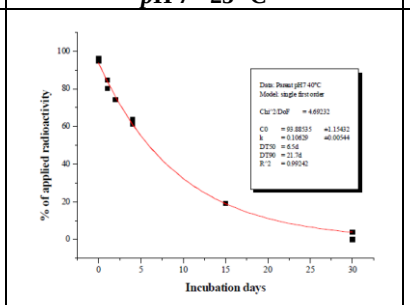
*p*H 7 - 25 °C



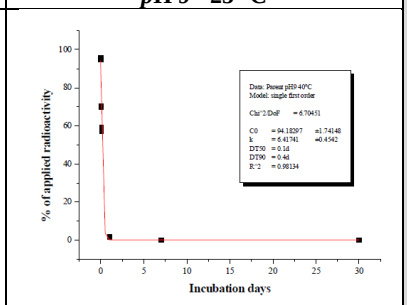
*p*H 9 - 25 °C



*p*H 4 - 40 °C

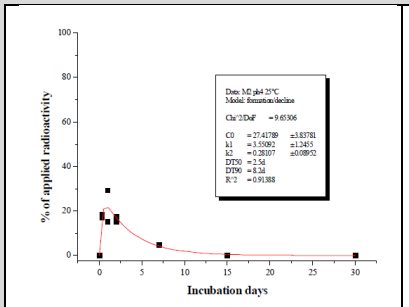


*p*H 7 - 40 °C



*p*H 9 - 40 °C

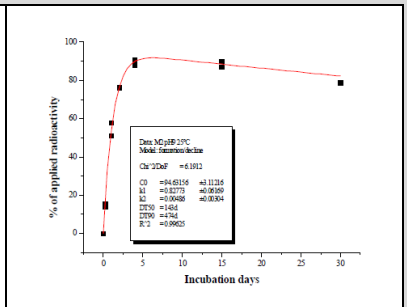
Table B.8.2.1.1-34 Dissipation fits for fenoxaprop-P-acid (AE F088406) at 25 and 40 °C <u>obtained by the applicant and agreed by the RMS AT</u>



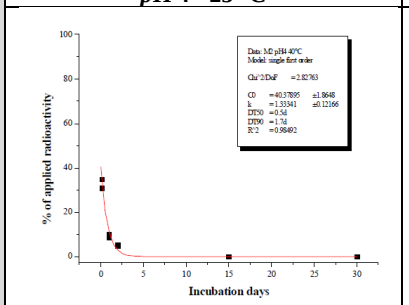
*p*H 4 - 25 °C

No reliable fit

*p*H 7 - 25 °C



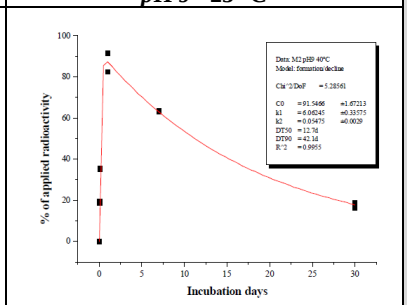
*p*H 9 - 25 °C



*p*H 4 - 40 °C

No reliable fit

*p*H 7 - 40 °C



*p*H 9 - 40 °C

- As already indicated in Van der Gaauw (2002) results on abiotic hydrolysis of fenoxaprop-P-ethyl (AE F046360) investigated in Van der Gaauw (2002), Fitzmaurice (2008) and in this study are somehow deviating. In particular, fenoxaprop-P-acid (AE F088406) was observed at *p*H 4 in this study as well, whereas this metabolite was hardly identified at *p*H 4 in the other two hydrolysis studies.

Author(s), year:	Adam, D. (2007)
Report/Doc. Number:	237 FPE, M-548134-01-1
Guideline(s):	OECD Guideline 111 (2004), Directive 92/69/EEC Part C.7, EPA Guideline OPPTS 835.2110
GLP:	Yes
Validity:	Yes
Status:	**New submission**

Executive Summary:

The hydrolysis of [UL-phenyl-^{14}C]-chlorobenzoxazolone (AE F054014) was investigated at a test concentration of 0.14 mg/L in sterile buffer solution of *p*H 4, 7 and 9 at 50 °C for 5 days in maximum.

The mean recovery of radioactivity in terms of mean values of two replicates was 96.5 to 102.5 % AR at *p*H 4, 100.0 to 102.1 % at *p*H 7 and 98.6 to 101.5 % at *p*H 9.

The decline of the test substance was negligible indicated by recoveries to range from 93.7 to 101.8 % AR by day 5 at all *p*H tested with no transformation products formed at significant level.

Consequently, no hydrolysis rates were determined since the test substance was hydrolytically stable under the conditions of the test.

Based on the results of the study, abiotic hydrolysis is unlikely to contribute to the overall elimination of chlorobenzoxazolone (AE F054014) from the aquatic environment.

Material and Methods:

Test Material:	[UL-phenyl-^{14}C]-chlorobenzoxazolone (AE F054014)
Specific radioactivity:	11.78 MBq/mg (318.38 µCi/mg)
Radiochemical purity:	100 % (HPLC)
Sample ID:	2525MFO007-6

Aqueous buffer
For investigations at three values of *p*H sterile aqueous buffer solutions of *p*H 4 (citrate), 7 (phosphate) and 9 (borate) were prepared. The concentration of the corresponding buffer solutions was 0.05 mol/L.

Experimental conditions
The test was performed at an initial concentration of 0.14 mg test substance/L thus corresponding to less than half the water solubility in sterile aqueous buffers. The final content of the co-solvent acetonitrile was 0.5 %. The test vessels containing 10 mL buffer solution each were incubated in the dark at 50 °C (pre-test) for five days in maximum. The *p*H and sterility of the test solutions was determined each at the start and at the end of the incubation period.

Sampling
Duplicate samples were removed for analysis at various sampling intervals.

Table B.8.2.1.1-35 Sampling intervals

Temperature	*p*H	**Sampling intervals** (days)
50 °C	4	0, 0.14, 1, 5
	7	0, 0.14, 1, 5
	9	0, 0.14, 1, 5

Analytical procedures
The total radioactivity was determined by liquid scintillation counting (LSC) followed by reversed-phase HPLC and ^{14}C-flow-through detection techniques as primary analytical method for separation and quantitation of

transformation products. Thin-layer chromatography (TLC) was performed as confirmatory method for selected samples.

The limit of quantitation (LOQ) was 0.5 % of AR, the corresponding limit of detection (LOD) was 0.3 % AR.

Kinetic evaluation
No kinetic evaluation for the rate of degradation was performed due to the stability of the test substance under the conditions of the test.

Results and Discussion:

Determinations confirmed the stability of *p*H in buffer solutions and their sterility throughout the incubation.

The material balance in terms of mean values of two replicates was 96.5 to 102.5 % AR at *p*H 4, 100.0 to 102.1 % at *p*H 7 and 98.6 to 101.5 % at *p*H 9.

The decline of the test substance was negligible under the conditions of the test as indicated by recoveries to range from 93.7 to 101.8 % AR by day 5 at all *p*H tested. Consequently, no transformation products were formed at significant level.

Table B.8.2.1.1-36 Transformation of [UL-phenyl-^{14}C]-chlorobenzoxazolone (AE F054014) in sterile aqueous buffer of *p*H 4 at 50 °C

Component	Rep. No.	Sampling interval (days) 0	0.1	1	5
Chlorobenzoxazolone (AE F054014)	1	99.5	98.0	102.6	100.6
	2	100.5	94.9	102.4	103.0
	mean	**100.0**	**96.5**	**102.5**	**101.8**
Total radioactivity	1	99.5	98.0	102.6	100.6
	2	100.5	94.9	102.4	103.0
	mean	**100.0**	**96.5**	**102.5**	**101.8**

n.a. = not applicable
n.d. = not detected
Values expressed as percentage of total applied radioactivity (AR)

Table B.8.2.1.1-37 Transformation of [UL-phenyl-^{14}C]-chlorobenzoxazolone (AE F054014) in sterile aqueous buffer of *p*H 7 at 50 °C

Component	Rep. No.	Sampling interval (days) 0	0.1	1	5
Chlorobenzoxazolone (AE F054014)	1	99.8	100.3	99.4	100.9
	2	100.2	101.1	101.6	101.0
	mean	**100.0**	**100.7**	**100.5**	**101.0**
Unknown[(a)]	1	n.d.	n.d.	n.d.	1.2
	2	n.d.	n.d.	n.d.	0.9
	mean	**n.a.**	**n.a.**	**n.a.**	**1.1**
Total radioactivity	1	99.8	100.3	99.4	102.1
	2	100.2	101.1	101.6	102.0
	mean	**100.0**	**100.7**	**100.5**	**102.1**

n.a. = not applicable
n.d. = not detected
(a) Reported as 'M1'
Values expressed as percentage of total applied radioactivity (AR)

Table B.8.2.1.1-38 Transformation of [UL-phenyl-^{14}C]-chlorobenzoxazolone (AE F054014) in sterile aqueous buffer of *p*H 9 at 50 °C

Component	Rep. No.	Sampling interval (days) 0	0.1	1	5
Chlorobenzoxazolone (AE F054014)	1	100.0	98.7	99.1	93.7
	2	100.0	98.5	99.0	93.6
	mean	**100.0**	**98.6**	**99.0**	**93.7**

Component	Rep. No.	Sampling interval (days) 0	0.1	1	5
Unknown[(a)]	1	n.d.	n.d.	2.2	5.7
	2	n.d.	n.d.	2.8	7.5
	mean	**n.a.**	**n.a.**	**2.5**	**6.5**
Total radioactivity	1	100.0	98.7	101.2	99.4
	2	100.0	98.5	101.8	101.1
	mean	**100.0**	**98.6**	**101.5**	**100.2**

n.a. = not applicable
n.d. = not detected
(a) Reported as 'M1 and M2'. Maximum occurrence of 4.8 % AR by day 5
Values expressed as percentage of total applied radioactivity (AR)

No hydrolysis rates were determined since the test substance was hydrolytically stable under the conditions of the test.

Conclusion:

Chlorobenzoxazolone (AE F054014) was stable under the conditions of hydrolysis in sterile aqueous buffer solution of *p*H 4, 7 and 9 at 50 °C. Consequently, no rates of hydrolysis and corresponding half-lives were determined. No transformation products were formed at significant level.

Comments RMS AT:

- The study follows OECD guideline 111and is considered reliable. The study confirms observations already made by Burgener (1999).

B.8.2.1.2. Direct photochemical degradation

Studies submitted for first Annex I inclusion:

- **Schwab (1993)**, investigating chlorophenyl labelled fenoxaprop-P-ethyl (AE F046360)
- **Burgener (1999)**, investigating chlorobenzoxazolone (AE F054014)

New studies submitted by the Fenoxaprop-P-ethyl Task Force:

- **Fitzmaurice (2008)**, investigating phenoxy labelled fenoxaprop-P-ethyl (AE F046360), supported by **Tarara (2016)**, elucidating an unknown photo-degradation product observed in Fitzmaurice (2008)
- **Fletcher & Gilbert (2008)**, investigating chlorophenyl labelled fenoxaprop-P-ethyl (AE F046360)
- **Adam (2008)**, investigating chlorobenzoxazolone (AE F054014)

Reference:	**Hoe 046360-^{14}C: Photodegradation of Fenoxaprop-P-ethyl in surface water, sterile buffer and distilled water**
Author(s), year:	Schwab, W. (1993c)
Report/Doc. Number:	A51353, M-132306-02-1
Guideline(s):	OECD Photodegradation of Chemicals in Water, Part A, 1992; US/EPA, N §161-2,1982; Japan/ACIS Degradation of Agricultural chemicals in water under exposure of light
GLP:	Yes
Validity:	Yes
Status:	**Previously submitted**

[The following study report is a copy/paste of the original text in the DAR for Annex I inclusion slightly amended in order to meet editorial settings and to improve readability]

Material and methods:

The photodegradation of UL-chlorophenyl-^{14}C labelled fenoxaprop-P-ethyl (AE F046360, called Hoe 046360 in the study report, initial test concentration 0.324 – 0.362 mg/L) was studied in aqueous solutions of i) natural surface water (filtered water from river „Nidda“, *p*H 9), ii) sterile acetate buffer (*p*H 5) and iii) distilled water (*p*H ~ 6.8).

Test solutions of the three separate series were continuously irradiated with polychromatic light (290 – 490 nm) of a xenon burner in two SUNTEST photoreactors (SUNTEST II and III) at 25 ± 2 °C for up to 144 hours (surface water) and 168 hours (acetate buffer and distilled water). Further dark control samples of each series were incubated under the same conditions like the irradiated test samples. In order to collect volatile degradation products a closed flow-through system with suitable absorption traps were used.

At appropriate time intervals irradiated and non-irradiated test samples and contents of volatile traps were taken and analysed by LSC (quantification), HPLC, TLC and GC/MS (analysis of photoproducts).

Findings:

Mean recoveries for all series were in the range of 94.4 % - 103.5 % of applied radioactivity. All test solutions of acetate buffer and distilled water remained sterile during the test period. For each photosystem (Suntest II and III) the light intensity was determined with a chemical actinometer to be approx. 3 times the value of the mean intensity at 52 ° N latitude on sea level in June.

Table B.8.2.1.2-1 Distribution of active substance and metabolites in surface water, sterile acetate buffer and distilled water solutions at the end of each test period (% AR)

Test medium	Time (hrs)	Test series	Fenoxaprop-P-ethyl (AE F046369)	Fenoxaprop-P-acid (AE F088406)	Chlorobenz-oxazolone (AE F054014)	Phenol metabolite (AE F040356)	Total unknowns	CO_2
Surface water (*p*H 9)	144	II	2.0	39.3	nd	2.1	45.3[(a)]	5.7
		III	2.4	40.3	2.3	3.2	37.6[(a)]	7.8
		Dark	2.2	95.0	1.5	nd	nd	0.1
Acetate buffer (*p*H 5)	168	II	59.7	nd	3.3	4.9	19.9[(b)]	6.1
		III	61.5	nd	8.2	3.5	18.8[(b)]	6.3
		Dark	85.2	nd	14.6	nd	nd	0.1
Distilled water (*p*H ~ 6.8)	168	II	74.3	7.3	2.0	5.4	2.4[(c)]	3.1
		III	66.6	4.7	5.2	2.7	11.9[(c)]	7.7
		Dark	85.7	5.8	3.4	nd	1.4[(c)]	0.1

nd denotes not determined
(a) Including metabolite fractions M1 (RRT 0.04) and M2 (RRT 0.06) (for details refer to comment section)
(b) Including metabolite fractions M1 (RRT 0.06), M2 (RRT 0.24) and M5 (RRT 0.89) (for details refer to comment section)
(c) Including metabolite fractions M1 (RRT 0.07) and M5 (RRT 0.91) (for details refer to comment section)

Table B.8.2.1.2-2 *DT50* and *DT90* values of fenoxaprop-P-ethyl (AE F046360) in different test media (surface water, sterile buffer and distilled water) assuming 1st order reaction kinetic and an average sunshine period of 12 hours per day

Test solution	Test series (Suntest)	*DT50 lab* (hrs)	*DT90* lab (hrs)	*DT50 lab* (d)	*DT50* sunlight (d)	*DT90* sunlight (d)
Surface water (*p*H 9)	II	25.6	85.1	1.07	7.1	23.5
	III	27.1	89.9	1.13	7.3	24.3
Sterile buffer (*p*H 5)	II	210.5	699.2	8.8	53.5	177.7
	III	259.4	861.7	10.8	61.4	203.9
Distilled water (*p*H ~ 6.8)	II	498.0	1654	20.8	127.8	424.6
	III	322.6	1072	13.4	81.5	270.6

Quantum yield calculation

Based on obtained data from the photolysis experiments in buffer solution (*p*H 5) and distilled water (*p*H ~ 6.8), the quantum yield was calculated with LOTUS program QUANTUS. The mean quantum yield Φ derived from two replicate series of samples was 5.11×10^{-6} (sterile buffer) and 2.88×10^{-6} (distilled water).

A comparison with dark controls showed that the degradation of fenoxaprop-P-ethyl (AE F046360) in natural surface water was not due to direct photolytic effects. Hydrolysis and indirect photolysis were responsible for degradation in alkaline natural surface water. Consequently, no quantum yield was determined for these conditions.

Conclusion:

Under test conditions in sterile aqueous buffer solutions at *p*H 5 fenoxaprop-P-ethyl (AE F046360) was moderately photolytically degraded (*DT50*: 53.5 and 61.4 d). In distilled water samples at neutral *p*H the test substance is comparatively stable to photolysis (*DT50*: 127.8 and 81.5 d). Rapid degradation was observed in surface water samples (*DT50*: 7.1 and 7.3 d), however degradation was not due to direct photolytic effects. Water-dissolved photosensitizers (indirect photolysis) in combination with alkaline conditions (hydrolysis) resulted in a rapid reduction of fenoxaprop-P-ethyl (AE F046360), forming fenoxaprop-P-acid (AE F088406), chlorobenzoxazolone (AE F054014) and the phenol metabolite (AE F040356). Additionally, hydroxybenzoxazolone (AE 0316854), a number of short chained aliphatic carboxylic acids and CO_2 were identified as metabolites under these conditions.

The mean quantum yields Φ were 5.11 x 10^{-6} (sterile buffer) and 2.88 x 10^{-6} (distilled water).

Sum up, it is unlikely, that direct photolytic degradation contributes to a major extent to the elimination of fenoxaprop-P-ethyl from the environment.

Comments RMS AT:

- The study is broadly in line with OECD guideline 316 and the OECD draft guideline on 'Phototransformation of Chemicals in Water - Direct and Indirect Photolysis' and is still considered reliable.
- The study summary provided for first Annex I inclusion does not give details on individual samples. This information is provided in the tables below.

Table B.8.2.1.2-3 Distribution of active substance and metabolites in surface water (*p*H 9) (% AR, numbers shaded in grey indicate exceedance of 10 % AR)

Test system	HAT	Fenoxaprop -P-ethyl (AE F046360)	M1[(a)] *(rel. RT 0.04)*	M2[(a)] *(rel. RT 0.06)*	Chlorobenz-oxazolone (AE F054014)	Phenol metabolite (AE F040356)	Fenoxaprop -P-acid (AE F088406)
Suntest II	**0**	100.0	n.d.	n.d.	n.d.	n.d.	n.d.
	4	79.0	n.d.	n.d.	n.d.	n.d.	20.7
	7	67.9	n.d.	n.d.	5.4	n.d.	26.5
	24	32.1	10.8	n.d.	5.7	n.d.	54.3
	48	12.5	15.2	7.9	n.d.	3.5	55.9
	72	8.8	13.9	9.0	3.1	5.1	54.7
	144	2.0	17.9	27.4	n.d.	2.1	39.3
Suntest III	**0**	97.4	n.d.	n.d.	n.d.	n.d.	2.7
	4	75.7	n.d.	n.d.	n.d.	n.d.	23.6
	7	67.7	0.8	1.4	1.5	n.d.	27.2
	24	33.3	8.6	3.2	n.d.	n.d.	55.2
	48	16.1	15.2	3.4	2.5	2.0	57.3
	72	9.3	16.9	8.8	n.d.	3.4	55.9
	144	2.4	19.2	18.4	2.3	3.2	40.3
Average of Suntest II & III	**0**	**98.7**	**0.0**	**0.0**	**0.0**	**0.0**	**1.4**
	4	**77.4**	**0.0**	**0.0**	**0.0**	**0.0**	**22.2**
	7	**67.8**	**0.4**	**0.7**	**3.5**	**0.0**	**26.9**
	24	**32.7**	**9.7**	**1.6**	**2.9**	**0.0**	**54.8**
	48	**14.3**	**15.2**	**5.7**	**1.3**	**2.8**	**56.6**
	72	**9.1**	**15.4**	**8.9**	**1.6**	**4.3**	**55.3**
	144	**2.2**	**18.6**	**22.9**	**1.2**	**2.7**	**39.8**
Dark	**0**	97.0	n.d.	n.d.	n.d.	n.d.	3.0

control	**4**	67.6	n.d.	n.d.	n.d.	n.d.	31.8
	7	61.7	n.d.	n.d.	n.d.	n.d.	39.4
	24	4.4	n.d.	n.d.	n.d.	n.d.	97.2
	48	6.1	n.d.	n.d.	n.d.	n.d.	93.6
	72	1.7	n.d.	n.d.	2.4	n.d.	95.3
	144	2.2	n.d.	n.d.	1.5	n.d.	95.0

(a) Highly polar peaks eluting with the void volume of the RP18 column (refer to comments below)

Table B.8.2.1.2-4 Distribution of active substance and metabolites in sterile acetate buffer (*p*H 5) (% AR, numbers shaded in grey indicate exceedance of 10 % AR)

Test system	HAT	Fenoxaprop-P-ethyl (AE F046360)	M1[(a)] *(rel. RT 0.06)*	Hydroxy-benzoxazolone (AE 0316854)[(b)]	Chlorobenz-oxazolone (AE F054014)	Phenol metabolite (AE F040356)	Acetate of phenol metabolite (AE F040356)[(c)]
Suntest II	**0**	100.0	n.d.	n.d.	n.d.	n.d.	n.d.
	4	99.5	n.d.	n.d.	n.d.	n.d.	n.d.
	7	92.8	n.d.	2.2	4.5	n.d.	n.d.
	24[(d)]	*120.6*	*n.d.*	*n.d.*	*8.3*	*n.d.*	*n.d.*
	48	85.3	1.9	2.1	7.2	0.5	2.0
	96	73.8	5.4	4.4	5.2	3.9	2.2
	168	59.7	10.4	4.6	3.3	4.9	4.9
Suntest III	**0**	97.7	n.d.	n.d.	2.4	n.d.	n.d.
	4	97.0	n.d.	n.d.	2.3	n.d.	n.d.
	7	93.8	n.d.	n.d.	5.7	n.d.	n.d.
	24	95.0	n.d.	n.d.	5.8	n.d.	n.d.
	48	81.7	2.9	4.8	6.9	2.9	n.d.
	96	78.5	2.2	2.5	7.6	3.5	2.1
	168	61.5	12.4	6.4	8.2	3.5	n.d.
Aver-age of Suntest II & III	**0**	**98.9**	**n.d.**	**n.d.**	**2.4**	**n.d.**	**n.d.**
	4	**98.3**	**n.d.**	**n.d.**	**2.3**	**n.d.**	**n.d.**
	7	**93.3**	**n.d.**	**2.2**	**5.1**	**n.d.**	**n.d.**
	24	**95.0**	**n.d.**	**n.d.**	**5.8**	**n.d.**	**n.d.**
	48	**83.5**	**2.4**	**3.5**	**7.1**	**1.7**	**2.0**
	96	**76.2**	**3.8**	**3.5**	**6.4**	**3.7**	**2.2**
	168	**60.6**	**11.4**	**5.5**	**5.8**	**4.2**	**4.9**
Dark control	**0**	100.0	n.d.	n.d.	n.d.	n.d.	n.d.
	4	96.9	n.d.	n.d.	n.d.	n.d.	n.d.
	7	98.9	n.d.	n.d.	n.d.	n.d.	n.d.
	24	95.6	n.d.	n.d.	5.0	n.d.	n.d.
	48	95.3	n.d.	1.5	5.8	n.d.	n.d.
	96	91.9	n.d.	n.d.	8.4	n.d.	n.d.
	168	85.2	n.d.	n.d.	14.6	n.d.	n.d.

(a) Highly polar peak eluting with the void volume of the RP18 column consisting of at least six compounds characterized as short-chain aliphatic carboxylic acids. Two of them were definitely identified as malonic acid and succinic acid by GC/MS.
(b) Metabolite M2 (rel. RT 0.24) identified as hydroxybenzoxazolone (AE 0316854)
(c) Metabolite M5 (rel. RT 0.89) identified as acetate of the phenol metabolite (AE F040356); considered an artefact formed in acetate buffer solution
(d) Considered an outlier

Table B.8.2.1.2-5 Distribution of active substance and metabolites in distilled water (*p*H ~ 6.8) (% AR, numbers shaded in grey indicate exceedance of 10 % AR)

Test system	HAT	Fenoxaprop-P-ethyl (AE F046360)	M1[(a)] *(rel. RT 0.07)*	Chlorobenz-oxazolone (AE F054014)	Phenol metabolite (AE F040356)	Fenoxaprop-P-acid (AE F088406)	M5 *(rel. RT 0.91)*
Suntest II	**0**	100.0	n.d.	n.d.	n.d.	n.d.	n.d.
	4	94.9	n.d.	n.d.	n.d.	n.d.	n.d.
	7	98.1	n.d.	n.d.	n.d.	n.d.	n.d.
	24	94.6	n.d.	n.d.	n.d.	3.7	n.d.
	48	98.0	n.d.	n.d.	n.d.	n.d.	n.d.
	96	96.4	n.d.	1.8	n.d.	2.9	n.d.
	168	74.3	2.4	2.0	5.4	7.3	n.d.

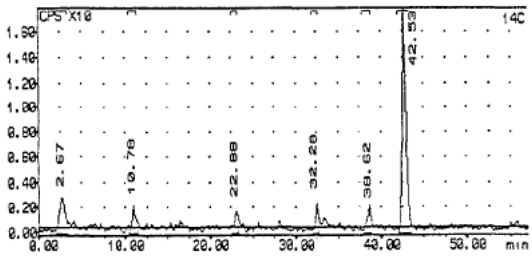
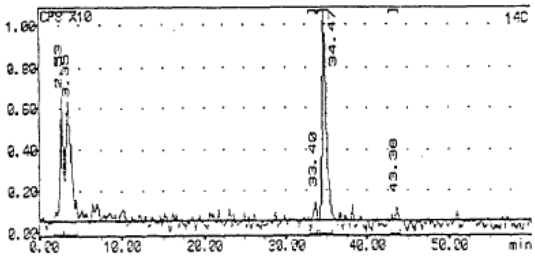
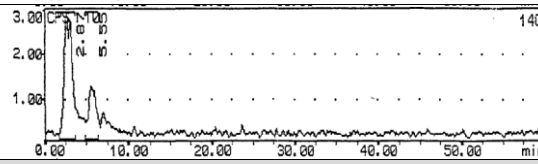
Suntest III	**0**	100.0	n.d.	n.d.	n.d.	n.d.	n.d.
	4	94.5	n.d.	2.4	n.d.	n.d.	n.d.
	7	95.9	n.d.	2.3	n.d.	n.d.	n.d.
	24	94.3	n.d.	4.5	n.d.	n.d.	n.d.
	48	87.7	n.d.	3.0	n.d.	4.9	n.d.
	96	84.6	2.4	2.7	1.6	4.8	n.d.
	168	66.6	9.6	5.2	2.7	4.7	2.3
Dark control	**0**	100.0	n.d.	n.d.	n.d.	n.d.	n.d.
	4	99.7	n.d.	n.d.	n.d.	n.d.	n.d.
	7	98.0	n.d.	n.d.	n.d.	n.d.	n.d.
	24	99.0	n.d.	n.d.	n.d.	n.d.	n.d.
	48	97.8	n.d.	n.d.	n.d.	n.d.	n.d.
	96	92.9	n.d.	1.9	n.d.	2.5	n.d.
	168	85.7	n.d.	3.4	n.d.	5.8	1.4

(a) Highly polar peaks eluting with the void volume of the RP18 column

- From the three photolysis experiments conducted (i.e. in surface water, acetate buffer solution and distilled water) the experiment conducted in **acetate buffer solution (*p*H 5)** is considered broadly in line with guidance on ***direct photolysis*** (as described in OECD guideline 316). In this experiment the highly polar metabolite fraction 'M1' (*rRT* 0.06) exceeded 10 % AR in both Suntest systems (maximum 11.4 % AR on average for both systems (Suntest II & III), also refer to HPLC chromatogram provided in the table below). In order to facilitate identification of transformation products additional irradiation experiments using exaggerated application rates were conducted in acetate buffer solutions (*p*H 5). These samples were blended with fenoxaprop-P-acid (AE F088406), used as a surrogate for the poorly soluble fenoxaprop-P-ethyl (AE F046360), and irradiated for 27 days. In this 27 day sample, highly polar fractions with a RT below approx. 10 min (including M1) were isolated and further identified by ion sensitive HPLC as a mixture of naturally occurring short chain carboxylic acids amongst them oxalic, malonic, succinic, acetic and citric acid, each ≤ 22.1 % of the total fraction. Thus, metabolite fraction M1 is not considered to obtain degradation products > 10 % AR on individual basis. Note that dissipation in the dark samples is considered in line with OECD guideline 111 on hydrolysis, thus adding an additional data set to the large number of hydrolysis data already available for fenoxaprop-P-ethyl (AE F046360).

- The photolysis experiment conducted **in surface water (*p*H 9)** is considered broadly in line with the (draft) guidance on ***indirect photolysis*** (as described in OECD draft guideline on Phototransformation of Chemicals in Water - Direct and Indirect Photolysis), thus related to the section on *indirect photochemical degradation* (B.8.2.1.3). In this experiment the highly polar metabolite fractions 'M1' (*rRT* 0.04) and 'M2' (*rRT* 0.06) exceed 10 % AR (18.6 % AR for M1, 22.9 % AR for M2, both with maxima at study end by 168 hrs). No dedicated experiment/analysis was performed to further elucidate these two fractions observed in this experiment. However, on basis of the additional exaggerated experiment conducted in acetate buffer solution (refer to comment above), it may be concluded that the highly polar fraction overserved in the acetate buffer solution, characterized further by ion-sensitive HPLC, also covers M1 and M2 (refer to HPLC chromatograms shown in the table below). In this respect, the RMS AT considers metabolite fraction M1 and M2 observed in the surface water experiment to mainly represent aliphatic short chain carboxylic acids as well. However, considering the difference in *p*H between the test systems and the sensitivity of fenoxaprop-P-ethyl (AE F046360) regarding *p*H dependent hydrolysis it remains unclear whether individual substances covered by the polar fractions M1 or M2 exceed 10 % of AR on individual basis. Notice that the complexity of indirect photolysis processes does not allow straightforward extrapolation of results from filtered xenon arc lamps to sunlight equivalents (as stated in the OECD draft guideline on Phototransformation of Chemicals in Water - Direct and Indirect Photolysis).

Table B.8.2.1.2-6 HPLC chromatograms of the 168-hrs acetate buffer solution (*p*H 5) sample, 144-hrs surface water (*p*H 9) sample and the polar fractions sample obtained in the exaggerated acetate buffer (*p*H 5) experiment (27 days irradiation)

HPLC chromatogram of the **acetate buffer solution (*p*H 5)** showing the highly polar fractions M1 (RT 2.67 min, *rRT* 0.06) - 168 hrs sample (Suntest II)	
HPLC chromatogram of the **surface water (*p*H 9)** showing the highly polar fractions M1 (RT 2.53 min, *rRT* 0.04) and M2 (RT 3.35 min, *rRT* 0.06) - 144 hrs sample (Suntest II)	
HPLC chromatogram of isolated polar fractions (RT < 10 min) observed in **acetate buffer solution (*p*H 5)**, further analysed by ion-sensitive HPLC - 27 days sample	

- The photolysis experiment conducted in **distilled water (pH ~ 6.8)** is considered **supplemental information only** as it does not follow any pertinent guidance.

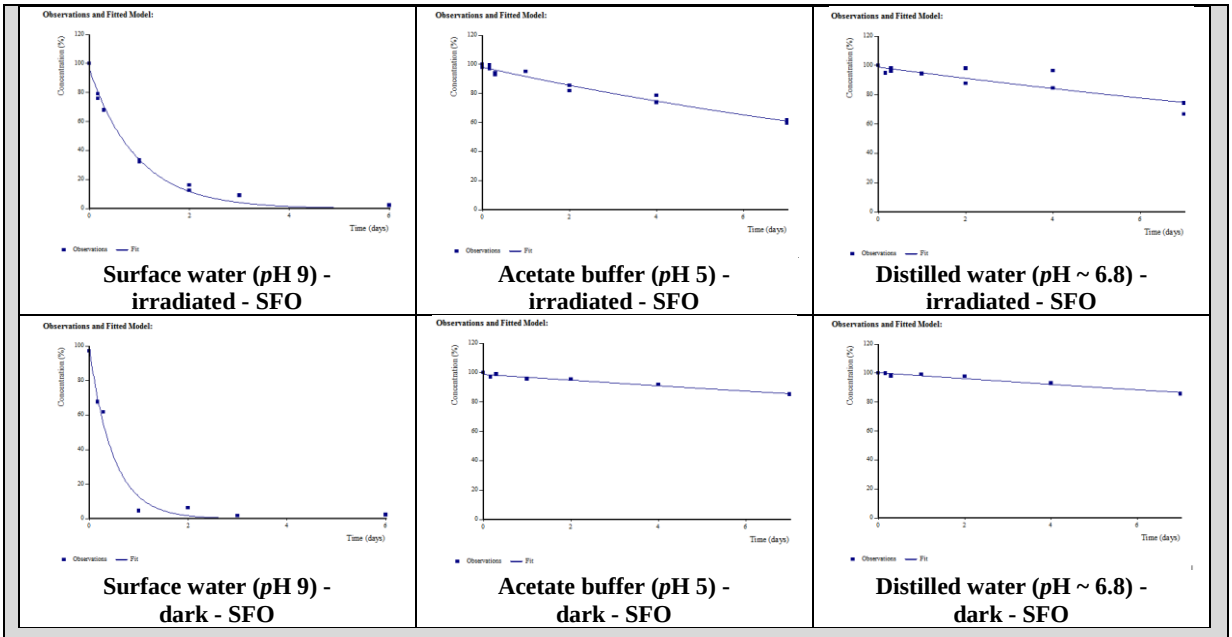
- The RMS AT re-evaluated dissipation rates of fenoxaprop-P-ethyl (AE F046360) in both, irradiated and dark samples, and calculated the *net* photolysis rate, as this was not done in the study report. Based on this re-calculation no impact of photolysis was observed for the experiment conducted in surface water (*p*H 9) at all as dissipation in dark samples was indeed faster than in irradiated samples. Net photolysis in the acetate buffer system (*p*H 5) was calculated to be 14.6 days, which gives a net photolysis rate under natural sunlight of 85.7 days. With respect to the dark dissipation rate of 34 days, irradiation has only a minor impact on the overall dissipation of fenoxaprop-P-ethyl (AE F046360) at a *p*H of 5.

Table B.8.2.1.2-7 Re-evaluated photolysis dissipation rates of fenoxaprop-P-ethyl (AE F046360) in surface water (*p*H 9), acetate buffer (*p*H 5) and distilled water (pH ~ 6.8) - RMS AT assessment

System	Treatment	*DT50* / *DT90* (d) experimental	χ^2 error (%)	*DT50* (d) sunlight (52 °N in June)[(a)]
Surface water (*p*H 9)	Irradiated	0.7 / 2.2	5.8	-
	Dark	0.3 / 1.1	11.1	-
	Net photolysis	**na**	**-**	**na[(b)]**
Acetate buffer (*p*H 5)	Irradiated	10.2 / 34	1.9	-
	Dark	34.0 / 113	0.8	-
	Net photolysis	**14.6 / 48.4**	**-**	**85.7**
Distilled water (*p*H ~ 6.8)	Irradiated	17.4 / 57.8	2.8	-
	Dark	33.3 / 111	0.9	-
	Net photolysis	**36.4 / 121**	**-**	**222**

na denotes not applicable
(a) Light intensity was determined with a chemical actinometer to be approx. 3 times the value of the mean intensity at 52 ° N latitude on sea level in June which finally gives a factor of approx. 6 assuming an average sunshine period of 12 hours per day
(b) The complexity of indirect photolysis processes does not allow straightforward extrapolation of results from filtered xenon arc lamps to sunlight equivalents (OECD draft guideline on Phototransformation of Chemicals in Water - Direct and Indirect Photolysis)

Table B.8.2.1.2-8 Fits on photolysis dissipation of fenoxaprop-P-ethyl (AE F046360) in the surface water (*p*H 9), acetate buffer (*p*H 5) and distilled water (*p*H ~ 6.8) - RMS AT assessment



Surface water (*p*H 9) - irradiated - SFO

Acetate buffer (*p*H 5) - irradiated - SFO

Distilled water (*p*H ~ 6.8) - irradiated - SFO

Surface water (*p*H 9) - dark - SFO

Acetate buffer (*p*H 5) - dark - SFO

Distilled water (*p*H ~ 6.8) - dark - SFO

Reference:	**Aqueous photolysis of ^{14}C-AE F054014 under laboratory conditions**
Author(s), year:	Burgener, A. (1999b)
Report/Doc. Number:	C006616, M-194301-01-1
Guideline(s):	SETAC, 1995; OECD guideline Document (97)21; EPA-540/9-82-021
GLP:	Yes
Validity:	Yes
Status:	**Previously submitted**

[The following study report is a copy/paste of the original text in the DAR for Annex I inclusion slightly amended in order to meet editorial settings and to improve readability]

Material and methods:

The rate of photolysis and the quantum yield of UL-chlorophenyl-^{14}C labelled chlorobenzoxazolone (AE F054014, test concentration 2.125 mg/L) were determined in sterile aqueous buffer solutions at *p*H 7 under continuous irradiation with simulated sunlight in a SUNTEST apparatus (light source: 1.8 kW xenon lamp: $\lambda > 290$ nm, intensity: 51 W/m² at 300 – 400 nm) for up to 15 days. Dark controls were incubated under the same conditions. In order to collect volatile degradation products a closed flow-through system with suitable absorption traps was used. At each sampling time interval the samples were analysed by LSC and TLC and/or HPLC. During the study temperature was maintained at 25 °C.

Findings:

The total recoveries were in a range of 92.5 % to 101.6 % of the initial concentration. No degradation occurred in the dark control samples. In irradiated test samples a complete degradation of chlorobenzoxazolone (AE F054014) was observed in the course of the study.

A total of 15 fractions and CO_2 were detected, whereas hydroxybenzoxazolone (AE 0316854), M2, M9 and M15 were identified as main components with peak values ≥ 10 %.

Table B.8.2.1.2-9 Distribution of ^{14}C-chlorobenzoxazolone (AE F054014) and metabolite fractions (> 10 %) in the irradiated buffer solutions

Fractions	sample	Irradiation time [d] 0	0.5	1	2	3	5	8	15
		Radioactivity in buffer solution (% applied)							
Chlorobenzoxazolone (AE 054014)	A	100.0	85.4	68.4	35.9	20.3	7.3	1.9	< 0.1
	B	100.0	83.8	66.4	31.9	17.9	5.7	1.3	< 0.1
	Mean	**100.0**	**84.6**	**67.4**	**33.9**	**19.1**	**6.5**	**1.6**	**< 0.1**
Hydroxybenzoxazolone (AE 0316854)	A	< 0.1	9.4	17.4	23.2	30.1	32.2	29.3	20.7
	B	< 0.1	8.8	16.5	21.2	23.1	20.2	14.1	6.0
	Mean	**< 0.1**	**9.1**	**17.0**	**22.2**	**26.6**	**26.2**	**21.7**	**13.3**
M2	A	< 0.1	< 0.1	3.1	5.7	7.4	12.2	11.1	10.9
	B	< 0.1	< 0.1	2.8	5.4	8.7	10.9	11.7	16.1
	Mean	**< 0.1**	**< 0.1**	**2.9**	**5.8**	**8.0**	**11.6**	**11.4**	**13.5**
M9	A	< 0.1	5.1	10.6	13.1	11.6	11.7	5.1	10.1
	B	< 0.1	6.4	13.5	16.9	16.1	12.5	16.5	11.7
	Mean	**< 0.1**	**5.8**	**12.1**	**15.0**	**13.9**	**12.1**	**10.8**	**10.9**
M15	A	< 0.1	< 0.1	< 0.1	7.5	8.3	9.9	12.1	10.2
	B	< 0.1	< 0.1	< 0.1	8.4	11.9	14.4	14.4	10.3
	Mean	**< 0.1**	**< 0.1**	**< 0.1**	**8.0**	**10.1**	**12.2**	**13.3**	**10.2**
CO_2		**-**	**-**	**0.5**	**1.7**	**3.1**	**6.1**	**9.6**	**12.1**

To identify the fractions M2, M9 and M15 further analysis by HPLC, TLC and HPLC/MS were performed: M2 and M15 could be separated into a number of components all accounting for less than 10 % of the total applied radioactivity. M9 (max. 15.0 % AR after 2 days) mainly consist of more than one component, whereas no individual fraction achieved amounts of > 10 % of AR. Further the characterisation by co-elution experiments with fumaric acids, succinic acid and maleic acid gave an indication that at least a part of the fractions of M2, M9 and M15 could be assigned to these short chain aliphatic compounds.

Additionally the *DT50* and the quantum yield were calculated: Assuming a pseudo first order reaction kinetic the *DT50* for the photolysis experiment was determined to be 1.42 d.

The quantum yield Φ was calculated to be 5.65×10^{-3}. This value was used for the estimations of the environmental half-life of chlorobenzoxazolone (AE F054014) with the computer program GC SOLAR at 50 °N for different seasons.

Table B.8.2.1.2-10 Theoretical environmental half life time of chlorobenzoxazolone (AE F054014) in surface water calculated with the computer program GC SOLAR

Latitude	*DT50* (d) Spring	Summer	Fall	Winter
40 °N	9.0	7.4	15.4	25.5
50 °N	10.4	7.8	23.3	50.6

Conclusion:

The metabolite chlorobenzoxazolone (AE F054014) was rapidly photolysed at *p*H 7 to at least 15 fractions (test temperature 25 °C). The major metabolite was hydroxybenzoxazolone (AE0316854, max. 26.6 %). Other fractions ≥ 10 % (M2, M9, M15) mainly consisted of various components which did not exceed 10 % of applied radioactivity. The photolytic half-life of chlorobenzoxazolone (AE F054014) was determined to be 1.42 d. For summer season at 50 °N an environmental half-life of 7.8 d was calculated.

Comments RMS AT:

- The study is broadly in line with OECD guideline 316 and is still considered reliable.
- The RMS AT re-evaluated the dissipation half-life of chlorobenzoxazolone (AE F054014) in line with pertinent guidance applying CAKE 3.3 yielding a *DT50* of 1.34 days (SFO, χ^2 error 6.1 %, excellent fit). This gives slightly revised theoretical half-life times of chlorobenzoxazolone (AE F054014) in surface water in range from 7.0 (summer, 40 °N) to 47.7 days (winter, 50 °N).
- It may be noted that results obtained in this study are substantially different from results obtained in

Adam (2008), where photolysis half-life of chlorobenzoxazolone (AE F054014) was only 0.11 days with a quantum yield of 0.151. Also refer to the summary section.

Reference:	**[^{14}C]-Fenoxaprop-P-ethyl: Aqueous photolysis in sterile buffer solution at pH 7**
Author(s), year:	Fitzmaurice, M. (2008b)
Report/Doc. Number:	CX/05/031, M-344639-01-1
Guideline(s):	US EPA Subdivision N, Section 161-2 (1982), SETAC Procedures, Part 10 (1995), OECD guideline, photo-transformation of chemicals in water - direct and indirect photolysis, draft (2000), US EPA OPPTS 835.2210 (1998)
GLP:	Yes
Validity:	Yes
Status:	**New submission**

Executive Summary:

The photolysis of [UL-phenoxy-^{14}C]-fenoxaprop-P-ethyl (AE F046360) was investigated in sterile aqueous buffer solution at *p*H 7 using artificial sunlight at a test concentration of 0.3 mg/L. Samples were continuously irradiated at 25 °C with artificial sunlight (< 290 nm cut-off filter) for 1.67 experimental days (40 experimental hours) in maximum, equivalent to ca 3.72 days of natural summer (June) sunlight at Phoenix, Arizona (USA).

The mean recovered radioactivity ranged from 94.3 to 97.5 % of applied radioactivity (AR) for irradiated samples and from 96.5 to 98.7 % for dark controls. Values of ^{14}C-fenoxaprop-P-ethyl (AE F046360) decreased rapidly from 92.5 % AR at time zero to 2.8 % after 40 hours of irradiation.

Irradiation resulted in formation of a compound observed at 17.7 % AR in maximum after six hours characterised as EHBPP[7] following a formal exchange of the chlorine atom in the active substance by a hydroxyl group. The complex pattern consisting of numerous minor phototransformation products included identified compounds such as fenoxaprop-P-acid (AE F088406), HOPP acid (AE F096918), phenolic metabolite (AE F040356), the ester compound AE F029062 and dissolved ^{14}C-CO_2 each accounting for 6.6 % AR or less in maximum for a single component. Unretained polar photolysis products not resolved by HPLC were separated by fractionation/TLC to result in none of the components to exceed 7.7 % AR at any sampling date.

For comparison, degradation in dark controls was negligible to form fenoxaprop-P-acid (AE F088406) and the ester AE F029062, each component not exceeding 7.1 % AR.

The direct photo-transformation of fenoxaprop-P-ethyl in sterile aqueous buffer solution (*p*H 7) was fast, resulting in a photolytic half-life of 0.68 environmental days referring to conditions of natural summer sunlight in June at Phoenix, Arizona, US (33.26 °N).

In case the contribution of biotic degradation can be excluded direct photolysis processes may contribute to the overall elimination of fenoxaprop-P-ethyl from the aquatic environment.

Material and Methods:

Test Material:	[UL-phenoxy-^{14}C]-fenoxaprop-P-ethyl (AE F046360)
Specific radioactivity:	5.84 MBq/mg (157.8 µCi/mg)
Radiochemical purity:	< 98 % (HPLC)
Sample ID:	BECH 1641

Buffer solution

The potential for direct photolysis of the test item was investigated in 0.025 M sterile aqueous buffer solution at

[7] Ethyl-2-[4-(6-hydroxybenzoxazol-2-yloxy)phenoxy]propanoate or ethyl-2-[4-(5-hydroxybenzoxazol-2-yloxy)-phenoxy]propanoate

*p*H 7. The phosphate buffer solution was sterilised by filtration through a sterile filter.

Experimental conditions
The test was performed with UL-phenoxy-^{14}C-fenoxaprop-P-ethyl (AE F046360) at an initial concentration of 0.3 mg/L. Photolysis was performed in sterilised glass vessels (static system) containing 18 mL aqueous buffer solution. Information from a preliminary test revealed that no traps to retain any evolved volatile components were required. The final concentration of the co-solvent acetonitrile in test solutions was 0.56 % (by vol.).

The samples were continuously irradiated in a ®Sun Test CPS+ system at 25 ± 1 °C with a xenon burner (range of wave length spectrum 290 to 800 nm, i.e. simulating natural sunlight) providing a light intensity of 465 W/m^2. One Suntest irradiation day was thus equivalent to 2.23 days sunlight at Phoenix, Arizona, USA, 33.26 °N at summer solstice. The UV radiation was cut-off by a filter to < 290 nm. In parallel, samples were incubated under the same conditions but in the absence of light thus serving as dark controls. Based on measurements of light intensity 40 hours of continuous light exposure in the ®Sun Test system was equivalent to 3.7 environmental days of natural sunlight at Phoenix Arizona.

Samples were irradiated continuously for 40 hours while dark controls were incubated for up to 45.5 hours in maximum. The sterility of the test solution and the *p*H was determined prior to study commencement and at the end of the study.

Additional samples were prepared and irradiated in order to isolate the major unidentified photolysis product EHBPP (see below).

Sampling
Duplicates of irradiated samples were removed for analysis after 0, 16, 20, 25, 30 and 40 hours, corresponding to 0.125, 0.25, 0.67, 0.83, 1.04, 1.25 and 1.67 days. In addition, single samples were taken after three and six hours. Dark controls were removed after 29 and 45.5 hours, thus corresponding to 1.21 and 1.90 days.

Analytical procedures
Samples were diluted to 20 mL with acetonitrile and radioactivity determined by liquid scintillation counting (LSC). Reversed-phase HPLC including ^{14}C-flow-through detection was used as primary analytical method for separation of transformation products. Representative samples were investigated by HPLC coupled with mass spectrometry (MS) for confirmation of identity of fenoxaprop-P-ethyl and major degradation products. Selected samples were re-analysed by thin-layer chromatography TLC to investigate fractions containing polar components.

The limit of quantitation (LOQ) was estimated for HPLC to 0.5 % of AR.

Kinetic evaluation
The kinetic evaluation was performed for the test substance following FOCUS guidance (FOCUS, 2006) by use of the software MatLab 7.0.4.365 including the KinGUI kinetics tool.

Results and Discussion:

The total irradiation time of 1.67 days (40 experimental hours) was equivalent to approximately 3.7 days sunlight (Phoenix, Arizona, USA) and thus included two half-lives for the test substance.

The *p*H of aqueous buffer was determined to 7.01 for irradiated samples and dark controls at the end of the study. Sterility of samples was confirmed throughout the study. The test was maintained at a temperature of 25 ± 1 °C throughout the study.

The material balances ranged from 94.3 to 97.5 % AR for irradiated samples and from 96.5 to 98.7 % AR in dark controls.

In irradiated samples, fenoxaprop-P-ethyl (AE F046360) was transformed rapidly from 92.5 % AR at time zero to 2.8 % following 40 hours of irradiation. Degradation in dark controls was negligible indicated by values of 92.5 % AR at time zero and 86.5 % after 46.5 hours of incubation.

Photo-transformation was extensive to result in numerous (> 50) minor products formed. One unknown

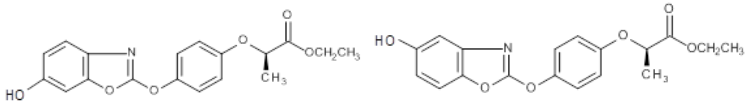
photolysis product was observed at a maximum of 17.7 % AR after six hours. Following separation and analysis the unknown was characterised to be a dechlorinated compound to result in two structural proposals, reported as two isomers of EHBPP.

The large number of minor photolysis products included dissolved $^{14}C\text{-}CO_2$ (maximum of 6.6 % AR after 40 hours), phenolic metabolite (AE F040356, maximum of 6.2 % after 16 hours) and an unknown component (RRT 0.93, maximum of 6.2 % after 20 hours). Fenoxaprop-P-acid (AE F088406) was observed at 2.4 % in maximum after three hours of irradiation.

In addition, a complex pattern of polar transformation products (retention times 0.07 – 0.10 min) was formed in the course of the study. A region with retention time 0.08 min had reached a maximum of 13.3 % AR after 40 hours. However, polar radioactivity in HPLC could be further separated by TLC with none of the components to exceed 7.7 % AR in the course of the study.

In the dark controls, AE F029062 and fenoxaprop-P-acid (AE F088406) were formed at 5.0 % and 7.1 % AR in maximum, respectively, after 46.5 hours.

Structures proposed for photo-transformation product EHBPP:



EHBPP Isomer I EHBPP Isomer II

Table B.8.2.1.2-11 Photo-transformation of [UL-phenoxy-^{14}C]-fenoxaprop-P-ethyl (AE F046360) in sterile aqueous buffer solution of *p*H 7; irradiated samples (numbers shaded in grey indicate exceedance of 10 % AR)

Component	Sample No.	43	44	Mean	45	46	51	52	Mean	53	54	Mean
	Time, hours	0	0	0	3	6	16	16	16	20	20	20
	RRT											
CO_2 related[(a)]	*0.05 - 0.07*	nd	nd	**nd**	**nd**	**nd**	1.9	3.1	**2.5**	3.3	2.6	**2.9**
Unknown[(a)]	*0.08*	nd	nd	**nd**	**nd**	**2.4**	5.5	4.3	**4.9**	7.6	7.2	**7.4**
Unknown[(a)]	*0.09 - 0.10*	nd	nd	**nd**	**nd**	**nd**	1.7	1.1	**1.4**	1.2	1.7	**1.5**
Unknown	*0.11 - 0.12*	nd	nd	**nd**	**nd**	**nd**	0.5	0.9	**0.7**	1.9	1.5	**1.7**
Unknown	*0.13 - 0.17*	nd	nd	**nd**	**nd**	**nd**	1.0	0.8	**0.9**	0.9	0.8	**0.9**
Unknown	*0.18 - 0.22*	nd	nd	**nd**	**nd**	**nd**	0.9	1.0	**0.9**	0.8	0.3	**0.6**
Unknown	*0.23 - 0.27*	nd	nd	**nd**	**nd**	**nd**	0.6	0.3	**0.5**	1.0	0.8	**0.9**
Unknown	*0.28 - 0.33*	nd	nd	**nd**	**nd**	**nd**	1.3	0.3	**0.8**	0.7	1.2	**0.9**
Unknown	*0.34 - 0.38*	nd	nd	**nd**	**nd**	**nd**	1.3	1.3	**1.3**	1.5	1.6	**1.5**
Unknown	*0.39 - 0.42*	nd	nd	**nd**	**nd**	**nd**	1.5	2.1	**1.8**	2.3	0.5	**1.4**
Unknown	*0.43 - 0.45*	nd	nd	**nd**	**nd**	**nd**	2.1	2.4	**2.2**	1.7	2.5	**2.1**
Unknown	*0.46 - 0.49*	nd	nd	**nd**	**nd**	**nd**	1.4	1.1	**1.3**	2.2	3.2	**2.7**
HOPP-acid (AE F096918)	*0.50*	nd	nd	**nd**	**nd**	**nd**	2.2	2.0	**2.1**	1.6	1.0	**1.3**
Unknown	*0.51 - 0.54*	nd	nd	**nd**	**nd**	**nd**	2.6	2.3	**2.5**	2.0	1.9	**1.9**
Unknown	*0.55 - 0.56*	nd	nd	**nd**	**nd**	**nd**	0.6	1.1	**0.9**	1.6	2.0	**1.8**
Unknown	*0.57 - 0.59*	nd	nd	**nd**	**nd**	**1.9**	3.6	2.1	**2.9**	4.4	2.0	**3.2**
Unknown	*0.60 - 0.61*	nd	nd	**nd**	**nd**	**nd**	3.2	3.2	**3.2**	2.4	3.9	**3.1**
Unknown	*0.62 - 0.64*	nd	nd	**nd**	**nd**	**1.6**	2.5	2.1	**2.3**	2.0	2.7	**2.3**
Unknown	*0.65 - 0.66*	nd	nd	**nd**	**1.0**	**2.2**	3.7	3.0	**3.4**	2.4	3.1	**2.8**
AE F029062	*0.68*	1.7	2.5	**2.1**	**3.1**	**3.3**	2.8	2.5	**2.7**	2.5	2.7	**2.6**
Unknown	*0.69 - 0.70*	nd	nd	**nd**	**nd**	**1.9**	4.0	3.9	**3.9**	4.4	3.4	**3.9**
Unknown	*0.71 - 0.72*	nd	nd	**nd**	**nd**	**nd**	1.3	0.9	**1.1**	1.2	1.4	**1.3**
Unknown	*0.73 - 0.74*	nd	nd	**nd**	**nd**	**nd**	2.0	2.8	**2.4**	3.4	2.7	**3.0**
Unknown	*0.75 - 0.80*	nd	nd	**nd**	**nd**	**nd**	3.1	1.6	**2.3**	2.5	3.0	**2.8**
EHBPP	*0.82*	nd	nd	**nd**	**8.5**	**17.7**	12.0	12.8	**12.4**	10.9	11.8	**11.3**
Phenol metabolite (AE F040356)	*0.84*	nd	nd	**nd**	**3.2**	**5.7**	5.7	6.2	**5.9**	5.8	6.0	**5.9**
Fenoxaprop-P-acid (AE F088406)	*0.86*	2.3	2.0	**2.1**	**2.4**	**1.0**	1.5	1.7	**1.6**	1.8	1.3	**1.5**
Unknown	*0.87 - 0.91*	nd	nd	**nd**	**nd**	**nd**	1.1	1.0	**1.1**	0.9	1.1	**1.0**

Unidentified	*0.93*	nd	nd	**nd**	**3.1**	**5.6**	5.5	6.7	**6.1**	5.7	6.7	**6.2**
AE F031886	*0.94*	nd	nd	**nd**	**1.4**	**nd**	nd	nd	**nd**	nd	nd	**nd**
Unknown	*0.95 - 0.99*	nd	nd	**nd**	**nd**	**nd**	0.1	0.3	**0.2**	0.2	0.5	**0.4**
Fenoxaprop-P-ethyl (AE F046360)	*1.00*	93.0	92.0	**92.5**	**74.6**	**54.0**	18.4	19.4	**18.9**	14.7	16.2	**15.4**
Total		97.0	96.5	**96.7**	**97.3**	**97.3**	95.5	94.3	**94.9**	95.1	97.0	**96.1**

n.d. = not detected or < 0.5 % AR
(a) Added by RMS AT: The polar material (*RRT* 0.05 - 0.10) isolated from samples No. 53, 47, 49 and 55 was separated into between 8 and 12 regions of radioactivity with a maximum occurrence of 7.7 % AR on basis of a single region (sample 55, 40 hrs).
EHBPP = ethyl-2-[4-(6-hydroxybenzoxazol-2-yloxy)phenoxy]propanoate, reporting name fenoxaprop-P-ethyl-dechloro-6-hydroxy, or ethyl-2-[4-(5-hydroxybenzoxazol-2-yloxy) phenoxy]propanoate, reporting name fenoxaprop-P-ethyl-dechloro-5-hydroxy
All values expressed as percentage of total applied radioactivity (AR)

Table B.8.2.1.2-12 **(*continued*) Photo-transformation of [UL-phenoxy-^{14}C]-fenoxaprop-P-ethyl (AE F046360) in sterile aqueous buffer solution of *p*H 7; irradiated samples (numbers shaded in grey indicate exceedance of 10 % AR)**

Component	**Sample No.**	47	48	**Mean**	49	50	**Mean**	55	56	**Mean**
	Time, hours	25	25	**25**	30	30	**30**	40	40	**40**
	RRT									
CO_2 related[(a)]	*0.05 - 0.07*	3.0	3.8	**3.4**	4.7	4.7	**4.7**	7.2	6.0	**6.6**
Unknown[(a)]	*0.08*	11.5	10.9	**11.2**	10.5	11.1	**10.8**	13.3	13.3	**13.3**
Unknown[(a)]	*0.09 - 0.10*	1.7	2.2	**2.0**	1.6	1.8	**1.7**	6.0	3.5	**4.7**
Unknown	*0.11 - 0.12*	2.7	3.2	**3.0**	2.8	1.3	**2.0**	1.9	2.8	**2.3**
Unknown	*0.13 - 0.17*	1.2	1.7	**1.4**	1.2	1.0	**1.1**	1.5	2.1	**1.8**
Unknown	*0.18 - 0.22*	1.0	0.5	**0.7**	1.0	1.3	**1.1**	2.0	1.1	**1.5**
Unknown	*0.23 - 0.27*	1.1	0.4	**0.8**	0.9	1.0	**1.0**	0.9	1.0	**0.9**
Unknown	*0.28 - 0.33*	0.3	0.8	**0.6**	1.0	0.9	**0.9**	1.8	1.1	**1.5**
Unknown	*0.34 - 0.38*	2.0	2.0	**2.0**	2.6	2.1	**2.3**	2.3	2.3	**2.3**
Unknown	*0.39 - 0.42*	3.4	3.9	**3.7**	3.2	3.4	**3.3**	3.1	2.5	**2.8**
Unknown	*0.43 - 0.45*	2.7	3.2	**2.9**	1.4	2.4	**1.9**	4.6	2.7	**3.6**
Unknown	*0.46 - 0.49*	1.1	2.8	**2.0**	4.0	3.3	**3.6**	5.1	4.2	**4.7**
HOPP-acid (AE F096918)	*0.50*	3.2	1.0	**2.1**	2.0	1.8	**1.9**	nd	2.9	**1.5**
Unknown	*0.51 - 0.54*	3.1	2.9	**3.0**	3.0	2.3	**2.6**	4.0	3.1	**3.6**
Unknown	*0.55 - 0.56*	3.3	1.3	**2.3**	1.3	1.8	**1.5**	3.1	1.8	**2.5**
Unknown	*0.57 - 0.59*	2.5	4.0	**3.3**	4.0	4.2	**4.1**	3.3	3.7	**3.5**
Unknown	*0.60 - 0.61*	3.0	2.7	**2.9**	2.1	3.7	**2.9**	2.4	4.9	**3.6**
Unknown	*0.62 - 0.64*	3.8	4.2	**4.0**	5.2	2.2	**3.7**	3.8	2.3	**3.1**
Unknown	*0.65 - 0.66*	5.0	3.0	**4.0**	1.9	3.1	**2.5**	1.5	2.4	**2.0**
AE F029062	*0.68*	4.4	2.2	**3.3**	4.0	2.4	**3.2**	2.2	1.9	**2.0**
Unknown	*0.69 - 0.70*	2.0	4.8	**3.4**	5.0	5.2	**5.1**	3.9	5.3	**4.6**
Unknown	*0.71 - 0.72*	1.9	1.1	**1.5**	1.7	1.3	**1.5**	2.2	0.9	**1.6**
Unknown	*0.73 - 0.74*	2.6	3.4	**3.0**	2.1	3.3	**2.7**	2.9	3.7	**3.3**
Unknown	*0.75 - 0.80*	3.6	3.5	**3.6**	3.1	4.0	**3.6**	3.0	3.8	**3.4**
EHBPP	*0.82*	8.2	6.0	**7.1**	7.1	7.4	**7.3**	3.1	4.3	**3.7**
Phenol metabolite (AE F040356)	*0.84*	5.7	5.0	**5.4**	5.3	4.7	**5.0**	4.4	4.7	**4.6**
Fenoxaprop-P-acid (AE F088406)	*0.86*	0.9	1.2	**1.1**	1.6	1.7	**1.6**	0.9	1.4	**1.2**
Unknown	*0.87 - 0.91*	1.7	0.9	**1.3**	0.6	0.9	**0.8**	0.7	0.8	**0.7**
Unidentified	*0.93*	4.8	4.9	**4.8**	5.0	5.4	**5.2**	3.3	4.0	**3.6**
AE F031886	*0.94*	nd	0.4	**0.2**	nd	0.5	**0.2**	nd	0.2	**0.1**
Unknown	*0.95 - 0.99*	0.6	0.3	**0.4**	0.6	nd	**0.3**	0.2	nd	**0.1**
Fenoxaprop-P-ethyl (AE F046360)	*1.00*	5.3	7.4	**6.4**	6.5	6.1	**6.3**	2.6	3.0	**2.8**
Total		97.2	95.7	**96.5**	97.0	96.1	**96.5**	97.0	97.5	**97.2**

n.d. = not detected or < 0.5 % AR
(a) Added by RMS AT: The polar material (*RRT* 0.05 - 0.10) isolated from samples No. 53, 47, 49 and 55 was separated into between 8 and 12 regions of radioactivity with a maximum occurrence of 7.7 % AR on basis of a single region (sample 55, 40 hrs).
EHBPP = ethyl-2-[4-(6-hydroxybenzoxazol-2-yloxy)phenoxy]propanoate, reporting name fenoxaprop-P-ethyl-dechloro-6-hydroxy, or ethyl-2-[4-(5-hydroxybenzoxazol-2-yloxy) phenoxy]propanoate, reporting name fenoxaprop-P-ethyl-dechloro-5-hydroxy
All values expressed as percentage of total applied radioactivity (AR)

Table B.8.2.1.2-13 Transformation of [UL-phenoxy-^{14}C]-fenoxaprop-P-ethyl (AE F46360) in sterile aqueous buffer solution of *p*H 7; dark controls

Component	Replicate	Sampling interval (days) 0	1.21	1.94
Fenoxaprop-P-ethyl (AE F046360)	1	93.04	87.14	86.62
	2	92.01	88.32	86.32
	mean	**92.52**	**87.73**	**86.47**
Fenoxaprop-P-acid (AE F088406)	1	2.28	5.96	6.81
	2	1.96	5.27	7.43
	mean	**2.12**	**5.61**	**7.12**
AE F029062	1	1.71	3.58	4.96
	2	2.50	3.47	4.98
	mean	**2.11**	**3.53**	**4.97**
Total radioactivity	1	97.0	96.7	98.4
	2	96.5	97.1	98.7
	mean	**96.8**	**96.9**	**98.6**

Values expressed as percentage of total applied radioactivity (AR)

Table B.8.2.1.2-14 Products of direct photochemical transformation of ^{14}C-fenoxaprop-P-ethyl (AE F046360) in sterile aqueous buffer solution of *p*H 7

Label position	Component	Maximum fraction (% AR)	Maximum occurrence after day[(a)]
UL-phenoxy	EHBPP[(b)]	17.66	0.25

(a) Total duration was 1.67 days (40 hours)
(b) EHBPP = ethyl-2-[4-(6-hydroxybenzoxazol-2-yloxy)phenoxy]propanoate, reporting name fenoxaprop-P-ethyl-dechloro-6-hydroxy, or ethyl-2-[4-(5-hydroxybenzoxazol-2-yloxy) phenoxy]propanoate, reporting name fenoxaprop-P-ethyl-dechloro-5-hydroxy

The degradation kinetics of fenoxaprop-P-ethyl (AE F046360) in irradiated samples and dark controls was calculated by applying the single first-order kinetic model.

For irradiated samples the half-life of fenoxaprop-P-ethyl (AE F046360) was 7.08 hours (0.66 days) and the value for the *DT90* was 23.52 hours (2.19 days).

When being corrected for the portion of biotic degradation, the half-life of fenoxaprop-P-ethyl (AE F046360) was 7.27 hours (0.68 days) associated by a *DT90* of 24.16 hours (2.25 days) under conditions of natural sunlight and at summer solstice (June) at Phoenix, Arizona, US (33.26 °N).

Table B.8.2.1.2-15 Half-lives of photo-transformation of fenoxaprop-P-ethyl (AE F046360) in sterile aqueous buffer solution of *p*H 7

System	Kinetic model	Hours *DT50*	Hours *DT90*	Equivalent Days Natural Sunlight *DT50*	Equivalent Days Natural Sunlight *DT90*	Degradation rate *k*/hour	χ^2 err.
Irradiated	SFO	7.08	23.52	0.66	2.19	0.0979	3.70
Dark control	SFO	267	886	-	-	0.0026	1.10
Net-photolytic[(a)]	**SFO**	**7.27**	**24.16**	**0.68**	**2.25**	**0.0953**	

(a) Corrected for the degree of degradation in dark controls

Conclusion:

The direct photo-transformation of fenoxaprop-P-ethyl (AE F046360) in sterile aqueous buffer solution (*p*H 7) was fast, resulting in a photolytic half-life of 0.68 environmental days referring to conditions of natural summer sunlight in June at Phoenix, Arizona, US (33.26 °N).

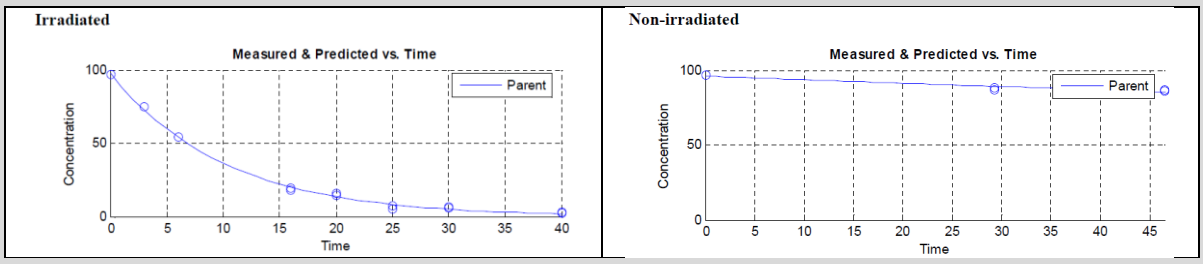
The photo-transformation in sterile buffer solution resulted in formation of numerous components with one major compound characterised as ethyl-2-[4-(6-hydroxybenzoxazol-2-yloxy)phenoxy]propanoate (isomer 1) or ethyl-2-[4-(5-hydroxybenzoxazol-2-yloxy)phenoxy]propanoate (isomer 2). Following full identification as isomer 1 (refer to Tarara, 2016) the compound was considered in aquatic risk assessment.

In case the contribution of biotic degradation can be excluded direct photolysis processes may contribute to the

overall elimination of fenoxaprop-P-ethyl (AE F046360) from the aquatic environment.

Comments RMS AT:

- The study is follows OECD guideline 316 and is considered reliable.
- Calculated photolysis half-life for fenoxaprop-P-ethyl (AE F0446360) is confirmed by the RMS AT. The fit for fenoxaprop-P-ethyl (AE F046360) in the irradiated and non-irradiated samples is given below.



Reference:	**Identification of an unknown photo-transformation product observed in aqueous photolysis in sterile buffer solution at pH 7**
Author(s), year:	Tarara, G. (2016)
Report/Doc. Number:	EnSa-16-0323, M-554364-01-1
Guideline(s):	Not applicable
GLP:	Yes
Validity:	Yes
Status:	**New submission**

Executive Summary:

The photo-transformation of [UL-phenoxy-^{14}C]-fenoxaprop-P-ethyl (AE F046360) had resulted in formation of numerous components while a major compound was characterised as 'EHBPP' consisting either of ethyl-2-[4-(6-hydroxybenzoxazol-2-yloxy)phenoxy]propanoate (Isomer I) or ethyl-2-[4-(5-hydroxybenzoxazol-2-yloxy)-phenoxy]propanoate (Isomer II, see Fitzmaurice, 2008).

The full identification was performed by separate synthesis of the two isomers to serve as authentic reference material following application of various analytical methods including HPLC/MS/MS and ^{1}H- and ^{13}C-NMR-spectroscopy. The key analytical data available for the Unknown component were then compared with those of authentic references. The structure of Unknown 'EHBPP' could thus be identified as ethyl-2-[4-(6-hydroxybenzoxazol-2-yloxy)phenoxy]propanoate (i.e. Isomer I, company code: BCS-CY11271[8]).

Material and Methods:

Solutions of each isomer were prepared in deuterated methanol (NMR) or in mixture with methanol (HPLC-MS/MS).

NMR investigations consisted of ^{1}H-NMR, Correlated Spectroscopy (i.e. ^{1}H, ^{1}H-COSY), Heteronuclear Single Quantum Correlation (HSQC) and Heteronuclear Multiple Bond Correlation (HMBC). HPLC-MS/MS investigations were performed following electro-spray ionisation.

Results and Discussion:

The spectroscopic information generated for each of the two isomers allowed for the comparison with

[8] The company code for the corresponding racemic mixture is BCS-CX38119.

spectroscopic data of the original sample generated in Fitzmaurice, 2008.

The molecular ion mass (MH+) of 344 was confirmed to be the same for the two isomers synthesized and the Unknown 'EHBPP'. In addition, the shift of signals in ^{1}H-NMR was nearly the same for protons 7 and 9 for all compounds. However, the difference in shift between the three compounds was significant for protons 16 and 19. Moreover, the shift of all signals in ^{1}H-NMR including their coupling pattern was the same for 'isomer 1' in contrast to 'isomer 2'.

Consequently, the unknown component characterized in Fitzmaurice, 2008, was fully identified as ethyl-2-[4-(6-hydroxybenzoxazol-2-yloxy)phenoxy]propanoate (i.e. Isomer I, BCS-CY11271).

Conclusion:

An unknown photo-transformation product characterized as 'EHBPP' previously was fully identified as ethyl-2-[4-(6-hydroxybenzoxazol-2-yloxy)phenoxy]propanoate (i.e. Isomer I, BCS-CY11271).

Comments RMS AT:

- None

Reference:	**[^{14}C]-fenoxaprop-P-ethyl: Photodegradation and quantum yield in sterile, aqueous solution**
Author(s), year:	Fletcher, T., Gilbert, J. (2008)
Report/Doc. Number:	268 FPE, M-548205-01-1
Guideline(s):	EC Directive 95/36/EC of July 1995, Amending Council Directive 91/414/EEC; Annex II, 7.2.1.2 Photochemical Degradation SETAC Procedures for assessing the Environmental Fate and Ecotoxicity of Pesticides, Section 10 (Aqueous Photolysis)
GLP:	Yes
Validity:	Yes
Status:	**New submission**

Executive Summary:

The photolysis of [UL-chlorophenyl-^{14}C]-fenoxaprop-P-ethyl (AE F046360) was investigated at a test concentration of 0.343 mg/L in sterile aqueous buffer solution of *p*H 7 using artificial sunlight (< 290 nm cut-off filter). Samples were continuously irradiated at 20 °C for seven experimental days (168 experimental hours) in maximum, equivalent to ca. 14 days of European summer sunlight.

The mean recovery of radioactivity ranged from 97.2 to 99.7 % of AR for irradiated samples while it was 98.1 % for dark controls. Values of ^{14}C-fenoxaprop-P-ethyl decreased from 95.4 % AR at time zero to 73.7 % after 7 days of irradiation.

Irradiation resulted in formation of a number of minor photo-transformation products accounting for 7.5 % AR in maximum or less for a single component.

The experimental *DT50* of fenoxaprop-P-ethyl was determined to 17.8 days by applying simple first order (SFO) kinetics. Considering light intensity used in the experiment to be the same as for outdoor conditions in the EU this was equivalent to ca. 17.8 days of European summer sunlight. No value of the *DT50* was determined for dark controls.

The quantum yield Φ was determined for [UL-chlorophenyl-^{14}C]-fenoxaprop-P-ethyl to be 0.040 molecules degraded/photon.

Direct photolysis is therefore expected to not contribute significantly to the overall elimination of fenoxaprop-P-ethyl from the aquatic environment.

Material and Methods:

Test Material:	[UL-chlorophenyl-^{14}C]-fenoxaprop-P-ethyl (AE F046360)
Specific radioactivity:	7.06 MBq/mg (190.8 µCi/mg)
Radiochemical purity:	97.5 %
Sample ID:	3039CAL001-2

Buffer solution
A 0.02 M aqueous phosphate buffer solution of *p*H 7 was prepared by adjusting a 0.02 M potassium dihydrogen phosphate solution to *p*H 7 using 2 M aqueous sodium hydroxide. The quantum yield was determined at *p*H 7 in a buffer/acetonitrile solution (1:1, by vol.).

Experimental conditions
The test was performed with UL-chlorophenyl-^{14}C-fenoxaprop-P-ethyl at an initial concentration of 0.343 mg/L. Photolysis was performed in sterilised glass vessels with quartz glass lids attached to a system of traps for volatiles. The final concentration of organic co-solvent in aqueous buffer solutions was < 1 %. Samples were continuously irradiated in a ®Suntest system at 20 ± 3 °C with a xenon burner simulating sunlight (range of wave length 290 to 800 nm) including filters for cut-off of UV radiation below 290 nm. The average intensity for wave length of 300 to 400 nm was 25.3 W/m^2, thus approximately equivalent to one European summer day. In parallel, two samples were incubated for seven days under the same conditions in the dark thus serving as dark controls.

Samples were continuously irradiated for 7 days in maximum while the dark controls were incubated in the dark for the same time.

The *p*H and sterility of samples was determined for irradiated samples and dark controls.

A UV-VIS absorption spectrum was recorded for a solution of 0.05 mg/mL fenoxaprop-P-ethyl in *p*H 7 in phosphate buffer at *p*H 7/acetonitrile (1:1, by vol.) for a wavelength range from 290 to 800 nm. Measurements were made at 2 nm intervals.

Sampling
Duplicate samples were removed for analysis after 0, 1, 2, 4 and 7 days of irradiation. Dark controls were removed after 7 days of incubation.

Analytical procedures
A portion of 8 mL of acetonitrile was added to each sub-sample prior to determination of radioactivity by LSC. Direct analysis of the aqueous solution was performed by HPLC coupled with ^{14}C-radio-detection. Sub-samples (ca. 10 g) of unit wash were concentrated, reconstituted in aqueous acetonitrile and analysed by LSC and HPLC. The purity of the test item and representative samples were re-analysed by thin-layer chromatography (TLC) as confirmatory method including appropriate reference standards.

Kinetic evaluation
The evaluation of fenoxaprop-P-ethyl degradation data was performed with the software Excel by using the SFO kinetic model. Values for half-lives and *DT90* were calculated for irradiated samples and dark controls.

Results and Discussion:

Based on the light intensity determinations the maximum irradiation time of seven days (168 experimental hours) was equivalent to approximately 7 days of European summer sunlight.

The *p*H was constant for irradiated samples and dark controls throughout the study.

Sterility of test solutions was confirmed by tests on bacterial colony formation on agar plates. The test temperature was 20 ± 3 °C for irradiated samples and 20 ± 2 °C for dark controls.

The material balances (mean of two replicates) ranged from 97.2 to 99.7 % AR for irradiated samples and it was 98.1 % for dark controls. Mineralisation to ^{14}C-carbon dioxide was 0.9 % AR after seven days of irradiation while formation of other volatiles was negligible (0.6 % AR in maximum).

For irradiated samples, values of fenoxaprop-P-ethyl decreased from 95.4 % AR at time zero to 73.7 % after seven days of irradiation. Fenoxaprop-P-ethyl in dark controls was 87.7 % after seven days of incubation.

Photo-transformation of fenoxaprop-P-ethyl resulted in up to eight minor metabolites. Chlorobenzoxazolone (AE F054014) and fenoxaprop-P-acid (AE F088406) were detected at 1.8 % (day 1) and 1.6 % AR (day 4) in maximum, respectively. Six unknown photo-transformation products were found to reach 7.5 % AR in maximum for a single component.

In dark controls, single metabolites were formed at or below 3.4 % AR.

No major and distinct transformation products were therefore observed assessment in environmental exposure assessment.

The quantum yield Φ for [UL-chlorophenyl-^{14}C]-fenoxaprop-P-ethyl was determined to 0.040 molecules degraded/photon.

Table B.8.2.1.2-16 Transformation of [UL-chlorophenyl-^{14}C]-fenoxaprop-P-ethyl (AE F046360) in sterile aqueous buffer solution of *p*H 7; <u>irradiated</u> and <u>dark control</u>

Component	Replicate No.	Sampling interval (days) 0	1	2	4	7	7 (dark)
Fenoxaprop-P-ethyl (AE F046360)	1	94.4	94.6	88.1	75.0	73.4	89.7
	2	96.4	90.7	89.5	84.7	74.0	85.6
	mean	**95.4**	**92.7**	**88.8**	**79.9**	**73.7**	**87.7**
Chlorobenzoxazolone (AE F054014)	1	1.4	0.6	0.5	0.6	0.7	3.0
	2	1.2	2.9	0.4	0.7	1.1	3.3
	mean	**1.3**	**1.8**	**0.5**	**0.7**	**0.9**	**3.2**
Fenoxaprop-P-acid (AE F088406)	1	0.2	n.d.	1.1	1.6	1.6	3.4
	2	n.d.	0.8	0.8	1.6	1.6	3.3
	mean	**0.1**	**0.4**	**1.0**	**1.6**	**1.6**	**3.4**
Largest unknown	1	- [B)]	- [C)]	4.8	7.0	7.4	n.a.
	2	- [C)]	- [C)]	4.3	4.5	7.5	n.a.
	mean	**n.c.**	**n.c.**	**4.6**	**5.8**	**7.5**	**n.a.**
Total of minor unknowns	1	0.1	3.9	4.3	12.1	10.6	0.3
	2	0.8	3.4	3.7	5.8	11.4	0.6
	mean	**0.5**	**3.7**	**4.0**	**9.0**	**11.0**	**0.5** [D)]
Radioactivity recovered from test solution	1	79.0	96.5	98.4	93.1	93.0	96.4
	2	78.2	87.6	95.1	92.9	94.5	93.0
	mean	**78.6**	**92.1**	**96.8**	**93.0**	**93.8**	**94.7**
Radioactivity recovered from test vessel wash	1	18.2	3.4	1.7	4.1	2.7	2.9
	2	20.6	10.7	4.0	5.2	2.4	3.8
	mean	**19.4**	**7.1**	**2.9**	**4.7**	**2.6**	**3.4**
^{14}C-Carbon dioxide	1	n.a.	n.d.	0.0	0.1	0.7	n.d.
	2	n.a.	n.d.	0.0	0.2	0.9	n.d.
	mean	**n.a.**	**n.d.**	**n.d.**	**0.2**	**0.8**	**n.d.**
Other volatiles [A)]	1	n.a.	n.d.	n.d.	n.d.	0.1	n.d.
	2	n.a.	0.9	n.d.	0.1	0.0	n.d.
	mean	**n.a.**	**0.5**	**n.d.**	**0.1**	**0.1**	**n.d.**
Total recovery	1	97.2	99.9	100.1	97.3	96.5	99.3
	2	98.8	99.2	99.1	98.4	97.8	96.8
	mean	**98.0**	**99.6**	**99.7**	**97.9**	**97.2**	**98.1**

n.a. = not applicable
n.d. = not detected or < 0.1 % AR
n.c. = not calculated
[A)] Quantifiable amounts of volatile radioactivity other than $^{14}CO_2$ were found in foam bungs only
[B)] no further unknowns present
[C)] all unknowns < 2 % AR
[D)] no unknowns > 0.3 % AR
All values expressed as percentage of total applied radioactivity (AR)

The rate of photo-transformation of fenoxaprop-P-ethyl (AE F046360) was calculated by applying the simple first-order kinetic model. No experimental *DT50* value was calculated for dark controls.

The experimental half-life was determined to 17.8 days for irradiated samples, equivalent of ca 17.8 days of European summer sunlight. The experimental *DT50* had not been corrected for biological degradation due to the insignificant degradation observed in dark controls.

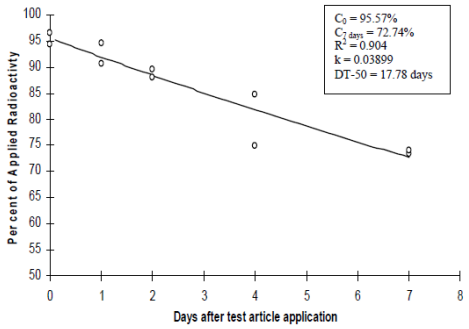
Conclusion:

The direct photo-transformation of fenoxaprop-P-ethyl in sterile buffer solution (*p*H 7) was slow, resulting in a half-life of 17.8 environmental days when referring to light conditions of European summer sunlight. Consequently, the irradiation resulted in no formation of photo-degradation products at significant level to be considered in aquatic risk assessment. Direct photolytic processes therefore contribute to a negligible extent to the overall elimination of fenoxaprop-P-ethyl from the aquatic environment.

The quantum yield Φ for [chlorophenyl-U-^{14}C]-fenoxaprop-P-ethyl was determined to 0.040 molecules degraded/photon.

Comments RMS AT:

- The study is follows OECD guideline 316 and is considered reliable.
- Calculated photolysis half-life for fenoxaprop-P-ethyl (AE F0446360) is confirmed by the RMS AT. The fit for fenoxaprop-P-ethyl (AE F046360) in the irradiated samples is given below. Note that the photolysis rate of 17.8 days is extrapolated beyond the study duration.



- The study authors did not calculate the net photolysis rate accounting for hydrolysis under non-irradiated (dark) conditions. However, as there is only one sampling point available for the dark control (i.e. 7 DAT with 87.7 % AR fenoxaprop-P-ethyl (AE F046360) remaining) no reliable dark hydrolysis rate can be calculated at all.
- The RMS AT notes that photolysis results for fenoxaprop-P-ethyl (AE F046360) in this study (lab photolysis *DT50* of 17.8 days) are substantially different from results obtained in Fitzmaurice (2008) (lab photolysis *DT50* of 0.7 days) conducted under the same conditions (*p*H 7, 0.02 M phosphate buffer) but with a different label. Also refer to the summary section.

Reference:	**^{14}C-6-chloro-2,3-dihydrobenzoxazol-2-one (metabolite of fenoxaprop-P-ethyl) - Aqueous photolysis and determination of the quantum yield**
Author(s), year:	Adam, A. (2008b)
Report/Doc. Number:	267 FPE, M-548198-01-1
Guideline(s):	OECD Guideline, Proposal for a new Guideline: Phototransformation of Chemicals in Water – Direct and Indirect Photolysis, draft document (2000),

	EPA-540/9-82-021, Section 161-2 (1982), EPA 540/09-90-078 (1989)
GLP:	Yes
Validity:	Yes
Status:	**New submission**

Executive Summary:

The photo-transformation of [UL-phenyl-^{14}C]-chlorobenzoxazolone (AE F054014) was investigated at a test concentration of 0.15 mg/L in sterile aqueous buffer solution at *p*H 7. Samples were continuously irradiated at 25 °C with artificial sunlight (< 290 nm cut-off filter) for seven experimental days (168 experimental hours) in maximum, equivalent to 16 environmental days when considering midsummer sunlight at latitudes 30 - 40 °N.

The mean recovered radioactivity ranged from 98.1 to 100.0 % of AR for irradiated samples and from 99.4 to 102.3 % for dark controls. Values of ^{14}C-chlorobenzoxazolone (AE F054014) decreased from 100.0 % AR at time zero to below the limit of detection after seven days of irradiation.

Irradiation resulted in formation of numerous radioactive fractions and components each to consist of multiple components. In dark controls, the ^{14}C-test substance was found to be stable.

The experimental *DT50* was determined to 0.11 days for chlorobenzoxazolone (AE F054014). The experimental half-life was equivalent to 0.25 days for midsummer natural light conditions at latitudes 30 - 40 °N.

The quantum yield Φ for photo-transformation was determined by actinometry to 0.151 molecules degraded/photon.

In case biotic degradation processes can be excluded, direct photolysis may therefore contribute to the overall elimination of chlorobenzoxazolone (AE F054014) from the aquatic environment.

Material and Methods:

Test Material:	[UL-phenyl-^{14}C]-chlorobenzoxazolone (AE F054014)
Specific radioactivity:	11.78 MBq/mg (318.3 µCi/mg)
Radiochemical purity:	100 % (HPLC)
Sample ID:	2525MFO007-6

Buffer solution
Sterile aqueous phosphate buffer solution of *p*H 7 was prepared by diluting aqueous solutions of 0.1 N sodium hydroxide and 0.1 M monopotassium phosphate with distilled water to reach a final concentration was 0.05 mol/L. Prior to further use the buffer solution was sterilized by autoclaving.

Experimental conditions
The test was performed with UL-chlorophenyl-^{14}C-chlorobenzoxazolone (AE F054014) at an initial concentration of 0.15 mg/L. Photolysis was performed in cylindrical vessels made of Pyrex glass and covered with quartz glass plates. The equipment was sterilized prior to use. The vessels were attached to traps for volatile components. The final concentration of organic co-solvent in the test solutions was 0.9 %. The samples were continuously irradiated in a Suntest system at 24.9 ± 0.1 °C with simulated sunlight (xenon burner, range of wave length spectrum 290 to 800 nm, i.e. simulating natural sunlight). Wave lengths below 290 nm were cut-off by the use of filters. By providing a light intensity of 52.9 W/m^2 one Suntest irradiation day was equivalent to 2.3 days of midsummer sunlight at latitudes 30 - 40 °N. Based on intensity measurements a continuous light exposure of seven days in maximum (168 experimental hours) was equivalent to 16 environmental days compared to light conditions at latitudes 30 - 40 °N. In parallel, dark controls were incubated under static conditions at the same temperature in the dark. The sterility of the test systems was determined at the start and the end of the irradiation or incubation.

Sampling
Duplicates of irradiated samples and dark controls were removed for analysis after 0, 2, 4, 6, 8 and 23 hours (corresponding to 0, 0.08, 0.17, 0.25, 0.33 and 0.96 days) and 3 and 7 days of irradiation and incubation.

Analytical procedures
Samples were analysed directly using LSC for determination of radioactivity. Reversed-phase HPLC with ^{14}C-flow-through detection techniques was used as analytical method for separation and quantitation of transformation products. Representative samples were additionally investigated by radio-TLC as confirmatory analytical method. The limit of detection (LOD) of radio-HPLC analysis was 0.3 % AR.

Kinetic evaluation
The evaluation of chlorobenzoxazolone degradation data was performed with the software Origin version 6.1 (Origin Lab Corporation, MA, USA) by using the SFO kinetic model.

Results and Discussion:

The total irradiation time of seven days (168 experimental hours) in maximum corresponded to 16 environmental days compared to light conditions at latitudes 30 - 40 °N.

The *p*H of aqueous phosphate buffer was constant for irradiated samples and dark controls throughout the study. Sterility of samples was confirmed by bacterial plate counts on agar plates. The test temperature was constant at 24.9 ± 0.1 °C for the irradiated samples and 25.0 ± 0.1 °C for dark controls.

The material balances ranged from 98.8 to 100.0 % AR for irradiated samples and from 99.5 to 102.3 % for dark controls. Mineralisation to ^{14}C-carbon dioxide was significant to amount to 38.0 % AR after seven days of irradiation while formation of other volatiles was insignificant. In irradiated samples, chlorobenzoxazolone (AE F054014) was transformed fast from 100.0 % AR at time zero to below the limit of detection (0.3 % AR) at the end of the irradiation period. Chlorobenzoxazolone (AE F054014) was stable in dark controls.

Irradiation resulted in a rather complex pattern of photo-degradation products consisting of at least sixteen radioactive fractions resolved by the HPLC analytical method. The polar radioactive fractions showed up at maximum amounts of 33.3 % (day 7) for M1, 39.8 % (day 0.96) for M2, 21.2 % (day 0.33) for M4, 16.5 % (day 7) for M9, 10.4 % (day 0.96) for M10 and 10.8 % AR (day 7) for M16. Major portions of components M2 and M4 declined rapidly within one day to be no more detectable after seven days of irradiation. As a representative for other sampling intervals, irradiated samples of day 7 were re-analysed by HPLC to show that polar radioactivity including fractions M1, M9 and M16 (retention time between 2.5 to 10 min) consisted of multiple components.

In dark controls, no notable degradation of chlorobenzoxazolone (AE F054014) was observed.

The quantum yield Φ for [UL-phenyl-^{14}C]-chlorobenzoxazolone (AE F054014) was determined to 0.151 molecules degraded/photon.

Table B.8.2.1.2-17 Phototransformation of [UL-phenyl-^{14}C]-chlorobenzoxazolone in sterile aqueous buffer solution of *p*H 7; irradiated

Component		Sampling interval (days)							
	Suntest	**0**	**0.08**	**0.17**	**0.25**	**0.33**	**0.96**	**3**	**7**
	Sunlight[(a)]	**0**	**0.20**	**0.39**	**0.59**	**0.79**	**2.26**	**7**	**17**
	Sunlight[(b)]	**0**	**0.19**	**0.38**	**0.57**	**0.75**	**2.17**	**7**	**16**
Chlorobenzoxazolone (AE F054014)	1	100.8	56.1	25.5	14.8	7.8	-	-	-
	2	99.2	66.6	42.1	27.1	14.8	-	-	-
	mean	**100.0**	**61.4**	**33.8**	**20.9**	**11.3**	**-**	**-**	**-**
Unknowns M1	1	-	3.1	2.1	6.5	5.6	18.2	27.7	34.3
	2	-	1.2	3.3	-	-	7.3	20.7	32.3
	mean	**-**	**2.1**	**2.7**	**3.2**	**2.8**	**12.7**	**24.2**	**33.3**
Unknowns M2	1	-	12.7	31.6	37.8	40.8	39.2	10.5	-
	2	-	11.9	20.4	27.2	37.3	40.5	12.8	-
	mean	**-**	**12.3**	**26.0**	**32.5**	**39.1**	**39.8**	**11.7**	**-**
Unknowns M4	1	-	14.3	21.7	20.4	22.5	12.1	-	-
	2	-	12.2	14.3	16.1	19.9	16.7	3.6	-
	mean	**-**	**13.3**	**18.0**	**18.3**	**21.2**	**14.4**	**1.8**	**-**
Unknowns M6	1	-	6.4	3.1	4.6	6.6	2.6	1.3	-
	2	-	1.7	6.0	5.0	5.2	2.5	2.3	-
	mean	**-**	**4.1**	**4.6**	**4.8**	**5.9**	**2.5**	**1.8**	**-**

Component		Sampling interval (days)							
	Suntest	**0**	**0.08**	**0.17**	**0.25**	**0.33**	**0.96**	**3**	**7**
	Sunlight[(a)]	**0**	**0.20**	**0.39**	**0.59**	**0.79**	**2.26**	**7**	**17**
	Sunlight[(b)]	**0**	**0.19**	**0.38**	**0.57**	**0.75**	**2.17**	**7**	**16**
Unknowns M9	1	-	-	2.3	-	-	-	15.4	14.8
	2	-	-	-	5.2	4.6	5.6	15.3	18.1
	mean	**-**	**-**	**1.1**	**2.6**	**2.3**	**2.8**	**15.3**	**16.5**
Unknowns M10	1	-	-	3.2	7.0	12.8	11.7	8.5	-
	2	-	-	4.3	6.5	6.6	9.1	5.5	-
	mean	**-**	**-**	**3.8**	**6.8**	**9.7**	**10.4**	**7.0**	**-**
Unknowns M13	1	-	-	3.2	2.9	-	4.2	4.2	-
	2	-	-	-	-	4.1	7.6	3.6	-
	mean	**-**	**-**	**1.6**	**1.5**	**2.0**	**5.9**	**3.9**	**-**
Unknowns M16	1	-	-	-	-	-	-	8.9	11.4
	2	-	-	-	-	-	-	10.2	10.2
	mean	**-**	**-**	**-**	**-**	**-**	**-**	**9.6**	**10.8**
Total radioactivity recovered from buffer solution	1	100.8	100.4	99.7	99.1	98.4	95.9	79.5	60.5
	2	99.2	99.5	100.1	99.1	98.5	96.1	81.7	62.1
	mean	**100.0**	**99.9**	**99.9**	**99.1**	**98.5**	**96.0**	**80.6**	**61.3**
^{14}C-Carbon dioxide	1	n.d.	< 0.1	< 0.1	0.2	0.4	3.6	18.9	38.4
	2	n.d.	< 0.1	< 0.1	0.2	0.4	2.8	16.0	37.7
	mean	**n.a.**	**< 0.1**	**< 0.1**	**0.2**	**0.4**	**3.2**	**17.5**	**38.0**
Other volatile radioactivity	1	n.d.	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
	2	n.d.	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
	mean	**n.a.**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**
Total recovery	1	100.8	100.4	99.8	99.3	98.8	99.5	98.4	99.0
	2	99.2	99.5	100.2	99.2	98.9	98.9	97.7	99.7
	mean	**100.0**	**100.0**	**100.0**	**99.3**	**98.8**	**99.2**	**98.1**	**99.4**

- = not detected
n.d. = not determined
n.a. = not applicable
(a) Summer sunlight time equivalent for latitude 50 °N
(b) Summer sunlight time equivalent for latitudes 30-40 °N
Values expressed as percentage of total applied radioactivity (AR)
Several other unknowns including M3, M5, M7, M8, M11, M12, M14 and M15 were detected to account each for less than 5 % AR for a single component.

Table B.8.2.1.2-18 Transformation of [UL-phenyl-^{14}C]-chlorobenzoxazolone in sterile aqueous buffer solution of pH 7; <u>dark controls</u>

Component	Sampling interval (days)							
	0	**0.08**	**0.17**	**0.25**	**0.33**	**0.96**	**3**	**7**
Chlorobenzoxazolone (AE F054014)	100.0	100.6	101.1	99.4	99.7	99.5	102.1	102.2
Total radioactivity recovered from buffer solution	100.0	100.6	101.1	99.4	99.7	99.5	102.1	102.2
^{14}C-Carbon dioxide	n.d.	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Other volatile radioactivity	n.d.	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Total recovery	**100.0**	**100.6**	**101.1**	**99.4**	**99.7**	**99.5**	**102.2**	**102.3**

n.d. = not determined
All values expressed as percentage of total applied radioactivity (AR)

For irradiated samples the experimental *DT50* for the chlorobenzoxazolone (AE F054014) was calculated by applying a simple first order kinetic model. No experimental *DT50* value was calculated for dark controls considering the stability of the compound under the conditions of the test. The experimental half-life was determined to 0.11 days associated with a *DT90* of 0.37 days. When transferring the result to outdoor conditions considering the (lower) light intensities of natural sunlight at latitudes 30 - 40 °N, this resulted in a half-life of 0.25 days. The corresponding *DT90* value was 0.83 days. The light intensity is comparable to southern European conditions, i.e. the light intensity at Athens, Greece, thus resulting in the same environmental half-life.

<u>Conclusion:</u>

The direct photo-transformation of chlorobenzoxazolone (AE F054014) in sterile aqueous buffer solution of *p*H 7 was fast to result in a photolytic half-life of 0.25 environmental days referenced to natural light conditions

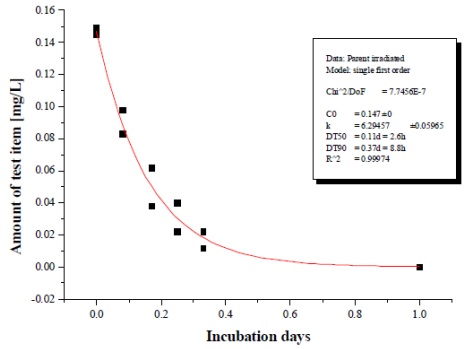
of latitudes 30 - 40 °N. The irradiation of ^{14}C-chlorobenzoxazolone in sterile buffer solution of *p*H 7 resulted in formation of numerous photo-degradation products with none to be considered in aquatic risk assessment.

In the absence of microbial degradation, direct photolysis processes may therefore contribute to a significant extent to the elimination of chlorobenzoxazolone (AE F054014) from the aquatic environment.

The quantum yield Φ was determined for [UL-phenyl-^{14}C]-chlorobenzoxazolone to 0.151 molecules degraded/photon.

Comments RMS AT:

- The study is follows OECD guideline 316 and is considered reliable.
- Calculated photolysis half-life for chlorobenzoxazolone (AE F054014) is confirmed by the RMS AT. The fit for the irradiated samples is given below.



- The RMS AT notes that results obtained in this study (lab photolysis *DT50* of 0.11 days, Φ = 0.151) are substantially different from results obtained in Burgener (1999) (lab photolysis *DT50* of 1.3 days, Φ = 0.0057) conducted under the same conditions (*p*H 7, 0.05 M phosphate buffer). Also refer to the summary section.

B.8.2.1.3. Indirect photochemical degradation

Indirect photolysis of the active substance fenoxaprop-P-ethyl (AE F046360) was investigated in non-sterile surface water (*p*H 9) following application of UL-chlorophenyl-^{14}C-labelled fenoxaprop-P-ethyl (AE F046360) and irradiation with a xenon arc lamp at 25 °C **(Schwab, 1993)**. For details refer to Schwab (1993), section B.8.2.1.2.

B.8.2.2. Route and rate of biological degradation in aquatic systems

B.8.2.2.1. 'Ready biodegradability'

No experimental data on ready biodegradability of fenoxaprop-P-ethyl (AE F046360) had been submitted within the process of Annex I inclusion.

New information submitted by the Fenoxaprop Task Force:

- **Hargreaves & Murphy (2005)**, investigating technical fenoxaprop-P-ethyl (AE F046360)

Reference:	**Fenoxaprop-P-ethyl technical: Determination of ready biodegradability by the CO_2 evolution (Modified Sturm) test**
Author(s), year:	Hargreaves, T. L., Murphy, C. M. (2005)
Report/Doc. Number:	151 FPE, M-548090-01-1
Guideline(s):	EC (2001), Directive 92/69/EEC, Annex V, Method C4-C, CO_2 Evolution Test OECD (1992), OECD 301B 'Ready Biodegradability, CO_2 Evolution Test (Modified Sturm Test)
GLP:	Yes
Validity:	Yes
Status:	**New submission**

Executive Summary:

The ready biodegradability of non-labelled active substance fenoxaprop-P-ethyl (AE F046360, technical grade) was investigated in a mineral medium inoculated by an activated sewage sludge at a nominal test concentration of 33.5 mg a.s./L under conditions of a 'CO_2 Evolution (Modified Sturm) Test' in its essential parts being identical with conditions of OECD 301 B. Samples were incubated at 20 - 23 °C in the dark for 28 days in maximum.

Fenoxaprop-P-ethyl technical was considered to be not ready biodegradable under the conditions of the test thus not fulfilling the criteria set according to OECD 301 B.

Material and Methods:

Test Material:	Fenoxaprop-P-ethyl (AE F046360) Technical
Chemical purity:	95.6 %
Sample ID:	660-PSH-45

Test system
The activated sludge used as origin for the inoculum in the test was collected from a wastewater treatment plant treating predominantly domestic sewage (Haddington Municipal Sewage Treatment Works, UK).

Experimental conditions
Samples of 2000 L mineral medium containing 20 mL inoculum were treated with the test substance to result in a nominal test concentration of 33.5 mg a.s./L. The samples were incubated in the dark at 20 - 23 °C for 29 days in maximum. Each sample was attached to a system of three traps, each containing 0.0125 M $Ba(OH)_2$ for determination of carbon dioxide formed in the course of the test. Each sample was purged with CO_2-free air.

In addition, samples containing the reference substance sodium benzoate, untreated blank controls and toxicity controls were incubated under the same conditions and measured at the same time points.

In a preliminary test inhibitory effects of fenoxaprop-P-ethyl (AE F046360) technical on the microbial inoculum were assessed.

Sampling and analytical procedures
Trap changes were conducted at 1, 4, 7, 11, 14, 18, 22, 27 and 29 days. Each sample trap was titrated against the indicator phenolphthalein solution with 0.05 M HCl (colour change pink to colourless). The *p*H was determined in each bioreactor on days 0, 28 and 29. After *p*H determination on day 29, the bioreactors were acidified by

concentrated aqueous hydrochloric acid to drive off any residual CO_2 in the system.

Evaluation
The weight of CO_2 evolved was calculated from the titre. The actual titre for each batch of $Ba(OH)_2$ prepared was used for the background titre value. The titre value for the test, reference and control vessels were calculated and subjected to the following equation:

$$\text{Weight } CO_2 \text{ produced (mg)} = 1.1 \times (\text{background titre} - \text{mL HCl titrated})$$

The net CO_2 production was then calculated by subtracting the control mean CO_2 production value from the test and reference item CO_2 values. The percentage biodegradation was calculated by comparing the actual CO_2 evolved in test and reference vessels with the theoretical CO_2 evolution ($ThCO_2$). This was calculated from the molecular weight and empirical formula of the test or reference item, as appropriate:

$$\% \text{ Degradation} = \text{mg } CO_2 \times 100 / (ThCO_2 \times \text{mg test substance added})$$

The test item was considered readily biodegradable if a transition from 10 % to 60 % (or greater) biodegradation was observed in a 10 day window during the 28 day test period. For a valid test, the reference item should be shown to be readily biodegradable.

Results and Discussion:

The temperature was maintained at 20 - 23 °C during the test. Biological activity of the inoculated mineral medium was confirmed by the degradation of the reference substance.

The reference substance was readily biodegradable since 68.2 % biodegradation was achieved on day 11, thus indicating sufficient microbial activity of the test system.

No toxicity of the test substance was observed in toxicity controls.

Fenoxaprop-P-ethyl technical did not exhibit notable biodegradation; the cumulative biodegradation at day 29 was determined to 3.9 %. Therefore, fenoxaprop-P-ethyl technical was not readily biodegradable under the conditions of the test.

Differences in CO_2 evolution between replicate test item bioreactors were greater than 20 % of the mean at day 29. However, as the test item exhibited only negligible biodegradation this difference is not considered to have had any impact on the outcome of the test also in view that other validity criteria for the test were met.

Conclusion:

Fenoxaprop-P-ethyl is considered to be not ready biodegradable under the conditions of a 'CO_2 Evolution (Modified Sturm) Test' thus not fulfilling the criteria set according to OECD 301 B.

Comments RMS AT:

- None

B.8.2.2.2. Aerobic mineralisation in surface water

Being a new data requirement this point had not been addressed in the existing dossier submitted within the process for Annex I inclusion.

In order to fulfil actual data requirements, new data were generated by performing two studies **(Telscher & Junge, 2016a; Telscher & Junge, 2016b)** following application of two positions of radiolabel each according to OECD Guideline 309.

Reference:	**[Chlorophenyl-UL-^{14}C]Fenoxaprop-P-ethyl: Aerobic mineralisation in surface water**
Author(s), year:	Telscher, M., Junge, T. (2016a)
Report/Doc. Number:	EnSa-15-0163, M-551145-01-1
Guideline(s):	OECD Test Guideline No. 309
GLP:	Yes
Validity:	Yes
Status:	**New submission**

Executive Summary:

The mineralisation of UL-chlorophenyl-^{14}C-labelled active substance fenoxaprop-P-ethyl (AE F046360) was investigated in non-sterile natural water at *p*H 8.0 at test concentrations of 10.0 µg a.s./L (low dose) and 103.7 µg a.s./L (high dose). Samples were incubated at 20 °C in the dark for 62 days in maximum. Microbial activity of the test water was demonstrated by incubation of UL-phenyl-^{14}C-labeled benzoic acid serving as reference.

The mean material balances of two duplicates ranged from 94.5 % to 104.5 % AR for low dose samples and from 94.8 % to 101.3 % for the high dose.

Values of the test substance in the test water decreased from 84.9 % of AR for the low dose (87.6 % for high dose) at time zero to below the LOQ of 1.1 % (0.4 % for high dose) each after 3 days of incubation.

UL-chlorophenyl-^{14}C labelled fenoxaprop-P-ethyl (AE F046360) was bio-transformed to fenoxaprop-P-acid (AE F088406, maximum: 101.4 % by day 3 for low dose, 98.6 % for high dose) and chlorobenzoxazolone (AE F054014, maximum: 36.8 % by day 52 for low dose, 7.8 % by day 14 for high dose) in the course of the study. Formation of carbon dioxide including other volatile components was low amounting to 1.2 % AR (low dose) and 2.0 % (high dose) each after 62 days of incubation.

Best fits to measured data were obtained by applying the simple first order (SFO) kinetic model for evaluation. The value of the *DT50* of fenoxaprop-P-ethyl under conditions of mineralization testing was calculated to be 0.4 days each for low and high dosed samples.

Material and Methods:

Test Material	[UL-chlorophenyl-^{14}C]-fenoxaprop-P-ethyl (AE F046360)
Specific radioactivity:	3.97 MBq/mg
Radiochemical purity:	> 98 % (HPLC)
	> 99 % (TLC)
Radiochemical purity:	> 99 % (HPLC-UV)
Ratio of enantiomers:	R : S = 99.3 : 0.7
Sample ID:	KML 9850

Test water
The natural water Wiehltalsperre used for the test was fresh collected from a reservoir serving as a source for drinking water at Reichshof, Northrhine-Westphalia, Germany.

Table B.8.2.2.2-1 Physico-chemical characteristics of test water

Water	Wiehltalsperre
*p*H	8.0
Redox potential Eobs (mV)	195
Oxygen saturation (%) / (mg/L)	97.4 / 11.4
Total organic carbon (TOC, mg/kg)	3
Dissolved Organic Carbon (DOC, mg/L)	3
Biochemical oxygen demand (BOD5;mg/L)	n.a.*
Total nitrogen (mg/L)	2.8
Total phosphorus (mg/L)	< 0.03

* not applicable due to low total organic carbon content

Before start of incubation the test water was passed through a 0.063 mm sieve.

Experimental conditions
Samples of 100 mL test water each were filled into 250 mL Erlenmeyer glass flasks with baffles and pre-equilibrated four days prior to treatment at approximate study conditions (darkness, 20 °C). The test was performed with UL-chlorophenyl-^{14}C-fenoxaprop-P-ethyl at initial concentrations of 10.0 µg/L (low dose) and 100 µg/L (high dose). Following application the samples were incubated in 'static' systems under gentle shaking and traps attached to collect ^{14}C-carbon dioxide and other volatiles, but being permeable to air. Samples were incubated at 20 ± 2 °C in the dark for 62 days in maximum.

In addition, samples containing biological controls were incubated under the same conditions and removed for analysis at selected time points. Biological controls contained the reference substance phenyl-UL-^{14}C-benzoic acid.

Sampling
Duplicate samples of each of the two test concentrations were removed for analysis after 0, 0.08, 0.17, 0.25, 1, 3, 7, 14, 20, 34, 41, 50 and 62 days of incubation. Samples for determination of microbial activity (biological controls) were investigated after 0 and 3 days of incubation. Finally, sterile controls were removed for analysis after 62 days of incubation. The complete samples were immediately processed and HPLC analysis was performed the same day. Therefore no additional investigations of storage stability were necessary. The *p*H, oxygen concentration and the redox potential was determined at each sampling interval.

Analytical procedures
Aliquots of the samples were concentrated prior to analysis while the water of low dose samples was concentrated prior to analysis by rotary evaporation (max. 40 °C, reduced pressure). The ^{14}C-material balance was established for each sample following analysis of the water and determination of volatile radioactivity in the traps. Following quantitation of radioactivity in water by LSC and concentration, analysis was performed by reversed phase HPLC and ^{14}C-flow-through detection techniques as the primary analytical method. For compounds isolated from selected samples identity of transformation products formed was confirmed by HPLC-MS/MS analysis.

The LOQ of the primary analytical method was estimated to 1.1 % AR for a compound in low dose and to 0.4 % for a compound in high dose samples.

Kinetic evaluation
The kinetic evaluation was performed for the active substance fenoxaprop-P-ethyl (AE F046360) with the software KinGUI II following FOCUS kinetic guidance (2011) to obtain best fits to the measured data.

Results and Discussion:

The temperature was maintained at 20 ± 2 °C during the test. Biological activity of the test water was confirmed by the degradation of reference substance UL-phenyl-^{14}C-benzoic acid within 3 days of incubation. The *p*H, oxygen concentration and redox potential of the test water was shown to be within the same range for treated samples and for untreated controls.

The mean material balances were 100.6 % ± 3.1 % AR for low dose samples and 98.6 % ± 2.3 % for the high dose demonstrating no significant losses of radioactivity from samples in the course of the test including processing till analysis.

Formation of ^{14}C-carbon dioxide was confirmed to be a minor transformation product to account for 1.2 % AR (low dose) and 2.0 % (high dose) at the end of the study, day 62. Formation of other volatile components was negligible amounting to < 0.1 % AR for the two concentrations tested.

Biotransformation of ^{14}C-labeled fenoxaprop-P-ethyl (AE F046360) resulted in a decline from 84.9 % AR at time zero to below the LOD of 0.7 % after 3 days for the low dose and from 87.6 % AR at time zero to below the LOD of 0.4 % after 3 days for the high dose. Being susceptible to abiotic hydrolysis some degradation of active substance was observed in sterile controls as documented by a recovery of 93.3 % AR (low dose) and 87.9 % (high dose) for the active substance after 62 days of incubation.

The initial step of abiotic and microbial-induced ester hydrolysis was fast to result in fenoxaprop-P-acid (AE F088406) as the predominant compound (maximum of 101.4 % for low dose by day 3, 98.6 % for high dose by day 3) followed by ether hydrolysis at the heterocyclic ether bond to form chlorobenzoxazolone (AE F054014, maximum of 36.8 % for low dose by day 50, 7.8 % for high dose by day 14). ^{14}C-carbon dioxide was observed as a minor transformation product under the conditions of the test. No minor components were observed.

The observation of carbon dioxide indicates the potential of fenoxaprop-P-ethyl (AE F046360) residues for mineralization in surface water to be clearly driven by microbial degradation.

The kinetic evaluation of the data resulted in *DT50* values of 0.4 days each for the two doses tested. The value was derived from the SFO kinetic model as best fits to measured data.

Table B.8.2.2.2-2 **Low dose: Degradation of [UL-chlorophenyl-^{14}C]-fenoxaprop-P-ethyl (AE F046360) under conditions of mineralization in aerobic surface water (mean of two replicates, numbers shaded in grey indicate exceedance of 5 % AR)**

Component		Sampling interval (days)						
		0	0.08	0.17	0.25	1	3	7
Fenoxaprop-P-ethyl	**Mean**	**84.9**	**74.1**	**66.0**	**64.3**	**18.3**	-	-
(AE F046360)	SD	± 0.1	± 3.6	± 2.1	± 6.8	± 7.6	n.a.	n.a.
Fenoxaprop-P-acid	**Mean**	**9.6**	**21.4**	**31.5**	**35.1**	**83.1**	**101.4**	**100.0**
(AE F088406)	SD	± 0.2	± 0.5	± 1.8	± 5.8	± 8.3	± 0.8	± 0.1
Chlorobenzoxazolone	**Mean**	-	-	-	-	-	**2.2**	**4.5**
(AE F054014)	SD	n.a.	n.a.	n.a.	n.a.	n.a.	± 0.2	± 0.4
Phenol metabolite	**Mean**	-	-	-	-	-	-	-
(AE F040356)	SD	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Total of unknown	**Mean**	-	-	-	-	-	-	-
radioactivity	SD	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Total radioactivity in water	**Mean**	**94.5**	**95.5**	**97.5**	**99.4**	**101.4**	**103.5**	**104.5**
	SD	± 0.2	± 3.1	± 0.4	± 1.0	± 0.7	± 1.0	± 0.2
^{14}C-CO_2 and other volatiles	**Mean**	**n.a.**	**n.a.**	**n.a.**	**n.a.**	**n.a.**	**n.a.**	**n.a.**
	SD	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Total radioactivity (%)	**Mean**	**94.5**	**95.5**	**97.5**	**99.4**	**101.4**	**103.5**	**104.5**
	SD	± 0.2	± 3.1	± 0.4	± 1.0	± 0.7	± 1.0	± 0.2

Values given as percentages of initially applied radioactivity
SD = standard deviation
n.a. = not applicable

Table B.8.2.2.2-3 **(*continued*) Low dose: Degradation of [UL-chlorophenyl-^{14}C]-fenoxaprop-P-ethyl (AE F046360) under conditions of mineralization in aerobic surface water (mean of two replicates, numbers shaded in grey indicate exceedance of 5 % AR)**

Component		Sampling interval (days)					
		14	20	34	41	52	62
Fenoxaprop-P-ethyl	**Mean**	-	-	-	-	-	-
(AE F046360)	SD	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Fenoxaprop-P-acid	**Mean**	**95.7**	**93.8**	**78.2**	**79.2**	**62.4**	**73.0**
(AE F088406)	SD	± 0.2	± 0.1	± 0.1	± 0.1	± 9.5	± 1.2
Chlorobenzoxazolone	**Mean**	**8.4**	**9.9**	**21.8**	**23.3**	**36.8**	**23.4**
(AE F054014)	SD	± 2.5	± 3.1	± 0.1	± 0.2	± 2.4	± 1.8
Phenol metabolite	**Mean**	-	-	-	-	-	-
(AE F040356)	SD	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Total of unknown	**Mean**	-	-	-	-	-	-
radioactivity	SD	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Total radioactivity in	**Mean**	**104.1**	**103.6**	**100.0**	**102.5**	**99.3**	**96.4**
water	SD	± 0.2	± 0.5	± 0.6	± 1.0	± 1.8	± 0.1
^{14}C-CO_2 and other	**Mean**	**n.a.**	**n.a.**	**n.a.**	**n.a.**	**n.a.**	**1.2**
volatiles	SD	n.a.	n.a.	n.a.	n.a.	n.a.	± 0.2
Total radioactivity (%)	**Mean**	**104.1**	**103.6**	**100.0**	**102.5**	**99.3**	**97.6**
	SD	± 0.2	± 0.5	± 0.6	± 1.0	± 1.8	± 0.4

Values given as percentages of initially applied radioactivity
SD = standard deviation
n.a. = not applicable

Table B.8.2.2.2-4 **<u>High dose</u>: Degradation of [UL-chlorophenyl-^{14}C]-fenoxaprop-P-ethyl (AE F046360) under conditions of mineralization in aerobic surface water (mean f two replicates, numbers shaded in grey indicate exceedance of 5 % AR)**

Component		Sampling interval (days)						
		0	0.08	0.17	0.25	1	3	7
Fenoxaprop-P-ethyl	**Mean**	**87.6**	**78.2**	**70.6**	**61.1**	**14.1**	**-**	**-**
(AE F046360)	SD	± 0.4	± 0.9	± 1.0	± 1.9	± 1.4	n.a.	n.a.
Fenoxaprop-P-acid	**Mean**	**8.2**	**20.1**	**27.3**	**35.8**	**85.6**	**98.6**	**97.3**
(AE F088406)	SD	± 0.2	± 0.3	± 0.9	± 1.2	± 1.5	± 0.2	± 0.1
Chlorobenzoxazolone	**Mean**	**0.5**	**0.5**	**0.7**	**0.6**	**1.0**	**2.0**	**3.5**
(AE F054014)	SD	± 0.0	± 0.1	± 0.1	± 0.0	± 0.0	± 0.2	± 0.0
Phenol metabolite	**Mean**	**-**	**-**	**-**	**-**	**-**	**-**	**-**
(AE F040356)	SD	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Total of unknown	**Mean**	**-**	**-**	**-**	**-**	**-**	**-**	**-**
radioactivity	SD	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Total radioactivity in	**Mean**	**96.2**	**98.8**	**98.7**	**97.5**	**100.8**	**100.6**	**100.8**
water	SD	± 0.2	± 0.6	± 0.0	± 0.6	± 0.1	± 0.3	± 0.1
^{14}C-CO_2 and other	**Mean**	**n.a.**	**n.a.**	**n.a.**	**n.a.**	**n.a.**	**n.a.**	**n.a.**
volatiles	SD	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Total radioactivity	**Mean**	**96.2**	**98.8**	**98.7**	**97.5**	**100.8**	**100.6**	**100.8**
(%)	**SD**	**± 0.2**	**± 0.6**	**± 0.0**	**± 0.6**	**± 0.1**	**± 0.3**	**± 0.1**

Values given as percentages of initially applied radioactivity
SD = standard deviation
n.a. = not applicable

Table B.8.2.2.2-5 **(*continued*) <u>High dose</u>: Degradation of [UL-chlorophenyl-^{14}C]-fenoxaprop-P-ethyl (AE F046360) under conditions of mineralization in aerobic surface water (mean of two replicates, numbers shaded in grey indicate exceedance of 5 % AR)**

Component		Sampling interval (days)					
		14	20	34	41	52	62
Fenoxaprop-P-ethyl	**Mean**	**n.a.**	**n.a.**	**n.a.**	**n.a.**	**n.a.**	**n.a.**
(AE F046360)	SD	-	-	-	-	-	-
Fenoxaprop-P-acid	**Mean**	**93.2**	**92.7**	**89.9**	**91.5**	**90.9**	**88.6**
(AE F088406)	SD	± 0.8	± 0.8	± 1.2	± 3.0	± 0.1	± 1.3
Chlorobenzoxazolone	**Mean**	**7.8**	**7.7**	**7.1**	**4.5**	**4.1**	**4.2**
(AE F054014)	SD	± 0.8	± 0.9	± 0.6	± 2.5	± 1.6	± 0.6
Phenol metabolite	**Mean**	**-**	**-**	**-**	**-**	**-**	**-**
(AE F040356)	SD	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Total of unknown	**Mean**	**-**	**-**	**-**	**-**	**-**	**-**
radioactivity	SD	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Total radioactivity in	**Mean**	**101.3**	**100.3**	**97.1**	**96.3**	**95.0**	**92.8**
water	SD	± 0.3	± 0.1	± 0.6	± 0.3	± 1.4	± 0.6
^{14}C-CO_2 and other	**Mean**	**n.a.**	**n.a.**	**n.a.**	**n.a.**	**n.a.**	**2.0**
volatiles	SD	n.a.	n.a.	n.a.	n.a.	n.a.	± 0.5
Total radioactivity	**Mean**	**101.3**	**100.3**	**97.1**	**96.3**	**95.0**	**94.8**
(%)	**SD**	**± 0.3**	**± 0.1**	**± 0.6**	**± 0.3**	**± 1.4**	**± 1.1**

Values given as percentages of initially applied radioactivity
SD = standard deviation
n.a. = not applicable

Table B.8.2.2.2-6 **Kinetic evaluation of degradation of [UL-chlorophenyl-^{14}C]-fenoxaprop-P-ethyl (AE F046360) in aerobic natural water under conditions of OECD 309 testing**

Compound / Dose	Kinetic Model	*DT50* (days)	*DT90* (days)	χ^2 error (%)	Visual assessment
Fenoxaprop-P-ethyl (AE F046360) / Low	SFO	0.4	1.4	5.1	O
Fenoxaprop-P-ethyl (AE F046360) / High	SFO	0.4	1.2	2.6	+

SFO = simple first order
Visual assessment: + = good, O = moderate, - = bad

<u>Conclusion:</u>

The overall mineralization of ^{14}C-chlorophenyl-fenoxaprop-P-ethyl (AE F046360) and its residues in non-sterile

natural water was moderate under the ‘pelagic’ conditions of the test.

While the initial step of microbial-induced ester hydrolysis was fast to result in fenoxaprop-P-acid (AE F088406) as the predominant compound (maximum of 101.4 % for low dose and 98.6 % for high dose each by day 3) followed by ether hydrolysis at the heterocyclic ether bond to form chlorobenzoxazolone (AE F054014, maximum of 36.8 % for low dose by day 50, 7.8 % for high dose by day 14).

^{14}C-carbon dioxide was observed as a minor transformation product under the conditions of the test.

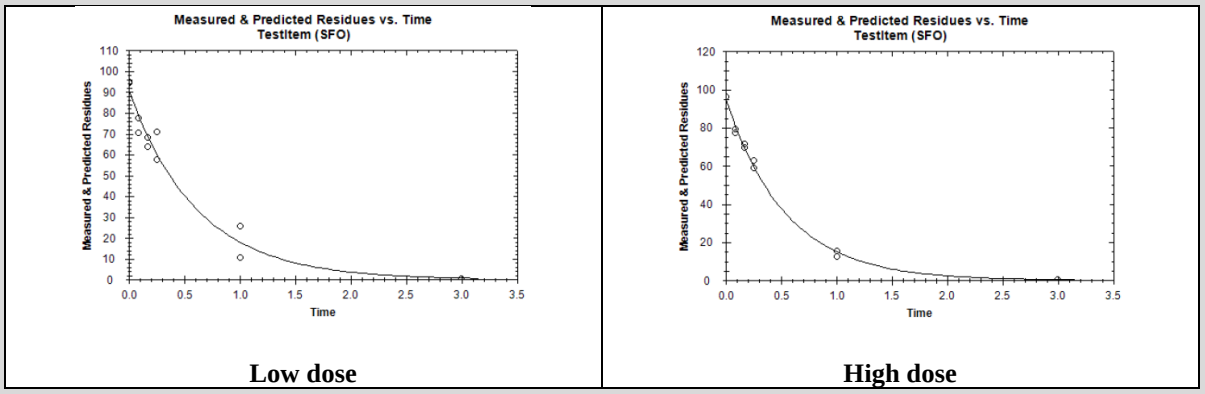
The *DT50* of fenoxaprop-P-ethyl (AE F046360) in water under conditions of aerobic mineralisation testing was calculated to be 0.4 days each for the low and high dose tested.

Results of mineralization tests in surface water thus contradict to the degradation behaviour observed in water/sediment tests, the latter indicating good degradability. When transferring this into an outdoor situation and considering the use of fenoxaprop-P-ethyl (AE F046360) as an agrochemical, the water/sediment test describes more realistic the situation after use, i.e. a flooded ditch adjacent to the field as ‘aquatic system’. In contrast tests according to OECD 309 were designed to reflect ‘open water’ which is, at least, not given for well degrading agrochemicals like for fenoxaprop-P-ethyl (AE F046360) following its intended use in cereals.

Comments RMS AT:

- The study follows OECD guideline 309 and is considered reliable.
- Fits for the kinetic evaluation of fenoxaprop-P-ethyl (AE F046360), not provided by the applicant in the study summary, are given below:

Table B.8.2.2.2-7 Degradation of fenoxaprop-P-ethyl (AE F046360) in aerobic natural water under conditions of OECD 309 testing - applicant assessment agreed by RMS AT



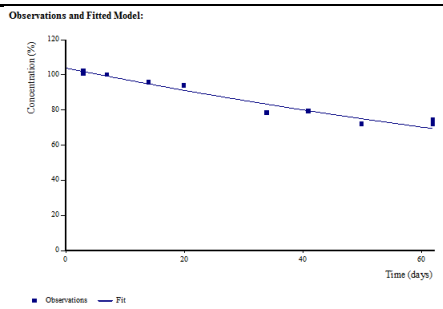
- Residue data of fenoxaprop-P-acid (AE F088406) in the low dose experiment allow for a kinetic assessment as well. This was done by the RMS AT in accordance with pertinent guidance applying SFO kinetics from the maximum occurrence (decline fit, CAKE 3.3), results are given in the following tables.

Table B.8.2.2.2-8 Degradation rate of fenoxaprop-P-acid (AE F088406) in aerobic natural water under conditions of OECD 309 testing - RMS AT assessment

Test system	*DT50* / *DT90* (d)	χ^2 error (%)	Kinetics
Low dose[(a)]	107 / 354	2.5	SFO (from max. occurrence)

(a) 50 DAT sample B omitted from fit (outlier)

Table B.8.2.2.2-9 Fits for the kinetic evaluation of degradation of fenoxaprop-P-acid (AE F088406) in aerobic natural water under conditions of OECD 309 testing - RMS AT assessment



Low dose

Reference:	**[Phenoxy-UL-^{14}C]Fenoxaprop-P-ethyl: Aerobic mineralisation in surface water**
Author(s), year:	Telscher, M., Junge, T. (2016b)
Report/Doc. Number:	EnSa-15-0232, M-553135-01-1
Guideline(s):	OECD Test Guideline No. 309
GLP:	Yes
Validity:	Yes
Status:	**New submission**

Executive Summary:

The mineralisation of UL-phenoxy-^{14}C-labeled active substance fenoxaprop-P-ethyl (AE F046360) was investigated in non-sterile natural water at *p*H 9.2 at test concentrations of 10.1 µg a.s./L (low dose) and 101.6 µg a.s./L (high dose).

Samples were incubated at 20 °C in the dark for 62 days in maximum. Microbial activity of the test water was demonstrated by incubation of UL-phenyl-^{14}C-labeled benzoic acid serving as reference.

The mean material balances of two duplicates ranged from 95.1 % to 110.6 % AR for low dose samples and from 95.4 % to 103.1 % for the high dose.

Values of the test substance in the test water decreased from 74.3 % of AR for the low dose (82.9 % for high dose) at time zero to below the LOQ of 0.7 % (0.2 % for high dose) each after 3 days of incubation.

UL-phenoxy-^{14}C labelled fenoxaprop-P-ethyl (AE F046360) was bio-transformed to fenoxaprop-P-acid (AE F088406, maximum: 98.0 % for low dose, 97.4 % for high dose, each by day 3) and HOPP-acid (AE F096918, maximum: 21.0 % by day 31 for low dose, 24.6 % by day 43 for high dose) in the course of the study. Formation of carbon dioxide including other volatile components was significant amounting in total to 19.3 % AR (low dose, sum of carbon dioxide in traps and dissolved in water) and 10.9 % (high dose) each after 62 days of incubation.

Best fits to measured data were obtained by applying bi-phasic kinetic model DFOP (low dose) and FOMC (high dose) for evaluation. The value of the *DT50* of fenoxaprop-P-ethyl (AE F046360) under conditions of mineralization testing was calculated to be 0.16 days for the low dose and to be 0.23 days for high dosed samples.

Material and Methods:

Test Material	[UL-phenoxy-^{14}C]-fenoxaprop-P-ethyl (AE F046360)
Specific radioactivity:	4.14 MBq/mg
Radiochemical purity:	> 98 % (HPLC) > 99 % (TLC)
Radiochemical purity:	> 98 % (HPLC-UV)
Sample ID:	KML 9800

Test water
The natural water Wiehltalsperre used for the test was fresh collected from a reservoir serving as a source for drinking water at Reichshof, Northrhine-Westphalia, Germany.

Table B.8.2.2.2-10 Physico-chemical characteristics of test water

Water	Wiehltalsperre
*p*H	9.2
Redox potential Eobs (mV)	193
Oxygen saturation (%) / (mg/L)	98.3 / 9.73
Total organic carbon (TOC, mg/kg)	2
Dissolved Organic Carbon (DOC, mg/L)	2
Biochemical oxygen demand (BOD5, mg/L)	n.a.*
Total nitrogen (mg/L)	2.4
Total phosphorus (mg/L)	0.07

*not applicable due to low total organic carbon content

Before start of incubation the test water was passed through a 0.063 mm sieve.

Experimental conditions
Samples of 100 mL test water each were filled into 250 mL Erlenmeyer glass flasks with baffles and pre-equilibrated three days prior to treatment at approximate study conditions (darkness, 20 °C). The test was performed with UL-phenoxy-^{14}C-fenoxaprop-P-ethyl (AE F046360) at initial concentrations of 10.1 µg/L (low dose) and 101.6 µg/L (high dose). Following application the samples were incubated in 'static' systems under gentle shaking and traps attached to collect ^{14}C-carbon dioxide and other volatiles, but being permeable to air. Samples were incubated at 20 ± 2 °C in the dark for 62 days in maximum.

In addition, samples containing biological controls were incubated under the same conditions and removed for analysis at selected time points. Biological controls contained the reference substance UL-phenyl-^{14}C-benzoic acid.

Sampling
Duplicate samples of each of the two test concentrations were removed for analysis after 0, 0.08, 0.17, 0.25, 1, 3, 7, 14, 20, 31, 43, 51 and 62 days of incubation. Samples for determination of microbial activity (biological controls) were investigated after 0 and 3 days of incubation. Finally, sterile controls were removed for analysis after 62 days of incubation. The complete samples were immediately processed and HPLC analysis was performed the same day. Therefore no additional investigations of storage stability were necessary. The *p*H, oxygen concentration and the redox potential was determined at each sampling interval.

Analytical procedures
Aliquots of the samples were concentrated prior to analysis while the water of low dose samples was concentrated prior to analysis by rotary evaporation (max. 40 °C, reduced pressure). The ^{14}C-material balance was established for each sample following analysis of the water and determination of volatile radioactivity in the traps. Following quantitation of radioactivity in water by LSC and concentration, analysis was performed by reversed phase HPLC and ^{14}C-flow-through detection techniques as the primary analytical method. For compounds isolated from selected samples identity of transformation products formed was confirmed by HPLC-MS/MS analysis.

The LOQ of the primary analytical method was estimated to 0.7 % AR for a compound in low dose and to 0.2 % for a compound in high dose samples.

Kinetic evaluation
The kinetic evaluation was performed for the active substance fenoxaprop-P-ethyl (AE F046360) with the software KinGUI II following FOCUS kinetic guidance (2011) to obtain best fits to the measured data.

Results and Discussion:

The temperature was maintained at 20 ± 2 °C during the test. Biological activity of the test water was confirmed by the degradation of reference substance UL-phenyl-^{14}C-benzoic acid within 3 days of incubation. The *p*H,

oxygen concentration and redox potential of the test water was shown to be within the same range for treated samples and for untreated controls.

The mean material balances were 99.0 % ± 3.9 % AR for low dose samples and 98.1 % ± 2.0 % for the high dose demonstrating no significant losses of radioactivity from samples in the course of the test including processing till analysis.

Formation of ^{14}C-carbon dioxide was confirmed to be a major transformation product to account in total for 19.3 % AR (low dose, sum of volatiles and in water) and 10.9 % (high dose) at the end of the study, day 62. Formation of other volatile components was negligible amounting to 1.9 % AR (day 7, low dose) or less for the two concentrations tested.

Biotransformation of ^{14}C-labeled fenoxaprop-P-ethyl (AE F046360) resulted in a decline from 74.3 % AR at time zero to below the LOD of 0.7 % after 3 days for the low dose and from 82.9 % AR at time zero to below the LOD of 0.2 % after 3 days for the high dose. Being susceptible to abiotic hydrolysis some to complete degradation of active substance was observed in sterile controls as documented by a recovery of 91.7 % AR (low dose) and below the LOD (high dose) for the active substance after 62 days of incubation.

The initial step of abiotic and microbial-induced ester hydrolysis was fast to result in fenoxaprop-P-acid (AE F088406) as the predominant compound (maximum of 98.0 % for low dose by day 3, 97.4 % for high dose by day 3) followed by ether hydrolysis at the heterocyclic ether bond to form HOPP-acid (AE F096918, maximum of 21.0 % for low dose by day 31, 24.6 % for high dose by day 43) thus being the corresponding 'counterpart' of chlorobenzoxazolone (AE F054014) after split of the molecule.

^{14}C-carbon dioxide was observed as a major transformation product (maximum: 19.3 % AR, low dose, sum of carbon dioxide in traps and dissolved in water) and 10.9 % (high dose) under the conditions of the test. Degradation was accompanied by formation of numerous minor components with none of the single components occurring at more than 4.8 % (low dose) or 4.1 % (high dose) in maximum in the course of the test.

The observation of a significant portion of carbon dioxide formed indicates the potential of fenoxaprop-P-ethyl (AE F046360) residues for mineralization in surface water to be clearly driven by microbial degradation.

The kinetic evaluation of the data resulted in *DT50* values of 0.16 days for low dosed samples and of 0.23 days for the high dosed. The values were derived from the DFOP (low dose) and the FOMC kinetic model (high dose) as best fits to measured data.

Table B.8.2.2.2-11 Low dose: Degradation of [UL-phenoxy-^{14}C]-fenoxaprop-P-ethyl (AE F046360) under conditions of mineralization in aerobic surface water (mean value of two replicates, numbers shaded in grey indicate exceedance of 5 % AR)

Component		Sampling interval (days)						
		0	0.08	0.17	0.25	1	3	7
Fenoxaprop-P-ethyl	**Mean**	**74.3**	**62.8**	**44.8**	**35.8**	**3.4**	**-**	**-**
(AE F046360)	SD	± 5.7	± 2.1	± 0.2	± 1.3	± 1.5	n.a.	n.a.
Fenoxaprop-P-acid	**Mean**	**20.0**	**34.5**	**53.9**	**60.3**	**97.8**	**98.0**	**96.2**
(AE F088406)	SD	± 5.6	± 1.7	± 0.5	± 1.1	± 3.5	± 0.6	± 0.3
HOPP-acid	**Mean**	**-**	**-**	**-**	**0.8**	**1.0**	**2.0**	**4.7**
(AE F096918)	SD	n.a.	n.a.	n.a.	± 0.1	± 0.1	± 0.2	± 0.4
Total of unknown	**Mean**	**0.8**	**-**	**-**	**-**	**-**	**-**	**-**
radioactivity[(a)]	SD	± 0.0	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Total radioactivity in	**Mean**	**95.1**	**97.6**	**99.0**	**97.2**	**102.2**	**100.0**	**100.9**
water[(b)]	SD	± 0.1	± 0.8	± 0.4	± 0.6	± 2.1	± 0.5	± 0.3
^{14}C-CO_2 and other	**Mean**	**n.a.**	**-**	**0.3**	**0.7**	**1.5**	**0.3**	**2.4**
volatiles[(c)]	SD	n.a.	n.a.	± 0.1	± 0.5	± 1.3	± 0.0	± 1.6
Total radioactivity	**Mean**	**95.1**	**97.7**	**99.3**	**97.9**	**103.7**	**100.3**	**103.3**
(%)	**SD**	**± 0.1**	**± 0.7**	**± 0.4**	**± 1.1**	**± 3.4**	**± 0.4**	**± 2.1**

Values given as percentages of initially applied radioactivity
SD = standard deviation
(a) No single component exceeded 4.8 % AR at any sampling interval (information added by RMS AT)
(b) Includes ^{14}C-CO_2 dissolved in water, no single component > 4.7 % AR
(c) Other volatiles to account for 1.9 % in maximum, day 7
n.a. = not applicable

Table B.8.2.2.2-12 ***(continued)*** **Low dose: Degradation of [UL- phenoxy-^{14}C]-fenoxaprop-P-ethyl (AE F046360) under conditions of mineralization in aerobic surface water (mean value of two replicates, numbers shaded in grey indicate exceedance of 5 % AR)**

Component		Sampling interval (days)					
		14	20	31	43	51	62
Fenoxaprop-P-ethyl	**Mean**	-	-	-	-	-	-
(AE F046360)	SD	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Fenoxaprop-P-acid	**Mean**	**91.7**	**79.1**	**65.3**	**57.5**	**40.4**	**29.9**
(AE F088406)	SD	± 1.3	± 2.9	± 2.0	± 11.9	± 1.6	± 14.1
HOPP-acid	**Mean**	**7.9**	**14.7**	**21.0**	**18.3**	**15.7**	**20.7**
(AE F096918)	SD	± 2.8	± 2.8	± 1.9	± 5.1	± 2.8	± 1.6
Total of unknown	**Mean**	-	**1.3**	**4.6**	**6.1**	**18.1**	**20.7**
radioactivity[(a)]	SD	n.a.	± 0.4	± 0.4	± 1.3	± 1.7	± 7.8
Total radioactivity in	**Mean**	**99.6**	**95.0**	**90.8**	**81.9**	**74.2**	**71.3**
water[(b)]	SD	± 1.5	± 0.3	± 0.5	± 5.5	± 6.1	± 4.7
^{14}C-CO_2 and other	**Mean**	**1.5**	**0.8**	**8.7**	**11.4**	**14.1**	**14.1**
volatiles[(c)]	SD	± 0.8	± 0.1	± 2.0	± 2.7	± 4.2	± 3.7
Total radioactivity	**Mean**	**101.2**	**96.0**	**110.6**	**107.0**	**108.0**	**105.0**
(%)	**SD**	**± 0.7**	**± 0.5**	**± 4.5**	**± 0.4**	**± 1.9**	**± 3.1**

Values given as percentages of initially applied radioactivity
SD = standard deviation
(a) No single fraction above 4.8 % AR at any sampling interval (information added by RMS AT)
(b) Includes ^{14}C-CO_2 dissolved in water
(c) Other volatiles to account for 1.0 % in maximum, day 14
n.a. = not applicable

Table B.8.2.2.2-13 **High dose: Degradation of [UL- phenoxy-^{14}C]-fenoxaprop-P-ethyl (AE F046360) under conditions of mineralization in aerobic surface water (mean value of two replicates, numbers shaded in grey indicate exceedance of 5 % AR)**

Component		Sampling interval (days)						
		0	0.08	0.17	0.25	1	3	7
Fenoxaprop-P-ethyl	**Mean**	**82.9**	**72.0**	**57.2**	**43.9**	**8.7**	-	-
(AE F046360)	SD	± 1.9	± 5.7	± 2.2	± 0.2	± 3.6	n.a.	n.a.
Fenoxaprop-P-acid	**Mean**	**11.8**	**24.4**	**39.7**	**52.4**	**89.5**	**97.4**	**96.2**
(AE F088406)	SD	± 1.3	± 5.0	± 1.5	± 0.1	± 3.6	± 0.1	± 0.4
HOPP-acid	**Mean**	-	-	**0.5**	**0.6**	**1.5**	**2.2**	**3.1**
(AE F096918)	SD	n.a.	n.a.	± 0.0	± 0.1	± 0.1	± 0.1	± 0.1
Total of unknown	**Mean**	**0.7**	**0.5**	**0.7**	**0.5**	**0.5**	-	-
radioactivity	SD	± 0.0	± 0.1	± 0.0	± 0.0	± 0.1	n.a.	n.a.
Total radioactivity in	**Mean**	**95.4**	**96.9**	**98.2**	**97.3**	**100.2**	**99.5**	**99.3**
water[(a)]	SD	± 0.6	± 0.6	± 0.6	± 0.2	± 0.2	± 0.2	± 0.4
^{14}C-CO_2 and other	**Mean**	**n.a.**	-	-	-	-	-	**0.1**
volatiles[(b)]	SD	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	± 0.0
Total radioactivity	**Mean**	**95.4**	**96.9**	**98.2**	**97.3**	**100.2**	**99.5**	**99.3**
(%)	**SD**	**± 0.6**	**± 0.6**	**± 0.6**	**± 0.2**	**± 0.2**	**± 0.2**	**± 0.4**

Values given as percentages of initially applied radioactivity
SD = standard deviation
(a) Includes ^{14}C-CO_2 dissolved in water
(b) Other volatiles to account for 0.1 % in maximum, day 51
n.a. = not applicable

Table B.8.2.2.2-14 ***(continued)*** **High dose: Degradation of [UL- phenoxy-^{14}C]-fenoxaprop-P-ethyl (AE F046360) under conditions of mineralization in aerobic surface water (mean value of two replicates, numbers shaded in grey indicate exceedance of 5 % AR)**

Component		Sampling interval (days)					
		14	20	31	43	51	62
Fenoxaprop-P-ethyl	**Mean**	**n.a.**	**n.a.**	**n.a.**	**n.a.**	**n.a.**	**n.a.**
(AE F046360)	SD	-	-	-	-	-	-
Fenoxaprop-P-acid	**Mean**	**89.9**	**86.8**	**76.8**	**62.4**	**76.3**	**72.7**
(AE F088406)	SD	± 0.5	± 3.7	± 3.5	± 15.6	± 0.3	± 1.6
HOPP-acid	**Mean**	**9.2**	**11.0**	**17.9**	**24.6**	**9.5**	**7.6**

(AE F096918)	SD	± 0.4	± 3.5	± 0.7	± 10.8	± 0.4	± 0.6
Total of unknown radioactivity	**Mean**	**-**	**0.5**	**2.2**	**2.2**	**3.9**	**2.3**
	SD	n.a.	± 0.0	± 1.1	± 0.4	± 1.0	± 0.5
Total radioactivity in water[(a)]	**Mean**	**99.1**	**98.3**	**96.8**	**89.2**	**89.7**	**82.7**
	SD	± 0.0	± 0.2	± 1.7	± 4.5	± 0.4	± 0.5
^{14}C-CO_2 and other volatiles[(b)]	**Mean**	**0.3**	**0.4**	**1.2**	**5.0**	**5.1**	**9.5**
	SD	± 0.0	± 0.0	± 0.7	± 1.5	± 1.1	± 0.1
Total radioactivity (%)	**Mean**	**99.3**	**98.8**	**100.1**	**101.2**	**101.8**	**103.1**
	SD	**± 0.0**	**± 0.2**	**± 2.8**	**± 0.4**	**± 2.8**	**± 0.7**

Values given as percentages of initially applied radioactivity
SD = standard deviation
(a) Includes ^{14}C-CO_2 dissolved in water
(b) Other volatiles to account for 0.1 % in maximum, day 51
n.a. = not applicable

Table B.8.2.2.2-15 Kinetic evaluation of degradation of [UL- phenoxy-^{14}C]-fenoxaprop-P-ethyl (AE F046360) in aerobic natural water under conditions of OECD 309 testing

Compound / Dose	Kinetic Model	*DT50* (days)	*DT90* (days)	χ^2 error (%)	Visual assessment
Fenoxaprop-P-ethyl / Low	DFOP	0.16	0.68	0.8	+
Fenoxaprop-P-ethyl / High	FOMC	0.23	0.94	1.6	+

SFO = simple first order
Visual assessment: + = good, O = moderate, - = bad

Conclusion:

The overall mineralization of ^{14}C-phenoxy-fenoxaprop-P-ethyl (AE F046360) and its residues in non-sterile natural water was significant under the 'pelagic' conditions of the test thus indicating a strong dependence on label position.

While the initial step of microbial-induced ester hydrolysis was fast to result in fenoxaprop-P-acid (AE F088406) as the predominant compound (maximum of 98.0 % for low dose and 97.4 % for high dose each by day 3) followed by ether hydrolysis at the heterocyclic ether bond to form HOPP-acid (AE F096918, maximum of 21.0 % for low dose by day 31, 24.6 % for high dose by day 43).

^{14}C-carbon dioxide was observed as a major transformation product (maximum: 19.3 % AR, low dose, sum of carbon dioxide in traps and dissolved in water) and 10.9 % (high dose) under the conditions of the test.

The *DT50* of fenoxaprop-P-ethyl (AE F046360) in water under conditions of aerobic mineralisation testing was calculated to be 0.16 days each for the low and to be 0.23 days for the high dose tested.

Results of mineralization tests in surface water thus contradict to the degradation behaviour observed in water/sediment tests, the latter indicating good degradability. When transferring this into an outdoor situation and considering the use of fenoxaprop-P-ethyl (AE F046360) as an agrochemical, the water/sediment test describes more realistic the situation after use, i.e. a flooded ditch adjacent to the field as 'aquatic system'. In contrast, tests according to OECD 309 were designed to reflect 'open water' which is, at least, not given for well degrading agrochemicals like for fenoxaprop-P-ethyl (AE F046360) following its intended use in cereals.

Comments RMS AT:

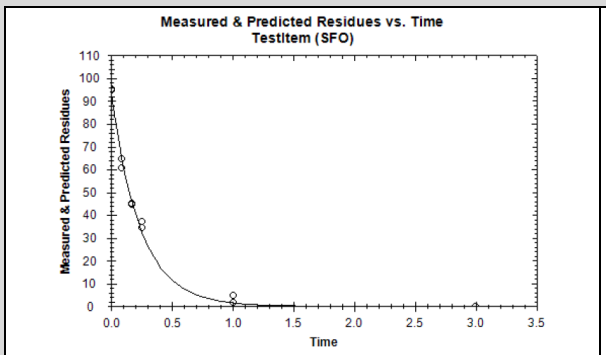
- The study follows OECD guideline 309 and is considered reliable.
- In view of the extremely short degradation time of fenoxaprop-P-ethyl (AE F046360) the RMS AT considers SFO kinetics equally appropriate for both dose experiments. Respective results (including kinetic fits, as already calculated by the applicant) are given below.

Table B.8.2.2.2-16 Degradation of fenoxaprop-P-ethyl (AE F046360) in aerobic natural water under conditions of OECD 309 testing - applicant assessment agreed by RMS AT

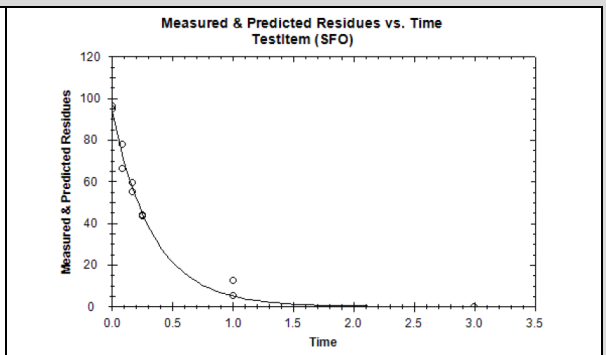
Compound / Dose	Kinetic Model	*DT50* (days)	*DT90* (days)	χ^2 error (%)	Visual assessment
Fenoxaprop-P-ethyl / Low	SFO	0.16	0.55	4.6	+
Fenoxaprop-P-ethyl / High	SFO	0.23	0.78	3.3	+

SFO = simple first order
Visual assessment: + = good, O = moderate, - = bad

Table B.8.2.2.2-17 Degradation fits of fenoxaprop-P-ethyl (AE F046360) in aerobic natural water under conditions of OECD 309 testing - applicant assessment agreed by RMS AT



Low dose (SFO)



High dose (SFO)

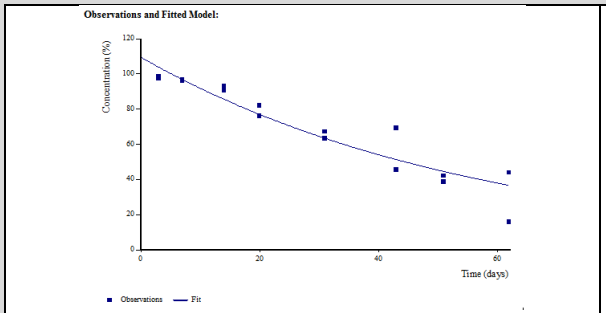
- Residue data of fenoxaprop-P-acid (AE F088406) allow for a kinetic assessment as well. This was done by the RMS AT in accordance with pertinent guidance applying SFO kinetics from the maximum occurrence (decline fit, CAKE 3.3), results are given in the following tables.

Table B.8.2.2.2-18 Kinetic evaluation of degradation of fenoxaprop-P-acid (AE F088406) in aerobic natural water under conditions of OECD 309 testing - RMS AT assessment

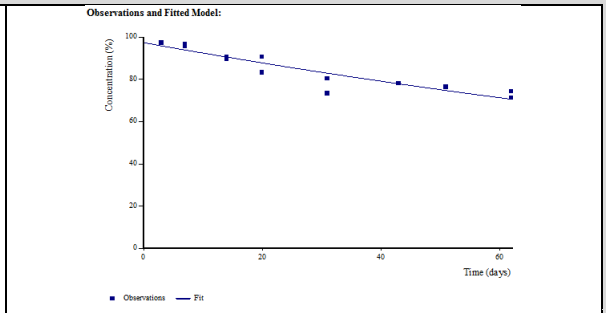
Test system	DT50 / DT90 (d)	χ^2 error (%)	Kinetics
Low dose	39.4 / 131	5.5	SFO (from max. occurrence)
High dose[(a)]	134 / 444	2.4	SFO (from max. occurrence)

(a) Omitting 43 DAT (A sample) as outlier

Table B.8.2.2.2-19 Fits for the kinetic evaluation of degradation of fenoxaprop-P-acid (AE F088406) in aerobic natural water under conditions of OECD 309 testing - RMS AT assessment



Low dose



High dose

B.8.2.2.3. Water/sediment studies

Studies submitted for first Annex I inclusion:

- **Tarara (2000)**, investigating chlorophenyl labelled fenoxaprop-P-ethyl (AE F046360) in two water/sediment systems
- **Fitzmaurice (2004)**, investigating phenoxy labelled fenoxaprop-P-ethyl (AE F046360) in two

water/sediment systems
- **Voelkel (2000)**, investigating chlorophenyl labelled fenoxaprop-P-ethyl (AE F046360) and phenoxy labelled, racemic fenoxaprop-ethyl (AE F033171) in one **anaerobic** water/sediment system

New information submitted by the Fenoxaprop Task Force:

- **Xu (2012)**, investigating chlorophenyl and phenoxy labelled fenoxaprop-P-ethyl (AE F046360) in two water/sediment systems
- **Mamouni (2008)**, investigating chlorophenyl and phenoxy labelled fenoxaprop-P-ethyl (AE F046360) in two water/sediment systems
- **Herrmann et al. (2016)**, re-evaluating the degradation/dissipation kinetics of fenoxaprop-P-ethyl (AE F046360) and metabolites in water/sediment system

Reference:	**[U-^{14}C-chlorophenyl]AE F046360: Degradation in two sediment/water-systems at 20 °C under aerobic conditions**
Author(s), year:	Tarara, G. (2000)
Report/Doc. Number:	C007688, M-227806-01-1
Guideline(s):	BBA: IV, 5-1; EU (=EEC): 95/36/EC; PMRA: (1991); USEPA (=EPA): N § 162-4
GLP:	Yes
Validity:	Yes
Status:	**Already submitted**

[The following study report is a copy/paste of the original text in the DAR for Annex I inclusion slightly amended in order to meet editorial settings and to improve readability]

Material and methods:

The aerobic aquatic metabolism and degradation of UL-^{14}C-chlorophenyl labelled fenoxaprop-P-ethyl (AE F046360, radiochemical purity 98 - 99 %) were studied in two different water-sediment systems. 0.06 mg test substance (field application rate 180 g/ha, full overspray, 30 cm water depth) were applied per kg water and test samples were incubated at 20 °C under aerobic conditions in darkness for up to 155 (199) days.

The sediment with associated water was sampled at two sites in natural environment:

- System 1: Rhine, old sidearm of the river Rhine, Trebur/Hohenau, Germany
- System 2: Nidda, sidearm of the river Nidda, Florstadt/Staden, Germany

After Sampling sediments were washed through a 2 mm sieve with corresponding water. Per test sample approx. 200 g of wet sediment was filled in laboratory glass flask (volume 500 mL) and filled up with approx. 300 g corresponding water. The ratio water/dry sediment was 2:1 for Rhine and 6:1 for Nidda, respectively. Flasks were closed with glass tubes filled with absorbing agents for CO_2 and other volatiles. In total 36 flask were prepared to determine the rate and route of degradation. Additional, flasks were incubated to generate material of potentially unknown metabolites (with exaggerated application rates: 10x and 100x) and flasks to determine the biomass at the beginning (0 d), after 155 d and the end of the study (199 d). Further 12 sterilised samples were set up to investigate the abiotic degradation processes under test conditions.

The test units were acclimatised to test conditions under carefully shaking by a horizontal shaker up to 21 d (Rhine) and 14 d (Nidda), respectively. During the acclimatisation period *p*H, O_2 content, redoxpotential were monitored until test systems were considered as equilibrated. Then the test substance was applied with a microlitre pipette to the surface of the water of each flask.

Duplicate samples were taken after two, four and six hours and 1, 2, 3, 7, 10 (only for Nidda system), 14, 21, 30, 42, 59, 90, 120, 155 and 199 days of incubation. Water and sediment phase were separated and dissolved radioactivity was analysed by HPLC and TLC. Non extractable residues in the sediment were characterised by Soxhlet extraction, acid hydrolysis (according the soil residue method), and fractionation of soil organic matter into humic- and fulvic acids.

Table B.8.2.2.3-1 Physical and chemical properties of the two test systems:

Matrix	Parameter	Location System 1: Rhine	Location System 2: Nidda
Water	Temperature (°C)*	16.6	2[(b)]
	*p*H ($CaCl_2$)[(a)]	7.3	6.8
	O_2-concentration [mg/L]* at surface/5 cm above sediment	8.8/8.7	9.1/6.8
	Total hardness °dH*	9.56	6.63
	Total organic carbon [mg C/L]	2.37	3.1
	Total nitrogen [%]	< 0.1	< 0.1
	Total phosphorous [mg/L]	< 3	< 3
Sediment	*p*H[(a)]	7.9	5.1
	C_{org} [%]	1.4	3.97
	Total nitrogen [%]	< 0.1	0.1
	Total phosphorus [g/kg]	101	831
	Redox potential [mV]*	+209	-51
	Cation exchange capacity [meq/100 g]	0.44	23.18
	Microbial biomass [mg C/100 g] after 0 d (untreated) / 160 d / 199 d	0 / 1.6 / 1.8	21 / 6.5 / 5.3
	Texture (US)	Sand	Silt loam
	Particle size distribution:		
	Sand [%]	99.6	9.2
	Silt [%]	0.1	67.1
	Clay [%]	1.2	23.7

(a) Parameter was measured shortly before collection of water/sediment samples
(b) Number as stated in the report (20 °C?)

Findings:

The two systems differed significantly in their texture, organic carbon content and microbial biomass.

During the study aerobic conditions in water and anaerobic conditions in sediment were established. However, in both systems the redox potential in the sediment increased slowly towards the end of the study (from day 90 in Rhine system, from day 155 in Nidda system). The *p*H values in water were in a range of 7.7 to 9.0 for Rhine and 7.4 to 8.6 for Nidda until day 42. Then for Nidda system more acidic conditions were observed, *p*H-values decreased to a minimum of *p*H 5.5 until the end of the test.

Results for material balance and distribution of radioactivity are summarised as mean measured values in the table below. Only degradation products which exceeded 10 % of AR are given.

Table B.8.2.2.3-2 Radioactivity distribution, partitioning and balance (% of applied radioactivity) during degradation in the water- and sediment phase within the Rhine and Nidda systems (mean of two replicates, numbers shaded in grey indicate exceedance of 5 % AR).

Time	Water	Ambient temp. extract	NER	CO_2	Total	Fenoxaprop-P-ethyl (AE F046360) Water	Fenoxaprop-P-ethyl (AE F046360) Sed.	Fenoxaprop-P-ethyl (AE F046360) Total system	Fenoxaprop-P-acid (AE F088406) Water	Fenoxaprop-P-acid (AE F088406) Sed.	Fenoxaprop-P-acid (AE F088406) Total system
System 1: Rhine (sand)											
2 h	94.8	10.3	0.6	< 0.1	105.7	50.3	3.6	**53.9**	43.5	6.5	**50.1**
4 h	89.3	9.6	0.8	< 0.1	99.7	32.6	2.3	**34.9**	55.8	7.2	**63.0**
6 h	90.4	7.7	0.7	< 0.1	98.8	30.7	1.6	**32.3**	57.4	5.9	**63.3**
1 d	92.8	6.5	2.8	< 0.1	102.1	4.1	0.3	**4.5**	87.1	5.7	**92.8**
2 d	87.6	7.0	4.3	< 0.1	98.9	0.4	0.2	**0.6**	85.7	6.3	**91.9**
3 d	86.2	8.9	4.7	< 0.1	99.8	-	0.2	**0.2**	84.2	8.0	**92.3**
7 d	73.7	12.6	11.0	0.2	97.5	-	0.1	**0.1**	70.8	11.6	**82.3**
14 d	44.5	17.6	34.5	1.3	97.9	-	-	**-**	39.6	12.6	**52.2**
21 d	35.5	15.3	39.2	2.7	92.7	-	-	**-**	25.3	11.3	**36.6**
30 d	23.2	14.9	52.4	4.1	94.6	-	-	**-**	9.2	8.2	**17.4**
42 d	14.4	7.4	68.7	5.2	95.7	-	-	**-**	-	3.4	**3.4**
59 d	11.5	4.6	75.0	9.7	100.8	-	0.1	**0.1**	-	0.8	**0.8**
90 d	10.8	3.8	71.8	9.7	96.1	-	-	**-**	-	0.6	**0.6**
120 d	10.2	3.4	60.0	13.8	87.4	-	-	**-**	-	0.6	**0.6**
155 d	9.3	2.4	64.7	19.5	95.9	-	-	**-**	-	0.3	**0.3**

199 d	10.5	2.0	54.9	27.6	95.0	-	-	-	-	0.7	**0.7**
199 d sterile	54.4	21.6	22.1	0.6	98.5	-	-	-	41.2	14.8	**56.3**
System 2: Nidda (silt loam)											
2 h	90.5	8.2	0.6	< 0.1	99.3	38.2	3.9	**42.1**	48.8	1.3	**50.1**
4 h	82.7	12.1	0.8	< 0.1	95.6	31.7	3.8	**35.5**	48.2	5.6	**53.8**
6 h	86.0	10.9	0.8	< 0.1	97.7	21.2	2.5	**23.7**	62.2	5.6	**67.9**
1 d	83.1	13.4	2.1	< 0.1	98.6	0.5	0.1	**0.6**	79.7	12.9	**92.7**
2 d	72.7	19.4	4.8	< 0.1	96.9	-	-	-	69.4	17.8	**87.2**
3 d	65.9	24.2	8.3	< 0.1	98.4	-	-	-	61.9	21.8	**83.6**
7 d	45.3	31.2	21.3	0.4	98.2	-	-	-	36.9	26.8	**63.7**
10 d	32.0	29.1	30.7	0.9	92.7	-	-	-	19.7	25.3	**45.0**
14 d	11.7	22.8	49.8	2.4	86.7	-	-	-	1.2	16.4	**17.6**
21 d	6.0	14.6	57.1	5.7	83.4	-	-	-	-	8.7	**8.7**
30 d	3.1	10.9	65.5	6.4	85.9	-	-	-	-	3.3	**3.3**
42 d	2.1	8.1	67.1	9.7	87.0	-	-	-	-	2.1	**2.1**
59 d	0.9	5.7	67.8	9.9	84.3	-	-	-	-	1.1	**1.1**
90 d	0.8	4.0	71.3	11.2	87.3	-	-	-	-	0.4	**0.4**
120 d	0.8	3.2	67.7	17.6	89.3	-	-	-	-	0.1	**0.1**
155 d	0.8	3.2	75.3	14.8	94.1	-	-	-	-	-	**-**
199 d	0.7	2.7	69.1	16.9	89.4	-	-	-	-	-	**-**
120 d sterile	17.3	55.6	22.2	0.4	95.4	-	-	-	7.9	19.9	**32.1**

Minor metabolites

In both systems up to nine radioactive compounds were found. Two were identified as chlorobenzoxazolone (AE F054014) and the phenol metabolite (AE F040356). None of the remaining non-identified compounds reached levels ≥ 10 % of applied radioactivity.

Table B.8.2.2.3-3 Maximum concentration (% of applied radioactivity) of metabolites chlorobenzoxazolone (AE F054014) and the phenol metabolite (AE F040356) in the water- and sediment phase within the Rhine and Nidda systems.

Metabolite	System	Water		Sediment	
		Max (%)	Time	Max (%)	Time
Chlorobenzoxazolone	Rhine	2.3	6 h	0.8	21 d
(AE F054014)	Nidda	5.0	10 d	1.5	10 d, 14 d
Phenol metabolite	Rhine	-	-	4.3	14 d
(AE F040356)	Nidda	0.2	10 d	2.6	30 d

Material balance

Recoveries in Rhine were generally ≥ 90 % of total applied radioactivity, except for day 120 when only 87.4 % were detected. From day 14 on in Nidda lower recoveries were found. It was concluded that increasing losses were due to higher metabolic activity and high overall turnover of test substance in this system, because material balance in comparable sterile samples was ≥ 90 %. Additional efforts were made to clarify the losses in recoveries by a re-determination of radioactivity in NER fraction, investigations on volatile components (additional sampling on day 71) and the determination of $^{14}CO_2$ dissolved as carbonates in the water phase, however the exact cause remained unknown.

Material balance in samples with exaggerated application rates (100x) were ≥ 90 %, whereas Nidda 10x samples showed similar deficiencies as determined for "normal" (1x) application rate (see above).

Route of degradation

No significant differences of the metabolic profile between the two systems were noted, but different quantities of individual metabolites were formed. In both systems the fast initial degradation step was the ester hydrolysis of fenoxaprop-P-ethyl (AE F046360) to fenoxaprop-P-acid (AE F088406). Further a cleavage of the two ether moieties in the molecule occurred and the chlorobenzoxazolone (AE F054014) was formed. In parallel, the phenol metabolite (AE F040356) was generated. Both metabolites did not exceed ≥ 10 % of applied radioactivity. In addition, the formation of a large portion of non-extractable residues (NER) and $^{14}CO_2$ was observed.

The metabolic profiles of exaggerated rates showed no significant differences in comparison to samples with 1x

application rate.

In sterile samples ester hydrolysis occurred very slowly compared to non-sterilised samples and test substance was even found until day 120 (Rhine) and day 30 (Nidda). Also the metabolites fenoxaprop-P-acid (AE F088406) and chlorobenzoxazolone (AE F054014) were found at comparable high amounts in both systems until the end of the study. This slower transformation reflects the diminished activity of esterase in the test systems and therefore it can be concluded that mainly biotic processes were responsible for the rapid degradation of fenoxaprop-P-ethyl (AE F046360).

Characterisation of NER
Soxhlet extraction: Extraction efficiency was very good and radioactivity additionally released was negligible (max. 1.6 % of total applied radioactivity).

Acid hydrolysis (according to soil residue method): Approx. half of residual radioactivity was found dissolved in acidic extract. Further efforts was made to characterise radioactivity in more detail, but the clean-up steps of samples showed difficulties, e.g. for Nidda samples with high organic matter content, a clean-up by soil phase extraction (SPE) failed. Therefore, a profiling of acidic extract without purification was conducted and results showed that only traces of chlorobenzoxazolone (AE F054014) were present and the major portion of radioactivity was not assignable to a distinct peak or component.

Organic matter fractionation: After treatment with aqueous sodium hydroxide solution approx. 16 – 20 % of total radioactivity from NER in sediment was detectable and was assigned to 8.9 – 17.7 % fulvic acids, 0.9 – 1.5 % beta humus and 0.5 – 1.4 % humic acids, respectively.

Conclusion:

In both systems fenoxaprop-P-ethyl (AE F046360) was rapidly hydrolysed to the main metabolite fenoxaprop-P-acid (AE F088406). Further chlorobenzoxazolone (AE F054014) and the phenol metabolite (AE F040356) were formed, but did not exceed the 10 % level.

The degradation of fenoxaprop-P-ethyl (AE F046360) and its metabolites was accompanied by the formation of high amounts of non-extractable radioactivity (Rhine: max. 75 % at day 59 and 54.9 % at end of study; Nidda: max.75.3 % at day 155 and 69.1 % at end of study) and CO_2 (Rhine: 27.6 %, Nidda: 16.9 %).

To sum up in water/sediment-systems under aerobic test conditions biotic processes in combination with hydrolysis were responsible for the rapid degradation of fenoxaprop-P-ethyl (AE F046360) and its metabolites.

Comments RMS AT:

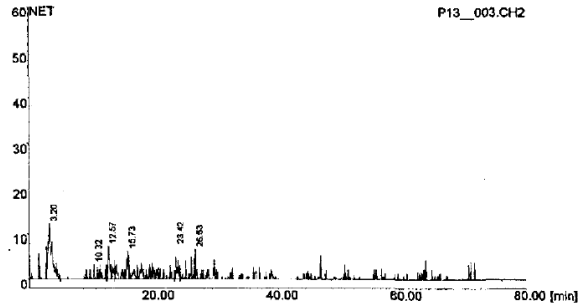
- The study broadly follows OECD guideline 308 and is still considered reliable.
- Mass balance was not sufficient (> 90 % AR) at all sampling times (particularly in the "Nidda" system). However, this is not considered to invalidate the study or parts of it as at later sampling times sufficient recover was reached indicating some problems with capturing volatiles and/or system setup tightness.
- Peak values for chlorobenzoxazolone (AE F054014) in the *total water/sediment system*, not mentioned in the summary above, were 2.4 % AR at 7 DAT and 6.5 % AR at 10 DAT for the Rhine and Nidda system, respectively. The corresponding values for the phenol metabolite (AE F040356) were 4.3 % AR at 14 DAT and 2.6 % AT and 30 DAT (Rhine/Nidda).
- Seven other unknown components were assigned to peaks nominated as 'U-1' to 'U-7'. U-1 was the largest component observed at maximum values of 6.0/3.2 % (Rhine/Nidda) in the course of the study. The RMS AT notes, that in the Rhine system U-1 actually exceeded 5 % of AR in more than two consecutive sampling points (refer to table below) thus formally triggering identification and exposure assessment according to Regulation (EU) No 283/2013. However, due to its distinct polar character in chromatography, U-1 is not regarded as one single compound (refer to example HPLC diagram below, Rhine system, water phase, 90 DAT). No other unknown metabolite fraction exceeded 5 % of AR in

the study or showed increasing tendency towards study end.

Table B.8.2.2.3-4 Residues of unknown polar metabolite fraction U-1 in the Rhine and Nidda system (numbers in grey indicated exceedance of 5 % AR).

DAT		2 hrs	4 hrs	6 hrs	1	2	3	7	10	14	21	30	42	59	90	120	155	199
Rhine	Wat.	-	-	-	-	-	-	-	na	1.4	2.8	5.5	5.6	5.1	3.4	4.3	4.1	5.5
	Sed.	-	-	-	-	0.1	-	-	na	-	0.3	0.5	0.5	0.4	0.4	-	-	0.1
	Tot.	**-**	**-**	**-**	**-**	**0.1**	**-**	**-**	**na**	**1.4**	**3.1**	**6.0**	**6.0**	**5.5**	**3.8**	**4.3**	**4.1**	**5.7**
Nidda	Wat.	-	-	-	-	-	-	1.4	1.8	3.2	2.4	0.9	0.6	0.2	0.1	0.2	na	na
	Sed.	-	-	-	-	-	-	-	-	-	0.3	0.5	0.7	0.3	0.1	0.1	na	na
	Tot.	**-**	**-**	**-**	**-**	**-**	**-**	**1.4**	**1.8**	**3.2**	**2.7**	**1.4**	**1.3**	**0.5**	**0.2**	**0.3**	**na**	**na**

Table B.8.2.2.3-5 Example HPLC diagram of the Rhine system, water phase, 90 DAT (unknown polar metabolite fraction U-1 with a RT of 3.2 min representing 3.4 % of AR)



- Residues of fenoxaprop-P-ethyl (AE F046360) and metabolites were kinetically re-assessed in Herrmann et al. (2016).

Reference:	**[^{14}C]-Fenoxaprop-P-Ethyl: Degradation and retention in two water/sediment systems**
Author(s), year:	Fitzmaurice, M. (2004)
Report/Doc. Number:	41428002, M-242393-01-1
Guideline(s):	OECD Guideline 308 (2002)
GLP:	Yes
Validity:	Yes
Status:	**Previously submitted**

[The following study report is a copy/paste of the original text in the DAR for Annex I inclusion slightly amended in order to meet editorial settings and to improve readability]

Material and methods:

The aerobic aquatic metabolism and degradation of UL-phenoxy-^{14}C-labelled fenoxaprop-P-ethyl (AE F046360, radiochemical purity > 98 %, enatiomeric purity: 99.5 %) were studied in two different water-sediment systems. The water/sediment systems were treated with 0.06 mg/L test substance (field application rate 180 g/ha, full overspray, 30 cm water depth) and test samples were incubated at 20 °C under aerobic conditions in darkness for up to 118 days.

The sediment with associated water was sampled at two sites in natural environment:

- System 1: Clayton Pond (04/039), pond at Clayton Farm, North Carolina, USA
- System 2: Roding River (04/044), from the river Roding at Boarded Barns Farm, Ongar, Essex, UK

After Sampling sediments were washed through a 2 mm sieve. Per test sample approx. 30 mm wet sediment and 120 mm water was put in specially adapted glass incubation flask (approximately 6 cm diameter). The ratio water/dry sediment was 4:1. All flasks were attached to the incubation system and were ventilated with moistened air. Each flask was connected with a series of three traps (1x ethylene glycol, 2x 2M potassium hydroxide solution). The test units were acclimatised to test conditions for at least 12 days. O_2 content, *p*H, redox potential and temperature were monitored during the acclimatisation period and at each sampling time. Duplicate samples (flasks and associated trap solutions) were taken after two, four and six hours and 1, 2, 3, 7, 10, 14, 30, 47 or 48, 62, 90, and 118 days of incubation. Water and sediment phase were separated by decantation and the radioactivity content was analysed by LSC and HPLC. Additionally selected samples were analysed by LC/MS to verify the identities of test substance and metabolites. Volatile trap solutions were removed for analysis at each sampling time and aliquots were taken to determine the radioactivity by LSC. The radioactivity in potassium hydroxide traps was confirmed as CO_2 with $BaCl_2$-precipitation. Non extractable residues in the sediment at the final sampling time were characterised by fractionation of sediment organic matter into humic- and fulvic acids and humin fraction.

Table B.8.2.2.3-6 Physical and chemical properties of the two test systems

Matrix	Parameter	Location	
		Clayton Pond	Roding River
Water	Temperature (°C)[(a)]	25	18
	*p*H	6.6	8.0
	O_2-content [%][(a)]	86	80
	Total hardness [mg/L $CaCO_3$][(a)]	28	370
	DOC [mg C/L]	10.1	15.1
	Total nitrogen [mg/L]	16.8	14.0
	Total phosphorous [mg/L]	0.1	0.3
Sediment	*p*H ($CaCl_2$)	4.4	7.2
	C_{org} [%]	0.8	2.2
	Total nitrogen [g/kg]	0.1	0.5
	Total phosphorus [mg/kg]	111.1	746.6
	Redox potential [mV] initial / final	-75 / -230	-5 / -226
	Cation exchange capacity [cmol+/kg]	3.5	15.3
	Microbial biomass [µg C/g sediment] initial / final	102.8 / 34.0	37.3 / 61.5
	Texture (USDA)	Loamy sand	Clay
	Particle size distribution:		
	Sand [%]	84.1	14.0
	Silt [%]	3.2	30.7
	Clay [%]	12.8	55.4

(a) Parameter was measured at sampling

Findings:

The two systems differed significantly in their texture, organic carbon content and microbial biomass.

The actual application rate of ^{14}C-Fenoxaprop-P-ethyl was determined to be 0.058 mg/L (97.3 % of the target application rate).

During the study aerobic conditions in water and anaerobic conditions in sediment were established. The *p*H values in water were in a range of 4.76 to 7.81 for Clayton Pond (04/039) and 7.58 to 8.38 for Roding River (04/044). For Clayton Pond system more acidic conditions were established until the end of the test.

Results for material balance and distribution of radioactivity are summarised as mean measured values in table below. Only degradation products which exceeded 10 % of applied radioactivity are mentioned.

Table B.8.2.2.3-7 Radioactivity distribution, partitioning and balance (% of applied radioactivity) during degradation in the water- and sediment phase within the Clayton Pond and Roding River systems (mean of two replicates, numbers shaded in grey indicate exceedance of 5 % AR).

Time	Water	Sediment	NER	CO_2	Total	Fenoxaprop-P-	Fenoxaprop-P-acid	HOPP-acid

						ethyl (AE F046360)			(AE F088406)			(AE F096918)		
						Wat.	Sed.	Tot.	Wat.	Sed.	Tot.	Wat.	Sed.	Tot.
System 1: Clayton Pond (loamy sand)														
2 h	96.9	4.8	0.3	0.0	102.0	70.9	nd	**70.9**	23.1	nd	**23.1**	nd	nd	nd
4 h	99.1	3.6	0.1	0.0	102.8	60.7	nd	**60.7**	35.8	nd	**35.8**	nd	nd	nd
6 h	99.9	2.8	0.0	0.0	102.7	28.7	nd	**28.7**	70.2	nd	**70.2**	nd	nd	nd
1 d	99.9	1.0	0.2	0.1	100.3	nd	nd	**nd**	95.0	nd	**95.0**	4.0	nd	**4.0**
2 d	94.3	4.4	1.1	0.1	99.9	nd	nd	**nd**	86.9	nd	**86.9**	7.4	nd	**7.4**
3 d	96.3	4.2	0.4	0.2	101.1	nd	nd	**nd**	90.8	nd	**90.8**	5.5	nd	**5.5**
7 d	88.6	9.0	2.2	0.7	100.5	nd	nd	**nd**	78.5	nd	**78.5**	10.2	nd	**10.2**
10 d	85.9	8.9	3.9	0.7	99.5	nd	nd	**nd**	75.3	8.9	**84.2**	10.7	nd	**10.7**
14 d	85.6	5.7	7.2	3.4	101.8	nd	nd	**nd**	78.5	3.5	**82.0**	7.2	0.4	**7.6**
30 d	69.4	13.7	10.7	5.7	99.6	nd	nd	**nd**	56.9	11.0	**67.9**	12.5	2.7	**15.2**
47 d	62.6	9.4	13.8	16.3	102.2	nd	nd	**nd**	43.9	9.4	**53.4**	18.7	nd	**18.7**
62 d	35.6	6.8	25.6	27.2	95.2	nd	nd	**nd**	10.6	3.3	**13.9**	22.9	3.4	**26.3**
90 d	34.0	7.7	26.2	25.9	93.9	nd	nd	**nd**	21.2	6.5	**27.7**	3.1	0.5	**3.5**
118 d	10.0	3.8	33.5	45.9	93.2	nd	nd	**nd**	4.0	nd	**4.0**	1.1	nd	**1.1**
System 2: Roding River (clay)														
2 h	100.9	2.8	0.3	0.0	104.0	81.4	nd	**81.4**	15.4	nd	**15.4**	nd	nd	**nd**
4 h	96.4	5.3	0.3	0.0	102.0	68.1	nd	**68.1**	24.3	nd	**24.3**	nd	nd	**nd**
6 h	96.9	6.2	1.0	0.0	104.1	65.9	nd	**65.9**	27.3	nd	**27.3**	nd	nd	**nd**
1 d	94.8	0.6	0.3	0.3	96.0	nd	nd	**nd**	94.8	nd	**94.8**	nd	nd	**nd**
2 d	97.1	2.3	0.6	0.3	100.4	nd	nd	**nd**	97.2	nd	**97.2**	nd	nd	**nd**
3 d	91.3	7.0	0.6	0.3	99.2	nd	nd	**nd**	91.4	nd	**91.4**	nd	nd	**nd**
7 d	88.8	7.0	0.9	1.8	98.5	nd	nd	**nd**	88.8	nd	**88.8**	nd	nd	**nd**
10 d	85.5	6.2	3.8	1.0	96.5	nd	nd	**nd**	83.8	nd	**83.8**	1.7	nd	**1.7**
14 d	85.5	5.4	3.8	3.0	97.7	nd	nd	**nd**	85.5	4.2	**89.7**	nd	nd	**nd**
30 d	79.5	6.6	4.8	5.1	96.0	nd	nd	**nd**	74.3	6.6	**81.0**	5.2	nd	**5.2**
47 d	30.7	8.2	28.7	28.2	95.7	nd	nd	**nd**	15.7	4.6	**20.3**	11.4	0.3	**11.6**
62 d	36.7	7.3	20.8	29.6	94.4	nd	nd	**nd**	30.7	5.5	**36.3**	4.1	1.7	**5.9**
90 d	22.3	5.1	20.1	46.5	93.9	nd	nd	**nd**	16.5	2.5	**18.9**	2.8	0.5	**3.3**
118 d	30.5	7.3	27.3	27.4	92.5	nd	nd	**nd**	17.5	3.1	**20.5**	3.2	0.7	**3.8**

-: not analysed; nd: not detected

Minor metabolites

In the Clayton Pond system nine non-identified radioactive compounds were found, none of which exceeded 3.5 % AR (in total system). In the Roding River system seven non-identified compounds were observed with a maximal individual level of 6.5 % AR (in total system).

Material balance

Recoveries in both systems were generally ≥ 90 % of total applied radioactivity.

Route of degradation

In both systems the fast initial degradation step was the ester hydrolysis of fenoxaprop-P-ethyl (AE F046360) to fenoxaprop-P-acid (AE F088406). Furthermore a cleavage of the two ether moieties in the molecule occurred and HOPP acid (AE F096918) was formed. A partitioning of fenoxaprop-P-acid (AE F088406) and HOPP-acid (AE F096918) between water and sediment was observed. Additionally the formation of non-extractable residues (NER) and $^{14}CO_2$ was noted.

Characterisation of NER

The results of distribution of bound residues (NER) at the end of the study are summarised in the table below.

Table B.8.2.2.3-8 Characterisation of NER Fraction at the end of the study

System	% of applied radioactivity				
	Bound	Fulvic acid	Humic acid	Humin	Total in fractions
Clayton Pond (04/039)	36.2	15.8	12.5	3.2	31.5
	30.9	10.3	14.5	2.2	27.1
Roding River (04/044)	26.0	3.7	2.0	3.3	9.0
	28.7	5.7	1.6	3.7	10.9

Conclusion:

In both systems fenoxaprop-P-ethyl (AE F046360) was rapidly hydrolysed to the main metabolite fenoxaprop-P-acid (AE F088406). A second major metabolite was identified as HOPP acid (AE F096918) with maximum amounts of 22.9 % (at day 62 in the Clayton Pond system) and 11.4 % (at day 47 in the Roding River system). Additionally the formation of non-extractable residues (NER) was noted: Clayton Pond: max. 33.5 % at day 118 and Roding River: max. 28.7 % at day 47 and 27.3 % at the end of the study. The mineralization to CO_2 was high with maximal amounts of 45.9 % at day 118 in the Clayton Pond system and 46.5 % at day 90 in the Roding River system. Thus mineralization was the major route of degradation of UL-phenoxy-^{14}C labelled fenoxaprop-P-ethyl (AE F046360) in both systems.

Comments RMS AT:

- The study broadly follows OECD guideline 308 and is still considered reliable.
- With a maximum occurrence of 6.5 % AR at study end in the total system of the Roding River system (118 DAT) unknown metabolite fraction 'RRT 0.1' exceeded 5 % AR at one sampling point. However, erratic occurrence of this fraction in this water/sediment system from DAT 48 onwards (4.0, nd, 2.3 and 6.5 % AR at 48, 62, 90 and 119 DAT, respectively) does not necessarily indicate that this highly polar fraction is *steadily increasing* towards study end. In the Clayton Pond system, this metabolite fraction was observed only at 90 and 118 DAT with 2.4 and 1.6 % AR, respectively. No other unknown metabolite fraction exceeded 5 % of AR or showed an increasing trend towards study termination.
- Residues of fenoxaprop-P-ethyl (AE F046360) and metabolites were kinetically re-assessed in Herrmann et al. (2016).

Reference:	**^{14}C-AE F046360/^{14}C-AE F033171: Degradation and Metabolism in an anaerobic aquatic system**
Author(s), year:	Voelkel, W. (2000)
Report/Doc. Number:	C007381, M-195784-01-1
Guideline(s):	USEPA (= EPA) Subdiv. IV, Section 162-3 Oct 1982, OECD Draft Oct. 1998, Guidelines for the Registration of Pesticides in Canada, Section C, Jul 1987
GLP:	Yes
Validity:	Supplemental information (refer to comment section)
Status:	**Previously submitted**

[The following study report is a copy/paste of the original text in the DAR for Annex I inclusion slightly amended in order to meet editorial settings and to improve readability]

Material and methods:

The rate of degradation, distribution and metabolism of [UL-chlorophenyl-^{14}C]-fenoxaprop-P-ethyl (AE F046360) and racemic [UL-phenoxy-^{14}C]-fenoxaprop-ethyl (AE F033171) were investigated in the aquatic model system Pond under anaerobic and sterile anaerobic conditions at a concentration of approx. 0.06 mg/kg water, equivalent to the maximum field rate of 0.18 kg/ha.

The samples were acclimatised to form anaerobic conditions in the dark for about one month. After establishment of the conditions required, the corresponding radio labelled test item was applied to the water surface and incubated at 20 °C and 7 °C in the dark. Volatile components formed were removed by flushing each sample periodically with nitrogen.

Non-sterile samples dosed with fenoxaprop-P-ethyl (AE F046360) and incubated at 20 °C were worked-up and analysed after 0, 0.17, 0.25, 1, 2, 3, 7, 14, 21, 27, 48, 64, 78, 97, 127, 163 and 238 days of incubation. Samples with the same label, but incubated at 7 °C were analysed after 0, 3, 7, 14, 21, 27, 48, 64, 78, 97, 127 and

163 days. The samples treated with racemic fenoxaprop-ethyl (AE F033171) at 20 °C were taken for analysis by days 1, 7, 14, 27, 64, 127 and 238. In addition, sterilised samples dosed with the fenoxaprop-P-ethyl (AE F046360) and incubated at 20 °C were taken for analysis after 0, 27 and 57 days.

The radioactivity in water and sediment was analysed separately by HPLC and TLC with radio analytical detection techniques. Sediment samples were analysed for extractable and non-extractable radioactivity and were submitted to an extraction with acetonitrile/water (80:20; v/v), several times until only 2 % AR were recovered in a single extraction step. The material balances and the distribution of radioactivity were established for each sampling interval. Non-extractable residues in the sediment were investigated by various methods including Soxhlet extraction, harsh acidic treatment and organic matter fractionation.

Table B.8.2.2.3-9 Specification of the water /sediment system Pond

Parameter	Water	Sediment
Origin	Ormalingen, BL, Switzerland	
Sediment type	na	Loam
*p*H	6.8	7.5
Total organic carbon (mg C/L)	2.6	na
Organic carbon (%)	na	5.95
Sand (0.050-2.000 mm) (%)	na	36.6
Silt (0.002-0.050 mm) (%)	na	41.1
Clay (< 0.002 mm) (%)	na	22.3
Cation exchange capacity (meq/100 g)	na	28.0

na = not applicable

Findings:

For the chlorophenyl-labelled test systems (fenoxaprop-P-ethyl (AE F0463609 applied), total mean recoveries were 97.0 ± 4.0 %, 101.1 ± 3.6 % and 97.2 ± 3.3 % at 20 °C, 7 °C and under sterile conditions, respectively. For the phenoxy-labelled test system (racemic fenoxaprop-ethyl (AE F033171) applied), the total mean recovery was 97.6 ± 3.4 %.

The radioactivity in the water phases of the chlorophenyl-labelled test systems decreased to 11.2 % (20 °C) and 26.3 % (7 °C) by day 127. For the phenoxy-labelled treated samples the radioactivity in the water decreased to 31.0 % by day 127. Concurrently, the radioactivity in the sediment (extractable and non-extractable) increased continuously reaching maximum values of 69.5 % (day 64, chlorophenyl-label, 20 °C), 70.4 % (day 163, chlorophenyl-label, 7 °C), 45.8 % (day 27, phenoxy-label) and 57.9 % for sterile test system by day 57.

The mineralization of the radioactive residues was significant in the chlorophenyl-labelled (20 °C) and even more in the phenoxy-labelled test systems incubated at 20 °C under non-sterile conditions. $^{14}CO_2$ accounted for 29.9 % of the applied radioactivity in the chlorophenyl-labelled test system at 20 °C and 61.8 % in the phenoxy-labelled system after 238 days of incubation. $^{14}CO_2$ formation was slow at low temperature and represented only 3.8 % after 163 days. Practically no $^{14}CO_2$ was detected under sterile conditions (< 0.1 %) when compared to the non-sterile system (3.5 %) within the same period.

The parent items fenoxaprop-P-ethyl (^{14}C-AE F046360, chlorophenyl-label) and racemic fenoxaprop-ethyl (^{14}C-AE F033171, phenoxy-label) were rapidly and completely transformed into the corresponding fenoxaprop acids AE F088406/AE F053022. AE F088406 or AE F053022 reached maximum values of up to 100.8 % of the applied radioactivity within several days. Dependent on label position, the fenoxaprop acids disappeared from the test systems via formation of up to 12 minor metabolites. However, their amounts did not exceed 5.5 % of the applied radioactivity. For the phenoxy-label, racemic HOPP-acid (AE F020686) was observed as a major metabolite. The formation of all components was followed by a significant mineralization to $^{14}CO_2$ or adsorption to sediment.

Table B.8.2.2.3-10 Time course of the degradation of ^{14}C-chlorophenyl-labelled fenoxaprop-P-ethyl (AE F046360) in a loamy water/sediment system under anaerobic conditions at 20 °C (% AR, values shaded in grey indicate exceedance of 5 % AR)

DAT	Fenoxaprop-P-ethyl (AE F046360)	Fenoxaprop-P-acid (AE F088406)	Chlorobenz-oxazolone (AE F054014)	Phenol metabolite (AE F040356)	NIR[(a)]	NER	$^{14}CO_2$	Total
0	78.9	18.2	-	-	0.3	0.3	n.d.	97.8
0.17	39.0	57.8	-	-	0.1	0.2	< 0.1	97.0
0.25	35.6	64.6	-	-	0.1	0.2	< 0.1	100.6
1	9.2	90.1	-	-	0.1	0.2	< 0.1	99.7
2	-	100.9	-	-	0.1	0.2	< 0.1	101.2
3	2.4	97.4	-		-	0.5	< 0.1	100.2
7	-	97.9	0.3	0.4	-	1.3	< 0.1	99.8
14	-	93.2	2.0	-	0.2	5.8	0.1	101.3
21	-	86.2	1.9	2.2	0.4	10.2	0.2	101.0
27	-	84.2	2.8	-	-	12.2	0.1	100.1
48	-	64.4	1.8	4.0	-	24.4	1.2	95.8
64	-	45.4	1.4	4.6	-	40.2	3.5	95.1
78	-	37.2	1.3	4.3	1.7	43.1	5.0	92.7
97	-	20.3	2.0	5.5	2.2	50.7	9.4	90.0
127		17.5	1.6	3.8	3.4	54.3	11.2	91.7
163		3.7	1.7	1.7	5.9	58.5	17.2	90.4
238	-	0.6	0.6	1.7	8.3	54.9	29.9	94.3

(a) Non-identified extractable residues consisting of numerous components

Table B.8.2.2.3-11 Time course of the degradation of ^{14}C-chlorophenyl-labelled fenoxaprop-P-ethyl (AE F046360) in a loamy water/sediment system under anaerobic conditions at 7 °C (% AR, values shaded in grey indicate exceedance of 5 % AR)

DAT	Fenoxaprop-P-ethyl (AE F046360)	Fenoxaprop-P-acid (AE F088406)	Chlorobenz-oxazolone (AE F054014)	Phenol metabolite (AE F040356)	NIR[(a)]	NER	$^{14}CO_2$	Total
0	81.6	15.6	-	-	-	0.4	-	97.6
3	10.1	88.5	-	-	-	0.5	-	99.1
7	-	100.3	0.3	0.1	0.1	0.9	-	101.7
14	-	98.7	1.5	-	0.2	2.2	-	102.6
21	-	97.9	1.4	-	0.4	2.6	-	102.2
27	-	105.7	0.4	-	-	3.3	-	109.4
48	-	94.5	1.3	1.2	-	7.6	0.1	104.7
64	-	90.8	1.0	-	-	9.8	0.2	101.9
78	-	84.1	1.5	1.1	0.9	11.8	0.7	100.2
97	-	75.7	1.7	2.6	0.9	18.3	1.3	100.5
127	-	69.1	2.1	2.0	-	21.6	2.4	97.1
163	-	55.9	1.5	0.7	-	34.6	3.8	96.4

(a) Non-identified extractable residues consisting of numerous components

Table B.8.2.2.3-12 Time course of the degradation of ^{14}C-phenoxy-labelled, racemic fenoxaprop-ethyl (AE F033171) in a loamy water/sediment system under anaerobic conditions at 20 °C (% AR, values shaded in grey indicate exceedance of 5 % AR)

DAT	Racemic fenoxaprop-ethyl (AE F033171)	Racemic fenoxaprop-acid (AE F053022)	Racemic HOPP-acid (AE F020686)	Phenol metabolite (AE F040356)	NIR[(a)]	NER	$^{14}CO_2$	Total
1	6.7	94.9	-	-	-	0.3	-	101.7
7	-	93.9	2.5	-	-	1.2	< 0.1	97.7
14	-	96.3	2.1	-	0.7	0.9	0.1	100.1
27	-	76.6	19.3	1.9	-	1.8	< 0.1	99.7
64	-	40.2	42.0	2.3	1.8	6.7	4.5	97.5
127	-	8.9	38.2	2.1	1.2	22.9	20.7	94.0

238	-	0.7	0.7	1.4	6.5	21.2	61.8	92.3

(a) Non-identified extractable residues consisting of numerous components

For samples incubated with the chlorophenyl-label, extractable radioactivity from sediment had maximum values of 37.7 % (20 °C, day 27) and 50.5% (7 °C, day 78), respectively. For samples with the phenoxy-label, a maximum value of 44.0 % of total applied dose was found by day 27. A major portion of radioactivity in the sediment was assigned to the fraction of non-extractables. For samples with the chlorophenyl-label, the non-extractables had reached a maximum of 59 % (chlorophenyl-label) and 23 % (phenoxy-label) at 20 °C by the end of the study. For the samples incubated at lower temperature, the total non-extractable radioactivity had increased to 34.6 % by day 163. For sterilised samples, the values never exceeded 5 % of the total applied dose at any time thus underlining that the formation of non-extractable residues is a microbial induced process.

For representative samples, Soxhlet as well as extractions under harsh reflux conditions were performed with aliquots each of the ambient-extracted and air-dried sediment. Soxhlet extractions of samples with the chlorophenyl label of days 48 and 238 released 6.8 % and 12.8 % of the radioactivity applied. This was followed by the release of 0.7 % and 6.5 % of the radioactivity applied under harsh reflux conditions for the same samples. In comparison, Soxhlet extractions with samples containing the phenoxy-label released 2.3 % of the radioactivity applied for the day 238. The harsh extraction conditions released an additional portion of 1.4 % only. An organic matter fractionation of samples of day 238 showed a partition into approx. 45.3 % and 18.0 % of the total applied dose for the humic acids and humin fractions for chlorophenyl and phenoxy-label, respectively. The radioactivity assigned to the fulvic acids fraction amounted to about 9.6 % and 3.1 % of the applied radioactivity for both radiolabels.

The degradation and mineralization of the major degradation product was significantly slower under sterile conditions thus proposing microbial induced processes for the overall conversion of fenoxaprop residues also under anaerobic conditions.

Conclusion:

Based on the metabolic patterns obtained, ^{14}C-labelled parent compounds fenoxaprop-P-ethyl (AE F046360) and racemic fenoxaprop-ethyl (AE F033171) were hydrolysed rapidly to fenoxaprop-P-acid (AE F088406) for the chlorophenyl-label or to racemic fenoxaprop-acid (AE F053022) for the racemic mixture of isomers with phenoxy-label. The fenoxaprop-acids were bound to the sediment or further degraded. In case of the phenoxy-label, racemic HOPP acid (AE F020686) was observed. For both label positions, a number of other minor components was formed in the course of the study being further mineralised to ^{14}C-carbon dioxide or adsorbed and bound to the sediment.

Comments RMS AT:

- The study broadly follows OECD guideline 308 and is still considered reliable. However, as conducted in **anaerobic** water/sediment systems the study is **considered supplemental information only**.
- The study was re-assessed for degradation rates by the RMS AT applying degradation pathway fit (SFO) with CAKE 3.3 in line with pertinent guidance. Notice that the fit on racemic HOPP acid (AE F020686) is not considered reliable (χ^2 error too high). Note that the limited dataset in the 7 °C did not allow for a robust fit of fenoxaprop-P-ethyl (AE F046360). The same is true for racemic fenoxaprop-ethyl (AE F033171) in the 20 °C study.

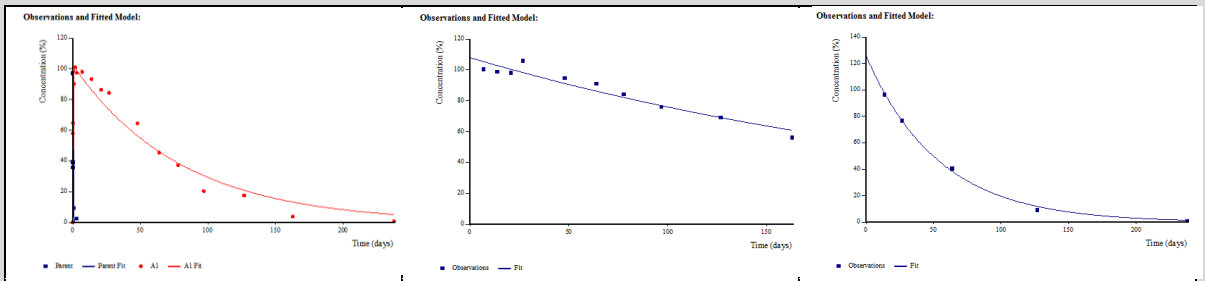
Table B.8.2.2.3-13 Degradation rates of fenoxaprop-P-ethyl (AE F046360) and fenoxaprop-P-acid (AE F088406) as well as racemic fenoxaprop-acid (AE F053022) in an anaerobic water/sediment system (whole system) - RMS AT assessment

Parent applied	T (°C)	Substance	*DT50 / DT90* (d)	ff	χ^2 error (%)	Kinetics
Fenoxaprop-P-ethyl (AE F046360)	20	Fenoxaprop-P-ethyl (AE F046360)	0.15 / 0.51	na	12.9	$P_{SFO} \rightarrow M_{SFO}$
		Fenoxaprop-P-acid (AE F088406)	55.3 / 184	1.0	8.9	
	7	Fenoxaprop-P-acid (AE F088406)	197 / 654	na	3.8	SFO[(a)]

Racemic fenoxaprop-ethyl (AE F033171)	20	Racemic fenoxaprop-acid (AE F053022)	37.2 / 124	na	3.0	SFO[(a)]

(a) Decline fit

Table B.8.2.2.3-14 Fits on degradation of fenoxaprop-P-ethyl (AE F046360) and fenoxaprop-P-acid (AE F088406) as well as racemic fenoxaprop-acid (AE F053022) in an anaerobic water/sediment system (whole system) - RMS AT assessment



Fenoxaprop-P-ethyl (AE F046360) applied, 20 °C	Fenoxaprop-P-ethyl (AE F046360) applied, 7 °C	Racemic fenoxaprop-ethyl (AE F033171) applied, 20 °C

Reference:	**[Phenoxy-UL-^{14}C] and [Chlorophenyl-UL-^{14}C]Fenoxaprop-P-ethyl: Aerobic aquatic metabolism in two sediment/water systems**
Author(s), year:	Xu, T. (2012)
Report/Doc. Number:	MEFPL007, M-431724-01-1
Guideline(s):	OECD 308 (2002), OPPTS 835.4300 Aerobic Aquatic Metabolism October (2008), PMRA DACO No. 8.2.3.5.6 (2003)
GLP:	Yes
Validity:	Yes
Status:	**New submission**

Executive Summary:

The biotransformation of [UL-phenoxy-^{14}C] and [UL-chlorophenyl-^{14}C]-fenoxaprop-P-ethyl (AE F046360) was studied in two differing US water-sediment systems: Lawrence and Goose River at 20 °C in the dark for 28 days in maximum.

For the silty clay loam system (Lawrence) the UL-phenoxy label mean material balances of two replicates ranged from 97.0 % to 103 %. The corresponding values after application of UL-chlorophenyl labelled fenoxaprop-P-ethyl (AE F046360) ranged from 100 % to 111 %. For the silt loam system (Goose River) the UL-phenoxy label mean material balances of two replicates ranged from 91.8 % to 104 %. The corresponding values after application of UL-chlorophenyl labelled fenoxaprop-P-ethyl (AE F046360) ranged from 89.9 % to 100 %. A full material balance was therefore established for all samples.

For the Lawrence system and the UL-phenoxy label, total radioactivity in water dissipated from 63.2 % at day zero to 3.4 % of AR after 28 days of incubation. Total radioactivity in sediment increased from 36.8 % at day zero to 53.2 % of AR by the end of the study. Non-extractable radioactivity in sediment increased from 2.1 % AR by day zero to 35.5 % at study termination. At the end of the study, radioactivity mineralised to ^{14}C-carbon dioxide amounted to 36.6 % AR while formation of other organic volatile components was negligible (< 0.1 %).

For the Lawrence system and the UL-chlorophenyl label, total radioactivity in water dissipated from 71.7 % at day zero to 4.2 % of AR after 28 days of incubation. Total radioactivity in sediment increased from 28.3 % at day zero to 91.7 % of AR by the end of the study. Non-extractable radioactivity in sediment increased from 1.6 % AR by day zero to 66.1 % at study termination. At the end of the study, radioactivity mineralised to ^{14}C-carbon dioxide amounted to 9.7 % AR while formation of other organic volatile components was negligible (< 0.1 %).

For the Goose River system and the UL-phenoxy label, total radioactivity in water dissipated from 60.9 % by day zero to 9.3 % of AR after 28 days of incubation. Total radioactivity in sediment increased from 39.1 % by day zero to 85.8 % at the end of the study. Non-extractable radioactivity in sediment increased from 0.5 % AR by day zero to 37.6 % at study termination. At the end of the study, radioactivity mineralised to ^{14}C-carbon dioxide amounted to 6.0 % AR while formation of other organic volatile components was negligible (< 0.1 %).

For the Goose River system and the UL-chlorophenyl label, total radioactivity in water dissipated from 69.2 % by day zero to 4.7 % of AR after 28 days of incubation. Total radioactivity in sediment increased from 30.8 % by day zero to 89.3 % at the end of the study. Non-extractable radioactivity in sediment increased from 0.2 % AR by day zero to 40.5 % at study termination. At the end of the study, radioactivity mineralised to ^{14}C-carbon dioxide amounted to 0.9 % AR while formation of other organic volatile components was negligible (< 0.1 %).

Metabolite fenoxaprop-P-acid (AE F088406) was found as a major transformation product in the Lawrence system for both positions of radiolabel tested amounting to 71.0/69.9 % AR in maximum (phenoxy-label/chlorophenyl label) in water each by day 0.5 and to 42.7/45.3 % in the sediment each by day 14. The same metabolite was found in the Goose River system amounting to 59.3 % AR and 58.3 % AR in maximum (phenoxy label, day 0.25/chlorophenyl label, day 1) and 49.9/45.8 % in the sediment each by day 7.

Only in sediment of the Goose River system, the phenol-type compound AE F040356 was found at 13.1/12.9 % AR in maximum (phenoxy label/chlorophenyl label) each by day 28. Also only in sediment of the Goose River system, chlorobenzoxazolone (AE F054014) was observed as a minor compound at 8.5 % AR in maximum by day 28.

Degradation was by a number of minor transformation products none exceeding 4.7 % (Lawrence) and 5.4 % (Goose River) for a single component at any sampling interval.

Material and Methods

Test Material
[UL-phenoxy-^{14}C]-fenoxaprop-P-ethyl (Ph label)
Specific radioactivity: 4.14 MBq/mg (111.9 µCi/mg)
Radiochemical purity: 100 %
Batch No. C-1142A

[UL-chlorophenyl-^{14}C]-fenoxaprop-P-ethyl (ClPh label)
Specific radioactivity: 3.97 MBq/mg (107.3 µCi/mg)
Radiochemical purity: > 98 %
Batch No. C-1143

Test System
The study was carried out with two contrasting water/sediment systems collected at two locations in the US. Water and sediment of each system were collected from the same area. While the Lawrence system was collected from the standing water of a pond, the Goose River system originated from flowing water. Sediments and water were collected from the top 0 to 20 cm and stored refrigerated less than 30 days prior to further processing. Before set-up of samples, the wet sediment was passed through a 2 mm sieve by use of the associated water.

Table B.8.2.2.3-15 Physico-chemical characteristics of associated sediments

Sediment	Goose River	Lawrence
Geographic location	Goose River, North Dakota, US River surrounded by agricultural area	Lawrence, Kansas, US Pond surrounded by agricultural area
Latitude and longitude	N 47°43.779’’ W 97°37.312’’	N 39°03.031' W 95°11.585’"
Texture class [USDA]	Silt loam	Silty clay loam
Sand (2000 - 50 µm) (%)	15.6	14.3
Silt (50 - 2 µm) (%)	76.9	48.0

Clay (< 2 µm) (%)	7.5	37.7
*p*H (0.01 M $CaCl_2$)	7.9	7.4
*p*H (water)	8.0	7.8
*p*H (saturated paste)	7.9	7.6
Organic matter (%)	7.0	3.2
Organic carbon (%)	4.1	1.8
Cation exchange capacity (meq/100 g sediment)	24	22.3
Bulk density (g/mL)	0.82	1.01
Microbial counts (CFU/g dry weight)		
Actinomycetes, Initial	968 000	74 500
Final	52 700	399 000
Fungi, Initial	8 070	993
Final	3 780	1 330
Bacteria, Initial	1 150 000	348 000
Final	39 800	339 000

Table B.8.2.2.3-16 Physico-chemical characteristics of water

Water	Goose River	Lawrence
Temperature at collection (°C)	not measured	not measured
*p*H	8.3	7.8
Hardness in mg equivalent (mg $CaCO_3$/L)	849	217
Calcium (mg/kg)	176	72
Magnesium (mg/kg)	98	9.1
Conductivity (mmhos/cm)	1.8	0.45
Total dissolved solids (mg/kg)	1566	320
Turbidity (NTU)	3.51	0.71
Alkalinity (mg $CaCO_3$/L)	352	213
Carbonates (meq/L)	1.17	0
Bicarbonates (meq/L)	7.05	4.25
Total Organic Carbon (TOC, mg/L)	11.8	4.4
Dissolved Organic Carbon (DOC, mg/L)	10.1	3.7
Total nitrogen (mg/kg)	< 0.2	1.1
Total phosphorus (mg/kg)	1.4	1.0

Experimental conditions

The tests were performed in individual cylindrical flasks each filled with sieved sediment to a depth of 2 cm. Associated water was added to each test vessel to result in a depth of 6 cm above the sediment zone. The sediment-to-water ratio was 1:3 (v/v) for Lawrence and 1:3.4 for Goose River systems. Each of the flow-through test vessels was attached to traps for volatile components formed, *i.e.* 2 M potassium hydroxide for ^{14}C-carbon dioxide and ethylene glycol/1M sulfuric acid for other volatiles. Two replicates per sampling interval were prepared for each position of radiolabel.

The nominal initial test concentration of 9 µg a.s./L was derived when assuming the single maximum treatment rate of 90 g a.s./ha in the field to be diluted in a one hectare pond with a water depth of 100 cm. An initial test concentration of 90 µg a.s./L was chosen to allow for sufficient analytical sensitivity and lower matrix effects.
Each sample was dosed by applying a solution of ^{14}C-fenoxaprop-P-ethyl (AE F046360) in ethanol dropwise onto the water surface to result in 14.8 to 16.4 µg test substance applied per test vessel.

Non-sterile, untreated samples were prepared in parallel for each water/sediment system for monitoring of total organic carbon (TOC) in the water and the microbial biomass in the sediment phase, respectively. One sample per water/sediment system was analysed at time zero and after 28 days of incubation.

The water/sediment samples were incubated under flow-through conditions at 20 ± 2 °C for a maximum period of 28 days.

Sampling

For each position of radiolabel duplicate samples were removed for analysis after 0, 0.08, 0.17, 0.25, 0.5, 1, 3, 7, 14, 21 and 28 days of incubation for Lawrence systems and after 0, 0.08, 0.17, 0.25, 1, 7, 14, 21 and 28 days of incubation for Goose River systems.

Analytical procedures

At each sampling interval, the *p*H and dissolved oxygen content were measured in the water phase. In addition, the redox potential was determined in the water phase and the sediment.

Water and sediment were separated by decantation followed by extraction of the sediment. Sediment was extracted exhaustively by shaking three times successively with aqueous acetonitrile (20:80, v/v) containing acetic acid (1 % by vol.) under ambient conditions. Sediments were microwave-extracted twice with acetonitrile in addition. Water samples were analysed by LSC and HPLC directly without concentration. Aliquots of ambient and microwave extracts were combined and concentrated by a factor of about three prior to HPLC analysis. Extracted sediment was air-dried prior to quantification of radioactivity *via* combustion and LSC. Volatile radioactivity in traps was determined by LSC. Identity of $^{14}C\text{-}CO_2$ was confirmed by co-precipitation with barium chloride solution. The radioactivity in liquid samples was directly determined by LSC while extracted sediment subject to combustion and determination of adsorbed ^{14}C-carbon dioxide by LSC.

Chromatographic investigations were performed by reversed phase HPLC as the primary analytical method using ^{14}C-flow through detection techniques.

Identification of transformation products was carried out by co-elution with authentic reference material and the investigation of selected isolated peaks by HPLC/MS.

Results and Discussion:

Findings

Following acclimation of samples and application of the test substance the test conditions were maintained throughout the incubation period.

Measurements of the redox potential in water and sediment and the oxygen content in the water indicated aerobic conditions for both water/sediment systems during incubation. The *p*H in the water of the two systems remained nearly constant in the course of incubation.

The results of microbial counts for actinomycetes, fungi and bacteria showed that biological activity of the test systems was given during the entire incubation period. From lower values in the Goose River system after 28 days of incubation a trend for a reduction could be derived. The decrease may be regarded as a typical situation within laboratory tests on soils and sediments with microbes suffering from a lack of nutrients when being held artificially in test flasks and separated from the outdoor environment.

Table B.8.2.2.3-17 Measurements of dissolved oxygen, *p*H and redox potential in the Lawrence system

Sampling interval (day)	----------Water----------			---------- Sediment ----------	
	Dissolved oxygen (mg/L)	*p*H	Redox E_h (mV)	*p*H	Redox E_h (mV)
0[(a)]	7.3	7.9	386	7.7	250
1[(a)]	7.5	8.0	298	7.7	218
3[(a)]	7.6	7.7	275	7.5	227
7[(a)]	7.8	7.9	336	7.5	238
14[(a)]	7.5	7.9	292	7.6	263
21[(b)]	8.3	8.4	345	7.2	339
28[(b)]	7.2	8.0	322	7.0	126
Maximum	7.2	7.7	275	7.0	126
Minimum	8.3	8.4	386	7.7	339
Average	7.6	8.0	322	7.5	238

E_h = Redox potential referring to the hydrogen standard electrode, consists of redox potential (E_{obs}) as measured with reference electrode (Ag/AgCl) and by adding a fixed value of +197 mV for the potential of the reference electrode (E_{ref}) used, i.e. $E_h = E_{obs} + E_{ref}$. E_{obs}

(a) Average of the average of two determinations per label position

(b) Average of two determinations from biomass samples

Table B.8.2.2.3-18 Measurements of dissolved oxygen, *p*H and redox potential in the Goose system

Sampling interval (day)	----------Water----------			---------- Sediment ----------	
	Dissolved oxygen	*p*H	Redox E_h (mV)	*p*H	Redox E_h (mV)

	(mg/L)				
0	6.6	8.7	262	8.6	274
1	7.7	8.7	258	8.7	187
7	7.4	9.0	289	9.0	293
14	7.0	8.7	333	8.7	336
21	7.5	8.5	279	8.3	214
28	7.9	8.4	308	8.4	315
Maximum	6.6	8.4	258	8.3	187
Minimum	7.9	9.0	333	9.0	336
Average	7.4	8.6	288	8.6	270

E_h = Redox potential referring to the hydrogen standard electrode, consists of redox potential (E_{obs}) as measured with reference electrode (Ag/AgCl) and by adding a fixed value of +197 mV for the potential of the reference electrode (E_{ref}) used, i.e. $E_h = E_{obs} + E_{ref}$. E_{obs}
Averages of two determinations from biomass samples

Data

Table B.8.2.2.3-19 Biotransformation of [UL-phenoxy-^{14}C]-fenoxaprop-P-ethyl (AE F046360) in the Lawrence water/sediment system at 20 °C (numbers shaded in grey indicate exceedance of 5 % AR)

Component/Matrix		Sampling interval (day)										
		0	**0.08**	**0.17**	**0.25**	**0.5**	**1**	**3**	**7**	**14**	**21**	**28**
Fenoxaprop-P-ethyl (AE F046360)	Water	63.2 ± 1.3	35.7 ± 3.4	15.9 ± 3.2	9.5 ± 2.1	3.0 ± 1.4	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	Sediment	23.4 ± 0.5	6.9 ± 0.4	3.7 ± 0.4	0.0 ± 0.0	0.5 ± 0.7	0.4 ± 0.5	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	Total	**86.6**	**42.6**	**19.6**	**9.5**	**3.5**	**0.4**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**
Fenoxaprop-P-acid (AE F088406)	Water	0.0 ± 0.0	32.4 ± 3.1	54.5 ± 2.3	61.8 ± 0.9	71.0 ± 1.1	70.1 ± 1.2	53.4 ± 1.7	38.2 ± 1.7	27.4 ± 1.4	15.9 ± 0.3	1.8 ± 2.5
	Sediment	10.0 ± 1.2	26.8 ± 0.6	24.2 ± 0.2	28.7 ± 1.0	22.8 ± 0.6	26.0 ± 0.7	39.3 ± 0.6	33.8 ± 0.8	42.7 ± 1.4	21.0 ± 0.1	13.3 ± 0.4
	Total	**10.0**	**59.1**	**78.7**	**90.5**	**93.7**	**96.1**	**92.6**	**72.0**	**70.1**	**36.9**	**15.0**
Total unidentified radioactivity[(a)]	Water	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.2	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.4 ± 0.5	0.0 ± 0.0	2.8 ± 0.1	0.0 ± 0.0
	Sediment	1.3 ± 1.8	0.0 ± 0.0	1.8 ± 0.3	0. ± 0.0	1.9 ± 2.7	0.9 ± 0.2	0.0 ± 0.0	9.5 ± 0.8	4.3 ± 2.9	4.6 ± 0.1	4.5 ± 0.0
	Total	**1.3**	**0.0**	**1.8**	**0.0**	**1.9**	**0.9**	**0.0**	**9.9**	**4.3**	**7.4**	**4.5**
Total extractable radioactivity	Water	63.2 ± 1.3	68.0 ± 0.3	70.3 ± 0.9	71.2 ± 1.2	74.0 ± 0.3	70.1 ± 1.2	53.4 ± 1.7	38.6 ± 2.2	27.4 ± 1.4	18.6 ± 0.3	3.4 ± 0.2
	Sediment	34.7 ± 0.1	33.7 ± 1.1	29.7 ± 0.6	28.7 ± 1.0	25.1 ± 2.7	27.3 ± 1.5	39.3 ± 0.6	43.3 ± 0.0	47.0 ± 1.5	25.6 ± 0.2	17.7 ± 0.5
	Total	**97.9**	**101.7**	**100.1**	**99.9**	**99.1**	**97.4**	**92.6**	**81.8**	**74.4**	**44.2**	**21.1**
CO_2 incl. other volatiles[(b)]		0.0 ± 0.0	0.1 ± 0.0	0.1 ± 0.1	0.1 ± 0.0	0.3 ± 0.0	0.4 ± 0.0	1.4 ± 0.1	3.1 ± 0.2	5.1 ± 0.3	25.5 ± 6.7	36.6 ± 1.2
Non-extract. residues		2.1 ± 0.7	1.5 ± 0.0	2.8 ± 0.3	3.0 ± 0.4	3.9 ± 0.9	5.5 ± 0.2	9.2 ± 0.3	15.8 ± 1.0	17.4 ± 0.0	28.8 ± 0.7	35.5 ± 0.4
Recovery total system		**100** ± 0.5	**103** ± 0.8	**103** ± 0.6	**103** ± 0.1	**103** ± 2.0	**103** ± 0.1	**103** ± 2.4	**101** ± 1.0	**97.0** ± 0.2	**98.7** ± 7.3	**93.3** ± 1.3

Mean values (mean ± standard deviation; n = 2) given as percentages of applied radioactivity (% AR)
Total system = water + sediment
n.a. = not analyzed; n.d. = not detected
(a) Total unidentified consisted of multiple components none exceeding 5.7 % AR for a single peak in the total system at any sampling interval (please refer to comment section)
(b) All values for other volatile radioactivity < 0.1 % AR

Table B.8.2.2.3-20 Biotransformation of [UL-chlorophenyl-^{14}C]-fenoxaprop-P-ethyl (AE F046360) in the Lawrence water/sediment system at 20 °C (numbers shaded in grey indicate exceedance of 5 % AR)

Component/Matrix		Sampling interval (day)										
		0	**0.08**	**0.17**	**0.25**	**0.5**	**1**	**3**	**7**	**14**	**21**	**28**
Fenoxaprop-P-ethyl (AE F046360)	Water	71.7 ± 3.4	21.9 ± 2.0	17.2 ± 1.0	8.5 ± 2.1	3.7 ± 0.1	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	Sediment	20.7	5.3	4.1	0.0	0.0	1.4	0.0	0.0	0.0	0.0	0.0

		± 2.1	± 0.9	± 0.5	± 0.0	± 0.0	± 1.9	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0
	Total	**92.4**	**27.2**	**21.4**	**8.5**	**3.7**	**1.4**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**
Fenoxaprop-P-acid (AE F088406)	Water	0.0 ± 0.0	37.9 ± 1.0	51.3 ± 2.5	63.2 ± 4.5	69.9 ± 1.7	68.0 ± 2.4	52.8 ± 1.8	36.4 ± 1.1	25.7 ± 0.6	17.5 ± 2.2	2.7 ± 0.7
	Sediment	6.0 ± 0.8	32.2 ± 2.4	24.6 ± 0.3	26.5 ± 1.2	22.4 ± 0.8	25.5 ± 0.2	36.5 ± 0.3	43.3 ± 1.9	45.3 ± 1.7	27.2 ± 1.6	17.3 ± 0.1
	Total	**6.0**	**70.2**	**75.9**	**89.7**	**92.3**	**93.5**	**89.3**	**79.7**	**71.1**	**44.7**	**20.0**
Total unidentified radioactivity[(a)]	Water	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	1.4 ± 0.2	1.4 ± 0.2
	Sediment	0.0 ± 0.0	3.1 ± 0.4	1.3 ± 1.8	3.0 ± 0.3	2.2 ± 0.1	3.5 ± 0.2	2.5 ± 0.6	3.0 ± 0.1	3.1 ± 0.0	8.3 ± 1.1	8.3 ± 0.5
	Total	**0.0**	**3.1**	**1.3**	**3.0**	**2.2**	**3.5**	**2.5**	**3.0**	**3.1**	**9.7**	**9.7**
Total extractable radioactivity	Water	71.7 ± 3.4	59.9 ± 1.0	68.6 ± 1.5	71.6 ± 2.5	73.6 ± 1.6	68.0 ± 2.4	52.8 ± 1.8	36.4 ± 1.1	25.7 ± 0.6	18.9 ± 2.4	4.2 ± 0.5
	Sediment	26.7 ± 1.3	40.6 ± 1.1	30.0 ± 2.6	29.6 ± 1.5	24.6 ± 0.9	30.4 ± 1.9	39.0 ± 1.0	46.3 ± 2.0	48.4 ± 1.6	35.5 ± 2.7	25.6 ± 0.4
	Total	**98.4**	**100.5**	**98.6**	**101.2**	**98.1**	**98.4**	**91.8**	**82.7**	**74.2**	**54.3**	**29.7**
CO_2 incl. other volatiles[(b)]		0.0 ± 0.0	0.1 ± 0.0	0.1 ± 0.0	0.1 ± 0.0	0.5 ± 0.0	0.3 ± 0.0	0.7 ± 0.1	1.0 ± 0.1	1.7 ± 0.5	9.3 ± 0.8	9.7 ± 1.0
Non-extract. residues		1.6 ± 0.6	2.5 ± 0.8	3.4 ± 0.9	3.0 ± 0.1	4.2 ± 0.3	7.3 ± 0.0	11.8 ± 0.4	18.8 ± 0.1	24.5 ± 0.9	47.2 ± 2.6	66.1 ± 1.5
Recovery total system		**100** ± 1.5	**103** ± 0.9	**102** ± 2.0	**104** ± 0.9	**103** ± 1.0	**106** ± 0.5	**104** ± 1.3	**103** ± 3.1	**100** ± 0.4	**111** ± 1.8	**106** ± 2.7

Mean values (mean ± standard deviation; n = 2) given as percentages of applied radioactivity (% AR)
Total system = water + sediment
n.a. = not analyzed; n.d. = not detected
(a) Total unidentified consisted of multiple components none exceeding 6.1 % AR for a single peak in the total system at any sampling interval (refer to comment section)
(b) All values for other volatile radioactivity < 0.1 % AR.

Table B.8.2.2.3-21 Biotransformation of [UL-phenoxy-^{14}C]-fenoxaprop-P-ethyl (AE F046360) in the Goose River water/sediment system at 20 °C (numbers shaded in grey indicate exceedance of 5 % AR)

Component/Matrix		Sampling interval (day)								
		0	**0.08**	**0.17**	**0.25**	**2**	**7**	**14**	**21**	**28**
Fenoxaprop-P-ethyl (AE F046360)	Water	59.3 ± 2.5	31.4 ± 1.1	17.4 ± 1.5	11.0 ± 1.8	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	Sediment	38.0 ± 5.0	30.4 ± 1.1	15.3 ± 9.6	6.8 ± 1.4	1.2 ± 1.7	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	Total	**97.3**	**61.9**	**32.7**	**17.7**	**1.2**	**0.0**	**0.0**	**0.0**	**0.0**
Fenoxaprop-P-acid (AE F088406)	Water	1.6 ± 0.9	36.5 ± 2.9	54.4 ± 0.2	59.3 ± 0.9	50.4 ± 2.5	25.1 ± 1.3	14.9 ± 1.6	10.8 ± 1.2	3.2 ± 1.4
	Sediment	0.6 ± 0.9	2.9 ± 0.5	11.8 ± 7.2	18.9 ± 1.1	39.8 ± 1.0	49.9 ± 0.9	40.5 ± 2.6	35.2 ± 4.3	24.2 ± 1.8
	Total	**2.2**	**39.4**	**66.1**	**78.2**	**90.2**	**75.0**	**55.4**	**46.0**	**27.5**
Phenol metabolite (AE F040356)	Water	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	Sediment	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	3.2 ± 0.5	7.6 ± 0.7	11.0 ± 0.4	13.1 ± 1.1
	Total	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**3.2**	**7.6**	**11.0**	**13.1**
Total unidentified radioactivity[(a)]	Water	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	1.3 ± 0.4	2.4 ± 0.4	5.4 ± 1.1	3.7 ± 5.3	6.0 ± 1.6
	Sediment	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	5.1 ± 2.0	1.5 ± 2.1	1.6 ± 2.3
	Total	**0.0**	**0.0**	**0.0**	**0.0**	**1.3**	**2.4**	**10.5**	**5.2**	**7.7**
Total extractable	Water	60.9 ± 3.4	67.9 ± 1.8	71.8 ± 1.3	70.3 ± 0.8	51.6 ± 2.9	27.5 ± 0.9	20.3 ± 0.6	14.5 ± 6.5	9.3 ± 3.0
	Sediment	38.6 ± 4.2	33.4 ± 0.6	27.1 ± 2.4	25.6 ± 0.3	41.0 ± 2.7	53.1 ± 0.4	53.2 ± 0.0	47.7 ± 6.8	38.9 ± 5.2
	Total	**99.5**	**101.3**	**98.9**	**95.9**	**92.7**	**80.7**	**73.5**	**62.2**	**48.2**
CO_2 incl. other volatiles[(b)]		0.0 ± 0.0	0.1 ± 0.0	0.1 ± 0.0	0.1 ± 0.0	0.2 ± 0.0	0.5 ± 0.0	0.5 ± 0.0	2.9 ± 2.0	6.0 ± 4.1
Non-extract. residues		0.5 ± 0.0	0.9 ± 0.0	3.8 ± 0.1	3.6 ± 0.6	11.2 ± 0.8	21.6 ± 1.2	24.6 ± 0.9	31.5 ± 5.2	37.6 ± 1.4

Recovery Total system	**100** ± 0.7	**102** ± 1.3	**103** ± 1.0	**99.6** ± 1.7	**104** ± 0.6	**103** ± 0.7	**98.7** ± 0.1	**96.7** ± 6.0	**91.8** ± 2.8

Mean values (mean ± standard deviation; n = 2) given as percentages of applied radioactivity (% AR)
Total system = water + sediment
n.a. = not analyzed; n.d. = not detected
(a) Total unidentified consisted of multiple components none exceeding 7.3 % AR for a single peak in the total system at any sampling interval (refer to comment section)
(b) All values for other volatile radioactivity < 0.1 % AR.

Table B.8.2.2.3-22 Biotransformation of [UL-chlorophenyl-^{14}C]-fenoxaprop-P-ethyl (AE F046360) in the Goose River water/sediment system at 20 °C (numbers shaded in grey indicate exceedance of 5 % AR)

Component/Matrix		Sampling interval (day) 0	0.08	0.17	0.25	1	7	14	21	28
Fenoxaprop-P-ethyl (AE F046360)	Water	66.7 ± 6.0	36.0 ± 5.7	15.9 ± 8.6	8.3 ± 1.3	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	Sediment	30.6 ± 2.6	26.2 ± 0.8	18.7 ± 3.6	10.8 ± 3.5	0.6 ± 0.9	0.8 ± 1.1	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	Total	**97.2**	**62.2**	**34.6**	**19.1**	**0.6**	**0.8**	**0.0**	**0.0**	**0.0**
Fenoxaprop-P-acid (AE F088406)	Water	2.6 ± 0.3	28.6 ± 6.7	45.2 ± 1.4	53.7 ± 3.7	58.3 ± 0.3	20.3 ± 0.6	11.4 ± 0.4	7.5 ± 1.3	4.7 ± 0.6
	Sediment	0.0 ± 0.0	2.7 ± 0.3	7.2 ± 0.1	17.2 ± 2.0	28.8 ± 1.0	45.8 ± 3.5	41.6 ± 4.0	27.3 ± 0.0	21.9 ± 0.7
	Total	**2.6**	**31.3**	**52.4**	**70.9**	**87.1**	**66.1**	**53.0**	**34.8**	**26.6**
Chlorobenzoxazolone (AE F054014)	Water	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	Sediment	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	1.6 ± 0.1	3.3 ± 0.8	2.5 ± 3.5	6.9 ± 1.2	8.5 ± 1.0
	Total	**0.0**	**0.0**	**0.0**	**0.0**	**1.6**	**3.3**	**2.5**	**6.9**	**8.5**
Phenol metabolite (AE F040356)	Water	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	Sediment	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	3.0 ± 0.7	7.2 ± 0.9	9.9 ± 0.6	12.9 ± 0.2
	Total	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**3.0**	**7.2**	**11.0**	**12.9**
Total unidentified radioactivity	Water	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	Sediment	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	2.0 ± 1.3	0.9 ± 1.3
	Total	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**2.0**	**0.9**
Total extractable	Water	69.2 ± 5.7	64.6 ± 1.1	61.1 ± 10.0	62.0 ± 2.4	58.3 ± 0.3	20.3 ± 0.6	11.4 ± 0.4	7.5 ± 1.3	4.7 ± 0.6
	Sediment	30.6 ± 2.6	28.9 ± 1.1	25.9 ± 3.6	28.1 ± 1.5	31.0 ± 0.0	52.8 ± 0.9	51.3 ± 1.5	46.1 ± 0.7	44.2 ± 0.8
	Total	**99.8**	**93.5**	**86.9**	**90.0**	**89.4**	**73.1**	**62.6**	**53.5**	**48.9**
CO_2 incl. other volatiles[(a)]		0.0 ± 0.0	0.1 ± 0.0	0.1 ± 0.0	0.1 ± 0.0	0.1 ± 0.0	0.2 ± 0.0	0.3 ± 0.0	0.6 ± 0.0	0.9 ± 0.0
Non-extract. residues		0.2 ± 0.0	1.0 ± 0.1	2.8 ± 1.3	2.8 ± 0.2	5.9 ± 0.6	22.2 ± 0.9	29.5 ± 0.7	37.2 ± 0.8	40.5 ± 0.3
Recovery Total system		**100** ± 3.1	**94.7** ± 2.1	**89.9** ± 7.6	**93.0** ± 0.7	**95.4** ± 0.4	**95.6** ± 0.6	**92.5** ± 1.2	**91.4** ± 1.2	**90.3** ± 1.1

Mean values (mean ± standard deviation; n = 2) given as percentages of applied radioactivity (% AR)
Total system = water + sediment
n.a. = not analyzed; n.d. = not detected
(a) All values for other volatile radioactivity < 0.1 % AR.

Mass balance

For the Lawrence system the total recovery of radioactivity in the individual test vessels ranged from 97.0 % of AR to 103 % for the phenoxy-label and from 100 % to 111 % for the chlorophenyl-label. The recovery in individual test vessels of the Goose River system ranged from 91.8 % to 104 % AR for Ph label and from 89.9 % to 100 % for ClPh label. The balances of radioactivity were therefore in an acceptable range for all sampling intervals and all positions of radiolabel indicating no significant losses of radioactivity during incubation and processing of samples.

Distribution of residues in water and sediment
In Lawrence systems, total ^{14}C-residues in the water phase decreased from 63.2 % (Ph label) and 71.7 % AR (ClPh label) at day zero to below the LOD (0.35 % AR) for both labels at the last sampling interval. Total extractable ^{14}C-residues in the sediment were 34.7 % (Ph label) and 26.7 % (ClPh label) by day zero to decrease to 3.4 % AR and 4.2 % after 28 days of incubation. Non-extractable radioactivity in the sediment increased from 2.1 % (Ph label) and 1.6 % (ClPh label) at day zero to 35.5 % AR and 66.1 % at study termination. At the end of the study, radioactivity found mineralised to CO_2 amounted to 36.6 % (Ph label) and 9.7 % (ClPh label).

In Goose River systems, total ^{14}C-residues in the water phase decreased from 60.9 % (Ph label) and 69.2 % AR (ClPh label) at day zero to 9.3 % and 4.7 % at the last sampling interval. Total extractable ^{14}C-residues in the sediment were 38.6 % (Ph label) and 30.6 % (ClPh label) by day zero and 38.9 % AR and 44.2 % after 28 days of incubation. Non-extractable radioactivity in the sediment increased from 0.5 % (Ph label) and 0.2 % (ClPh label) at day zero to 37.6 % AR and 40.5 % at study termination. At the end of the study, radioactivity found mineralised to CO_2 amounted to 6.0 % (Ph label) and 0.9 % (ClPh label).

The decline of total radioactivity from the water phase was paralleled by an increase in the sediment with the decrease from the water phase being more significant for samples of the Goose River system, i.e. the system with the higher organic matter content.

Metabolite fenoxaprop-P-acid (AE F088406) was formed as a predominant compound for both positions of radiolabel applied reaching in the Lawrence system maximum values of 96.1 % (Ph label) and 93.5 % (ClPh label) in total systems after one day of incubation. Formation of fenoxaprop-P-acid (AE F088406) was also significant in the Goose River system at maximum values of 90.2 % (Ph label) and 87.1 % (ClPh label) in total systems each at day one after application.

Dependent on radiolabel position a number of minor transformation products was detected in both water/sediment systems tested. None of the individual components exceeded 7.3 % of AR in total systems in the course of the study.

Volatile radioactivity
The formation ^{14}C-carbon dioxide was dependent on position of radiolabel to start after one to 7 days of incubation for both water/sediment systems investigated. Levels of ^{14}C-carbon dioxide reached their maximum of 36.6 % AR (Ph label) and 9.7 % (ClPh label) after 28 days in the Lawrence system. For the Goose River system the maximum values were 6.0 % AR (Ph label) and 0.9 % (ClPh label) after 28 days.

Formation of other volatile components was insignificant by accounting for less than 0.1 % AR at any sampling interval in the course of the study.

Fenoxaprop-P-ethyl and its residues were therefore subject to extensive further transformation in water/sediment systems till mineralisation.

Transformation of test substance
Fenoxaprop-P-ethyl was transformed by a microbial-induced hydrolytic step (ester hydrolysis) to its metabolite fenoxaprop-P-acid (AE F088406) in both water/sediment systems tested. Formation of fenoxaprop-P-acid (AE F088406) was rapid and predominant in the Lawrence total system with maximum values of 96.1 % AR (Ph label) and 93.5 % (ClPh label) each after one day and for the Goose River total system the maximum values found were 90.2 % AR (Ph label) and 87.1 % (ClPh label) each after one day.

The further conversion of fenoxaprop-P-acid proceeded *via* formation of the phenolic compound AE F040356 as a microbially-mediated step. AE F040356 was observed in the sediment of the Goose River system only at maximum values of 13.1 % AR (Ph label) and 12.9 % (ClPh label) each after 28 days of incubation. In parallel, residues of fenoxaprop-P-ethyl underwent microbial degradation at the heterocyclic ether bond to form, after a split of the molecule, chlorobenzoxazolone (AE F054014). Chlorobenzoxazolone (AE F054014) was observed at maximum values of 8.5 % after 28 days of incubation formed in the sediment of the Goose River system only when applying the chlorophenyl labelled test substance.

In addition, minor components were observed with none of the individual components accounting for more than 5.4 % AR in maximum at a single event for the two positions of radiolabel applied in the course of the study. Mechanisms of dissipation from the water body to the sediment as well as degradation therefore contributed to

the elimination of the parent substance from the total systems to result in the formation of NER and ^{14}C-carbon dioxide as terminal products of biotransformation.

Table B.8.2.2.3-23 Metabolites of fenoxaprop-P-ethyl (AE F046360) formed under conditions of water/sediment testing; maximum values of occurrence

Component	Label	Maximum occurrence (% AR)			System
		Water	Sediment	Total[(a)]	
Fenoxaprop-P-acid (AE F088406)	Phenoxy	71.0 (d0.5)	42.7 (d 14)	**93.7 (d 0.5)**	Lawrence
	Chlorophenyl	69.9 (d0.5)	45.3 (d 14)	**93.5 (d 1)**	Lawrence
	Phenoxy	59.3 (d0.25)	49.9 (d 7)	**90.2 (d 2)**	Goose River
	Chlorophenyl	58.3 (d1)	45.8 (d 7)	**87.1 (d 1)**	Goose River
Chlorobenzoxazolone (AE F054014)	Phenoxy	-	-	-	Lawrence
	Chlorophenyl	-	-	-	Lawrence
	Phenoxy	-	-	-	Goose River
	Chlorophenyl	-	8.5 (d 28)	**8.5 (d 28)**	Goose River
Phenol metabolite (AE F040356)	Phenoxy	-	-	-	Lawrence
	Chlorophenyl	-	-	-	Lawrence
	Phenoxy	-	13.1 (d 28)	**13.1 (d 28)**	Goose River
	Chlorophenyl		12.9 (d 28)	**12.9 (d 28)**	Goose River
Unknowns, minor	Phenoxy	2.8 (d 21)	2.8 (d 21)	**5.7 (d 21)**	Lawrence
	Chlorophenyl	1.4 (d 21)	4.7 (d 21)	**6.1 (d 21)**	Lawrence
	Phenoxy	5.4 (d 14)	1.9 (d 14)	**7.3 (d 14)**	Goose River
	Chlorophenyl	0.8 (d 21)	1.2 (d 21)	**1.2 (d 21)**	Goose River

(a) Not necessarily the sum of maximum fractions in water and sediment at the same sampling interval due to possibility of maximum occurrence at different sampling intervals

Conclusion:

Once applied to water surfaces fenoxaprop-P-ethyl (AE F046360) was rapidly eliminated from the water phase *via* sorption processes to the sediment. The processes were paralleled by a fast microbial induced hydrolysis to result in fenoxaprop-P-acid (AE F088406) as a predominant metabolite in both water/sediment systems (maxima at 71.0 % in water (Ph label, day 0.5, Lawrence system), 49.9 % in sediment (Ph label, day 7, Goose River system) and at 93.7 % in total systems (Ph label, day 0.5, Lawrence system).

Fenoxaprop residues were further microbially converted *via* formation of the phenol metabolite (AE F040356; maximum: 13.1 %, day 28) in the sediment of the Goose River system while the phenol metabolite (AE F040356) was not observed in Goose River water or samples of the Lawrence system.

In parallel, residues of fenoxaprop-P-acid (AE F088406) were microbially transformed *via* a split of the molecule to form chlorobenzoxazolone (AE F054014, maximum: 8.5 %, day 28) in the sediment of the Goose River system while chlorobenzoxazolone (AE F05014) was not observed in Goose River water or samples of the Lawrence system.

The degradation proceeded also via formation of minor metabolites to finally result in non-extractable residues (NER) and ^{14}C-carbon dioxide as terminal products of metabolic transformation under conditions of water/sediment testing.

Sorption of fenoxaprop-P-ethyl and fenoxaprop-P-acid to the sediment proceeded rapidly in the two water/sediment systems.

Comments RMS AT:

- The study follows OECD guideline 308 and is considered reliable.
- Mass balance was slightly below 90 % AR in one sampling date (one replicate only). This is not considered to invalidate the study or parts of it.
- Residue data on unidentified minor metabolite fractions (HPLC peaks, called 'minors') are not sufficiently addressed in the applicant summary above. Therefore, information is provided here more

in detail for metabolite fractions which in the *total* system exceed 5 % at least at one sampling point. The RMS AT agrees with the applicant that none of these unidentified fractions triggers further action in relation to Regulation (EU) No 283/2013.

Table B.8.2.2.3-24 Unidentified metabolite fractions in the Lawrence water/sediment system exceeding 5 % AR in the total system (numbers in grey indicate exceedance of 5 % AR)

Component (label) / Matrix		Sampling interval (day) 0	0.08	0.17	0.25	0.5	1	3	7	14	21	28
Minor 1 (Ph)	Water	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	2.8	0.0
	Sediment	0.0	0.0	1.0	0.0	0.4	0.0	0.0	1.5	0.0	3.0	4.5
	Total	**0.0**	**0.0**	**1.0**	**0.0**	**0.4**	**0.0**	**0.0**	**1.5**	**0.0**	**5.7**	**4.5**
Minor 2 (ClPh)	Water	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.4	0.0
	Sediment	0.0	0.0	0.0	0.0	0.0	0.3	0.0	3.0	0.0	4.7	2.8
	Total	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.3**	**0.0**	**3.0**	**0.0**	**6.1**	**2.8**

Table B.8.2.2.3-25 Unidentified metabolite fractions in the Goose River water/sediment system exceeding 5 % AR in the total system (numbers in grey indicate exceedance of 5 % AR)

Component (label) / Matrix		Sampling interval (day) 0	0.08	0.17	0.25	2	7	14	21	28
Minor 2 (Ph)	Water	0.0	0.0	0.0	0.0	1.3	2.4	5.4	2.0	1.2
	Sediment	0.0	0.0	0.0	0.0	0.0	0.0	1.9	1.5	1.6
	Total	**0.0**	**0.0**	**0.0**	**0.0**	**1.3**	**2.4**	**7.3**	**3.5**	**2.9**

- Data on enantiomer (R/S) analysis, conducted within this study, is missing in the applicant summary. Therefore, this information is provided here: No enantiomer interconversion of fenoxaprop-P-ethyl (R-isomer AE F046360) to the S-isomer fenoxaprop-M-ethyl[9] (AE F085791) was observed in this study. For fenoxaprop-P-acid (R-isomer AE F088406, S-isomer AE F088405) no interconversion was indicated in the Lawrence water/sediment systems, with the S-to-R isomer ratios < 0.06. Some interconversion was noted in the Goose River test systems with the S-to-R isomer ratio reaching 0.18 at Day 28.

- Residues of fenoxaprop-P-ethyl (AE F046360) and metabolites were kinetically re-assessed in Herrmann et al. (2016).

Reference:	**^{14}C-Fenoxaprop-P-ethyl: Route and rate of degradation in aerobic aquatic sediment systems**
Author(s), year:	Mamouni, A. (2008)
Report/Doc. Number:	265 FPE, M-548188-01-1
Guideline(s):	OECD Guideline 308 (2002)
GLP:	Yes
Validity:	Yes
Status:	**New submission**

amended with

Reference:	**^{14}C-Fenoxaprop-P-ethyl: Route and rate of degradation in aerobic aquatic sediment systems - Report Amendment 1**
Author(s), year:	Crowe, A. (2018)
Report/Doc. Number:	DR26BS, B49937, M-548188-02-1
Guideline(s):	Not applicable (amendment)
GLP:	Yes
Validity:	Yes
Status:	**New submission**

[9] Also called fenoxaprop-N-ethyl in some reports

Executive Summary:

The biotransformation of [UL-phenoxy-^{14}C]- and [UL-chlorophenyl-^{14}C]-fenoxaprop-P-ethyl (AE F046360) was studied in two differing water-sediment systems 'River' and 'Pond' at 20 °C in the dark for 103 days.

For the loamy sand system (River) and the UL-phenoxy-label material balances ranged from 94.7 % to 99.8 %. The corresponding values after application of UL-chlorophenyl-labelled fenoxaprop-P-ethyl (AE F046360) were from 95.9 % to 102.7 %. For the silt loam system (Pond) and the UL-phenoxy-label mean material balances of two replicates ranged from 93.5 % to 102.6 %. The corresponding values after application of UL-chlorophenyl-labelled fenoxaprop-P-ethyl (AE F046360) ranged from 95.6 % to 101.0 %. A full material balance was therefore established for all samples.

For the River system and the UL-phenoxy-label, total radioactivity in water dissipated from 77.6 % at day zero to 2.1 % of AR after 103 days of incubation. Total radioactivity in sediment increased from 19.0 % at day zero to 41.5 % of AR by the end of the study. Non-extractable radioactivity in sediment increased from 1.9 % AR by day zero to 37.8 % at study termination. At the end of the study, radioactivity mineralised to ^{14}C-carbon dioxide amounted to 56.1 % AR while formation of other organic volatile components was negligible (< 0.1 %).

For the River system and the UL-chlorophenyl-label, total radioactivity in water dissipated from 73.6 % at day zero to 3.9 % of AR after 103 days of incubation. Total radioactivity in sediment increased from 22.4 % at day zero to 76.9 % of AR by the end of the study. Non-extractable radioactivity in sediment increased from 1.6 % AR by day zero to 65.6 % at study termination. At the end of the study, radioactivity mineralised to ^{14}C-carbon dioxide amounted to 19.6 % AR while formation of other organic volatile components was negligible (< 0.1 %).

For the Pond system and the UL-phenoxy-label, total radioactivity in water dissipated from 79.7 % by day zero to 1.0 % of AR after 103 days of incubation. Total radioactivity in sediment increased from 18.6 % by day zero to 33.7 % at the end of the study. Non-extractable radioactivity in sediment increased from 2.1 % AR by day zero to 30.4 % at study termination. At the end of the study, radioactivity mineralised to ^{14}C-carbon dioxide amounted to 67.9 % AR while formation of other organic volatile components was negligible (< 0.1 %).

For the Pond system and the UL-chlorophenyl-label, total radioactivity in water dissipated from 77.8 % by day zero to 3.4 % of AR after 103 days of incubation. Total radioactivity in sediment increased from 19.1 % by day zero to 72.9 % at the end of the study. Non-extractable radioactivity in sediment increased from 1.8 % AR by day zero to 65.9 % at study termination. At the end of the study, radioactivity mineralised to ^{14}C-carbon dioxide amounted to 21.5 % AR while formation of other organic volatile components was negligible (< 0.1 %).

Metabolite fenoxaprop-P-acid (AE F088406) was found as the predominant transformation product in the River system for both positions of radiolabel tested amounting to 73.8/84.1 % AR in maximum (phenoxy-label/chlorophenyl-label) in water each by day 1 and to 22.8/27.6 % in the sediment each by day 8. The same metabolite was found in the Pond system amounting to 83.6/85.1 % AR in maximum (phenoxy-label/chlorophenyl-label) each by day 1 in water and 24.9/28.1 % in the sediment each by day 14. Fenoxaprop-P-acid (AE F088406) was further degraded to HOPP-acid (AE F096918) and chlorobenzoxazolone (AE F054014). HOPP-acid (AE F096918) reached maxima of 21.1 % (River) and 9.2 % (Pond) on day 0.17 and then declined to low levels (< 2 %) by day 8. However these maximum values may represent an overestimation as these samples were partitioned which may have led to degradation of the fenoxaprop-P-acid (AE F088406). Chlorobenzoxazolone (AE F054014) reached maxima of 6.4 % (River) and 6.7 % (Pond) on day 0.17 and then declined to low levels (< 2 %) by day 1. In addition, several unidentified metabolites were detected in the water phases which all remained below 9 % of applied radioactivity.

Material and Methods:

Test Material

[UL-phenoxy-^{14}C]-fenoxaprop-P-ethyl (Ph label)

Specific radioactivity:	5.39 MBq/mg
Radiochemical purity:	100 % (HPLC)
Batch No.	199044/A

[UL-chlorophenyl-^{14}C]-fenoxaprop-P-ethyl (ClPh label)

Specific radioactivity: 6.96 MBq/mg
Radiochemical purity: 98.9 % (HPLC)
Batch No. 199026/A

Test System
The study was carried out with two contrasting water/sediment systems collected at two locations in Switzerland. Water and associated sediment of each system were collected from the same area. The systems were "River" and "Pond" thus originating from flowing water (river Rhine) and the standing water of a pond (Fröschweiher pond). Water was collected about 20 cm below the surface while sediments were from top 10 cm. Before set-up of samples, the wet sediment was passed through a 2 mm sieve by use of the associated water.

Table B.8.2.2.3-26 Physico-chemical characteristics of associated sediments

Sediment	River	Pond
Geographic location	Rhine River, Mumpf, AG, Switzerland	Fröschweiher Pond, Möhlin, AG, Switzerland
Latitude and longitude	not reported	not reported
Texture class [USDA]	loamy sand	silt loam
Sand (2000-50 µm) (%)	74.8	14.2
Silt (50-2 µm) (%)	21.6	64.1
Clay (< 2 µm) (%)	3.6	21.7
*p*H (not specified)	7.40	7.18
Organic matter (%)	2.1	5.3
Organic carbon (%)	1.23	3.1
Microbial biomass (mg microbial C/100 g dry weight):		
Initial, post handling	57.4	107.1
Initial, start of incubation	48.2	77.0
Final, end of incubation	105.4	217.5

Table B.8.2.2.3-27 Physico-chemical characteristics of test water

Water	River	Pond
Temperature at collection (°C)	16.9	16.8
*p*H at collection	7.97	7.76
Redox potential at collection (mV)	219	216
Oxygen content at collection (mg/L)	9.26	8.08
Total Organic Carbon at start (TOC, mg/L)	3.15	5.50

Experimental conditions
The tests were performed in individual cylindrical flasks each filled with sieved sediment to a depth of 2 cm. Associated water was added to each test vessel to result in a depth of 7 cm above the sediment zone. The sediment-to-water ratio was about 1:4 (v/v) for the two systems. Each of the flow-through test vessels was attached to traps for volatile components formed, *i.e.* 2 M sodium hydroxide for ^{14}C-carbon dioxide and ethylene glycol for other volatiles. One replicate per sampling interval was prepared for each position of radiolabel and per system.

An initial nominal test concentration of 60 µg a.s./L was chosen to allow for sufficient analytical sensitivity and lower matrix effects.

Each sample was dosed by applying a solution of ^{14}C-fenoxaprop-P-ethyl in acetone dropwise onto the water surface to result in 37 µg test substance applied per test vessel.

Non-sterile, untreated samples were prepared in parallel for each water/sediment system for monitoring of organic carbon content in the water and the microbial biomass in the sediment phase, respectively. One sample per water/sediment system was analyzed at time zero and after 100 or 103 days of incubation.

The water/sediment samples were incubated under flow-through conditions at 20 ± 2 °C for a maximum period of 103 days (River) or 100 days (Pond).

Sampling

For each position of radiolabel single samples were removed for analysis after 0, 0.17, 1, 8, 14, 27, 57 and 103 days of incubation for River systems and after 0, 0.17, 1, 8, 14, 27, 57 and 100 days of incubation for Pond systems.

Analytical procedures
At each sampling interval, the *p*H and dissolved oxygen content were measured in the water phase. In addition, the redox potential was determined in the water phase and the sediment.

Water was removed from the sediment with a pipette followed by extraction of the sediment. Thereafter, the water phase was acidified by addition of 1 M hydrochloric acid. Sediment was extracted exhaustively by shaking two times successively with aqueous acetonitrile (20:80, v/v) at ambient temperature for 30 min. At day 8 and the following sediments were additionally Soxhlet-extracted with aqueous acetonitrile (20:80, v/v) for four hours. Water samples from time zero, 0.17 and 1 were extracted by twice partitioning an aliquot into ethyl acetate followed by quantitation with LSC and HPLC as primary analytical method and TLC of selected samples. Water phases from later time points were concentrated under reduced pressure at about 35 °C. HPLC analysis of the phenoxy label treated samples from 0.17 and 1 day was performed on the concentrated organic phase. HPLC analysis of all other samples was performed on the water phase. Aliquots of ambient and microwave extracts of sediments were combined and concentrated prior to HPLC analysis. Extracted sediment was air-dried prior to quantification of radioactivity *via* combustion and LSC. Volatile radioactivity in traps was determined by LSC. Identity of $^{14}C\text{-}CO_2$ was confirmed by co-precipitation with barium chloride solution.

The radioactivity in liquid samples was directly determined by LSC while extracted sediment was subject to combustion and determination of adsorbed ^{14}C-carbon dioxide by LSC.

Chromatographic investigations were performed by reversed phase HPLC as the primary analytical method using ^{14}C-flow through detection techniques while normal phase TLC/phosphor imaging for ^{14}C-detemination was performed with selected samples as confirmatory method.

Identification of transformation products was carried out by co-elution with authentic reference material.

Results and Discussion:

Findings
Following acclimation of samples and application of the test substance the test conditions were maintained throughout the incubation period.

Measurements of the redox potential in water and sediment and the oxygen content in the water indicated aerobic conditions for both water/sediment systems during incubation.

The *p*H in the water of the two systems remained in narrow range of about 8.1 to 8.4 in the course of incubation. The results of microbial biomass determination showed that biological activity of the test systems was given during the entire incubation period. No decrease of microbial biomass was observed thus no obvious suffering of microbes from lack of nutrients when being held artificially in test flasks and kept separately from the outdoor environment.

Table B.8.2.2.3-28 Measurements of dissolved oxygen, *p*H and redox potential in treated River system (sample A/B)

Sampling interval (day)	---------- Water ----------			Sediment
	Dissolved oxygen (mg/L)	***p*H**	**Redox E_h** (mV)	**Redox E_h** (mV)
0	8.8/8.4	8.40/8.46	194/167	-96/-98
0.17	7.2/8.5	8.05/8.38	130/126	-94/-73
1	8.7/8.3	8.48/8.27	185/218	-75/-91
8	8.0/7.5	8.30/8.21	189/214	-98/-89
14	7.4/7.7	8.12/8.14	155/152	-110/-123
27	8.5/8.7	8.16/8.24	122/120	-76/-96
57	8.5/8.6	8.18/8.24	227/229	-92/-94
103	7.9/8.4	8.06/8.16	196/198	-168/-156

Average	**8.2**	**8.24**	**176**	**-102**
SD	0.5	0.12	38	27

E_h = Redox potential referring to the reference electrode (Ag/AgCl)
SD = standard deviation

Table B.8.2.2.3-29 Measurements of dissolved oxygen, *p*H and redox potential in treated Pond system (sample A/B)

Sampling interval (day)	Water: Dissolved oxygen (mg/L)	Water: *p*H	Water: Redox E_h (mV)	Sediment: Redox E_h (mV)
0	8.5/8.2	8.45/8.53	200/150	-103/-93
0.17	7.3/8.6	8.13/8.43	125/140	-75/-68
1	8.8/8.4	8.32/8.31	171/182	-92/-78
8	8.0/7.0	8.36/8.19	211/211	-98/-91
14	7.0/7.3	8.18/8.24	152/142	-123/-140
27	7.9/7.0	8.27/7.71	136/136	-105/-145
57	8.6/8.5	8.22/8.30	234/231	-100/-98
100	8.5/8.9	8.34/8.37	182/179	-107/-117
Average	**8.0**	**8.27**	**174**	**-102**
SD	0.7	0.18	36	21

E_h = Redox potential referring to the reference electrode (Ag/AgCl)
SD = standard deviation

Data

Table B.8.2.2.3-30 Biotransformation of [UL-phenoxy-^{14}C]-fenoxaprop-P-ethyl (AE F046360) in the River water/sediment system at 20 °C (values shaded in grey indicate exceedance of 5 % AR)

Component/Matrix		Sampling interval (day) 0	0.17[a]	1[a]	8	14	27	57	103
Fenoxaprop-P-ethyl (AE F046360)[b]	Water	77.6	66.9	6.0	-	-	-	-	-
	Sediment	17.1	3.9	0.4	-	-	-	-	-
	Total	**94.7**	**70.7**	**6.4**	**-**	**-**	**-**	**-**	**-**
Fenoxaprop-P-acid (AE F088406)[b]	Water	-	3.8	73.8	55.6	42.0	4.4	-	-
	Sediment	-	3.1	7.6	22.8	21.3	8.8	3.5	2.4
	Total	**-**	**6.9**	**81.4**	**78.4**	**63.3**	**13.2**	**3.5**	**2.4**
HOPP-acid (AE F096918)[b]	Water	-	21.1	9.6	-	0.6	0.7	0.3	0.2
	Sediment	-	-	-	0.3	0.4	-	0.6	0.1
	Total	**-**	**21.1**	**9.6**	**0.3**	**1.0**	**0.7**	**0.9**	**0.3**
Total unidentified[b]	Water	-	-	-	-	2.4	2.2	1.3	0.4
	Sediment	-	-	0.2	0.7	2.0	2.6	1.2	1.3
	Total	**-**	**-**	**0.2**	**0.7**	**4.4**	**4.8**	**2.5**	**1.7**
Total extractable	Water	77.6	91.7	90.8	55.6	45.0	14.4	3.7	2.1
	Sediment	17.1	6.9	8.2	24.9	23.8	11.4	5.3	3.7
	Total	**94.7**	**98.7**	**99.0**	**80.5**	**68.8**	**25.9**	**9.0**	**5.8**
Dissolved CO_2[c]	Water	n.d.	n.d.	n.d.	n.d.	n.d.	4.8	0.7	1.0
Bound residues[d]	Water	n.d.	n.d.	n.d.	n.d.	n.d.	2.3	1.3	0.1
CO_2 incl. other volatiles[e]		n.p.	< 0.1	< 0.1	4.4	10.9	25.6	48.2	56.1
Non-extract. residues		1.9	0.7	1.5	10.0	20.2	43.3	40.3	37.8
Recovery total system[b]		**96.5**	**99.3**	**99.1**	**95.0**	**99.8**	**94.7**	**97.5**	**99.8**

Values given as percentages of applied radioactivity (% AR)
Total system = water + sediment
n.a. = not analysed
n.d. = not detected
n.p. = not performed
(a) Water phase samples considered to result in unreliable residues for fenoxaprop-P-acid (AE F088406) and other metabolites due to sample handling (Crowe, 2018, amendment No.1) - refer to comment section
(b) Corrected by Crowe (2018), amendment No. 1, individual unknown fraction not exceeding 2.2 % in the total system
(c) Data added by the RMS AT
(d) Adsorbed to the water dissolved organic matter, data added by the RMS AT
(e) All values for other volatile radioactivity < 0.1 % AR.

Table B.8.2.2.3-31 Biotransformation of [UL-chlorophenyl-^{14}C]-fenoxaprop-P-ethyl (AE F046360) in the River water/sediment system at 20 °C (values shaded in grey indicate exceedance of 5 % AR)

Component/Matrix		Sampling interval (day) 0	0.17	1	8	14	27	57	103
Fenoxaprop-P-ethyl (AE F046360)	Water	72.2	71.3	-	-	-	-	-	-
	Sediment	20.5	1.9	0.6	-	-	-	-	-
	Total	**92.7**	**73.2**	**0.6**	**-**	**-**	**-**	**-**	**-**
Fenoxaprop-P-acid (AE F088406)	Water	-	16.3	84.1	42.5	29.0	9.3	-	-
	Sediment	-	1.1	10.4	27.6	27.0	13.3	3.0	4.4
	Total	-	**17.4**	**94.5**	**70.0**	**56.1**	**22.6**	**3.0**	**4.4**
Chlorobenzoxazolone (AE F054014)[a]	Water	-	6.4	-	0.7	1.7	0.6	-	0.2
	Sediment	-	-	0.2	1.0	1.0	1.2	1.0	2.1
	Total	**-**	**6.4**	**0.2**	**1.8**	**2.8**	**1.8**	**1.0**	**2.3**
Total unidentified[a]	Water	1.4	-	-	1.3	2.5	4.6	2.3	1.3
	Sediment	0.3	-	0.6	1.2	2.4	2.7	1.6	3.3
	Total	**1.7**	**-**	**0.6**	**2.5**	**4.9**	**7.3**	**3.9**	**4.7**
Total extractable	Water	73.6	94.1	84.1	45.4	33.7	18.2	4.2	4.9
	Sediment	20.8	2.9	11.9	29.8	30.5	17.8	6.7	11.3
	Total	**94.3**	**97.0**	**96.0**	**75.2**	**64.1**	**35.9**	**10.9**	**16.2**
Dissolved CO_2[b]	Water	n.d.	n.d.	n.d.	n.d.	n.d.	1.6	0.9	0.7
Bound residues[c]	Water	n.d.	n.d.	n.d.	n.d.	n.d.	1.2	0.4	0.5
CO_2 incl. other volatiles[d]		n.p.	< 0.1	< 0.1	1.7	1.8	5.8	16.5	19.6
Non-extract. residues		1.6	0.4	5.0	25.7	30.3	56.0	70.1	65.6
Recovery total system		**95.9**	**97.4**	**101.0**	**102.7**	**96.3**	**97.7**	**97.5**	**101.5**

Values given as percentages of applied radioactivity (% AR)
Total system = water + sediment
n.a. = not analysed
n.d. = not detected
n.p. = not performed
(a) Corrected by Crowe (2018), amendment No. 1, individual unknown fraction not exceeding 2.9 % in the total system
(b) Data added by RMS AT
(c) Adsorbed to the water dissolved organic matter, data added by RMS AT
(d) All values for other volatile radioactivity < 0.1 % AR.

Table B.8.2.2.3-32 Biotransformation of [UL-phenoxy-^{14}C]-fenoxaprop-P-ethyl (AE F046360) in the Pond water/sediment system at 20 °C (values shaded in grey indicate exceedance of 5 % AR)

Component/Matrix		Sampling interval (day) 0	0.17[a]	1[a]	8	14	27	57	100
Fenoxaprop-P-ethyl (AE F046360)	Water	79.7	76.2	-	-	-	-	-	-
	Sediment	16.5	2.2	-	-	-	-	-	-
	Total	**96.3**	**78.4**	**-**	**-**	**-**	**-**	**-**	**-**
Fenoxaprop-P-acid (AE F088406)	Water	-	6.2	83.6	62.9	37.3	11.4	-	-
	Sediment	-	3.4	9.2	24.3	24.9	18.3	3.4	2.2
	Total	-	**9.7**	**92.8**	**87.2**	**62.1**	**29.7**	**3.4**	**2.2**
HOPP-acid (AE F096918)[b]	Water	-	9.2	3.4	1.0	1.3	1.8	0.2	-
	Sediment	-	-	-	0.5	0.3	1.0	-	0.3
	Total	-	**9.2**	**3.4**	**1.0**	**1.6**	**2.8**	**0.2**	**0.3**
Total unidentified[b]	Water	-	-	-	-	4.9	8.9	1.3	-
	Sediment	-	-	0.3	1.5	3.2	3.3	3.3	0.9
	Total	**-**	**-**	**0.3**	**1.5**	**8.0**	**12.2**	**4.6**	**0.9**
Total extractable	Water	79.7	91.6	87.0	63.9	43.4	28.1	5.0	1.0
	Sediment	16.5	5.7	9.5	26.3	28.3	22.6	6.7	3.3
	Total	**96.3**	**97.2**	**96.5**	**90.2**	**71.7**	**50.7**	**11.7**	**4.3**
Dissolved CO_2[c]	Water	n.d.	n.d.	n.d.	n.d.	n.d.	2.9	1.7	n.d.
Bound residues[d]	Water	n.d.	n.d.	n.d.	n.d.	n.d.	3.2	1.8	n.d.
CO_2 incl. other volatiles[e]		n.p.	< 0.1	0.1	1.2	10.2	17.9	47.2	67.9
Non-extract. residues		2.1	1.0	2.4	6.3	13.6	25.3	34.6	30.4
Recovery total system		**98.3**	**98.2**	**99.0**	**97.7**	**95.5**	**93.9**	**93.5**	**102.6**

Values given as percentages of applied radioactivity (% AR)
Total system = water + sediment
n.a. = not analysed
n.d. = not detected

n.p. = not performed
(a) Water phase samples considered to result in unreliable residues for fenoxaprop-P-acid (AE F088406) and other metabolites due to sample handling (Crowe, 2018, amendment No.1) - refer to comment section
(b) Corrected by Crowe (2018), amendment No. 1, individual unknown fraction not exceeding 3.3 % in the total system except for M12 (27 DAR, 8.2 % AR)
(c) Data added by the RMS AT
(d) Adsorbed to the water dissolved organic matter, data added by the RMS AT
(e) All values for other volatile radioactivity < 0.1 % AR

Table B.8.2.2.3-33 Biotransformation of [UL-chlorophenyl-^{14}C]-fenoxaprop-P-ethyl (AE F046360) in the Pond water/sediment system at 20 °C (values shaded in grey indicate exceedance of 5 % AR)

Component/Matrix		Sampling interval (day)							
		0	**0.17**	**1**	**8**	**14**	**27**	**57**	**100**
Fenoxaprop-P-ethyl (AE F046360)	Water	76.3	67.8	-	-	-	-	-	-
	Sediment	17.1	2.0	0.2	-	-	-	-	-
	Total	**93.3**	**69.8**	**0.2**	**-**	**-**	**-**	**-**	**-**
Fenoxaprop-P-acid (AE F088406)[(a)]	Water	-	17.6	85.1	42.5	46.2	6.1	-	-
	Sediment	-	3.5	9.7	21.9	28.1	15.8	2.2	0.5
	Total	**-**	**21.1**	**94.8**	**64.4**	**74.3**	**21.9**	**2.2**	**0.5**
Chlorobenzoxazolone (AE F054014)[(a)]	Water	-	6.7	-	0.9	0.9	1.2	-	-
	Sediment	-	-	0.2	0.8	1.0	1.9	0.9	1.1
	Total	**-**	**6.7**	**0.2**	**1.6**	**1.9**	**3.2**	**0.9**	**1.1**
Total unidentified[(a)]	Water	1.6	-	-	2.0	1.7	4.7	2.7	3.0
	Sediment	0.3	-	0.7	1.7	1.7	4.7	3.6	4.4
	Total	**1.9**	**-**	**0.7**	**3.8**	**3.4**	**9.5**	**6.3**	**7.3**
Total extractable	Water	77.8	92.1	85.1	45.4	49.5	15.2	4.2	3.4
	Sediment	17.3	5.5	10.9	24.3	30.7	22.4	6.7	7.0
	Total	**95.2**	**97.6**	**96.0**	**69.8**	**80.2**	**37.6**	**10.9**	**10.4**
Dissolved CO_2[(b)]	Water	n.d.	n.d.	n.d.	n.d.	n.d.	1.6	0.8	0.2
Bound residues[(c)]	Water	n.d.	n.d.	n.d.	n.d.	n.d.	0.9	0.6	0.1
CO_2 incl. other volatiles[(d)]		n.p.	< 0.1	< 0.1	1.3	1.3	5.4	15.9	21.5
Non-extract. residues		1.8	0.9	5.0	25.0	18.3	52.6	72.2	65.9
Recovery total system		**97.0**	**98.6**	**101.0**	**96.1**	**99.9**	**95.6**	**99.0**	**97.8**

Values given as percentages of applied radioactivity (% AR)
Total system = water + sediment
n.a. = not analysed
n.d. = not detected
n.p. = not performed
(a) Corrected by Crowe (2018), amendment No. 1, individual unknown fraction not exceeding 3.5 % in the total system
(b) Data added by the RMS AT
(c) Adsorbed to the water dissolved organic matter, data added by the RMS AT
(d) All values for other volatile radioactivity < 0.1 % AR

Mass balance

For the River system the total recovery of radioactivity in the individual test vessels ranged from 94.7 % of AR to 99.8 % for the phenoxy-label and from 95.9 % to 102.7 % for the chlorophenyl-label. The recovery in individual test vessels of the Pond system ranged from 93.5 % to 102.6 % AR for the phenoxy-label and from 95.6 % to 101.0 % for the chlorophenyl-label. The balances of radioactivity were therefore in an acceptable range for all sampling intervals and all positions of radiolabel indicating no significant losses of radioactivity during incubation and processing of samples.

Distribution of residues in water and sediment

In River systems, total ^{14}C-residues in the water phase decreased from 77.6 % (Ph label) and 72.2 % AR (ClPh label) at day zero to 2.1 % and 4.9 % at the last sampling interval, day 103. Total extractable ^{14}C-residues in the sediment were 17.1 % (Ph label) and 20.8 % (ClPh label) by day zero to decrease to 3.7 % AR and 11.3 % after 103 days of incubation. Non-extractable radioactivity in the sediment increased from 1.9 % (Ph label) and 1.6 % (ClPh label) at day zero to 37.8 % AR and 65.6 % at study termination. At the end of the study, radioactivity found mineralised to CO_2 amounted to 56.1 % (Ph label) and 19.6 % (ClPh label).

In Pond systems, total ^{14}C-residues in the water phase decreased from 79.7 % (Ph label) and 77.8 % AR (ClPh label) at day zero to 1.0 % and 3.4 % at the last sampling interval, day 100. Total extractable ^{14}C-residues in the sediment were 16.5 % (Ph label) and 17.3 % (ClPh label) by day zero and 3.3 % AR and 7.0 % after 100 days of

incubation. Non-extractable radioactivity in the sediment increased from 2.1 % (Ph label) and 1.8 % (ClPh label) at day zero to 30.4 % AR and 65.9 % at study termination. At the end of the study, radioactivity found mineralised to CO_2 amounted to 67.9 % (Ph label) and 21.5 % (ClPh label).

The decline of total radioactivity from the water phase was paralleled by a fast increase in the sediment with the decrease from the water phase being comparable for the two water/sediment test systems.

Metabolite fenoxaprop-P-acid (AE F088406) was formed as a predominant compound for both positions of radiolabel applied reaching in the River total system maximum values of 81.4 % (Ph label) and 94.5 % (ClPh label) each after one day of incubation. Formation of fenoxaprop-P-acid (AE F088406) was also significant in the Pond total system at maximum values of 92.8 % (Ph label) and 94.8 % (ClPh label) each at day one after application.

Fenoxaprop-P-acid (AE F088406) was degraded to form HOPP-acid (AE F096918) and chlorobenzoxazolone (AE F054014). In samples treated with phenoxy labelled fenoxaprop-P-ethyl (AE F046360), HOPP-acid (AE F096918) was detected at maximum amounts of 21.1 % and 9.2 % of the applied radioactivity in the River and Pond systems after four hours and then declined to less than 4 % by day 57. The high levels observed at 4 hours and 1 day were considered to be due to degradation of fenoxaprop-P-acid (AE F088406) during processing of the water samples which resulted in unreliable values. In samples treated with chlorophenyl labelled fenoxaprop-P-ethyl (AE F046360), chlorobenzoxazolone (AE F054014) was detected at maximum amounts of 6 - 7 % after 4 hours and then declined to lower levels ≤ 3.2 %) throughout the remainder of the incubation. In addition, numerous minor unidentified degradation products were detected, none individually exceeding 9 % of applied radioactivity in either system.

Volatile radioactivity

The formation ^{14}C-carbon dioxide was dependent on position of radiolabel to start by days one to 8 for both water/sediment systems investigated. Levels of ^{14}C-carbon dioxide reached their maximum of 56.1 % AR (Ph label) and 19.6 % (ClPh label) after 103 days in the River system. For the Pond system the maximum values were 67.9 % AR (Ph label) and 21.5 % (ClPh label) after 103 days.

Formation of other volatile components was insignificant by accounting for less than 0.1 % AR at any sampling interval in the course of the study.

Fenoxaprop-P-ethyl (AE F046360) and its residues were therefore subject to extensive transformation in water/sediment systems till mineralisation.

Transformation of test substance

Fenoxaprop-P-ethyl (AE F046360) was transformed by a microbial-induced hydrolytic step (ester hydrolysis) to its metabolite fenoxaprop-P-acid (AE F088406) in both water/sediment systems tested. Formation of fenoxaprop-P-acid (AE F088406) in total the River system was rapid and predominant to result in maximum values of 81.4 % AR (Ph label) and 94.5 % (ClPh label) each after one day and in total the Pond system in 92.8 % AR (Ph label) and 94.8 % (ClPh label) each after one day.

Fenoxaprop-P-acid (AE F088406) was further degraded to form HOPP-acid (AE F096918) and chlorobenzoxazolone (AE F054014). HOPP-acid (AE F096918) was detected at maximum amounts of 21.1 % and 9.2 % of the applied radioactivity in the River and Pond systems after four hours and then declined to less than 4 % by day 57. The high levels observed at 4 hours and 1 day were considered to be due to degradation of fenoxaprop-P-acid (AE F088406) during processing of the water samples which resulted in unreliable values. Chlorobenzoxazolone (AE F054014) was detected at maximum amounts of 6 - 7 % after 4 hours and then declined to lower levels ≤ 3.2 %) throughout the remainder of the incubation. In addition, numerous minor unidentified degradation products were detected, none individually exceeding 9 % of applied radioactivity in either system.

Mechanisms of dissipation from the water body to the sediment as well as degradation therefore contributed to the elimination of the parent substance from the total systems to result in the formation of NER and ^{14}C-carbon dioxide as terminal products of biotransformation.

Table B.8.2.2.3-34 Metabolites of fenoxaprop-P-ethyl (AE F046360) formed under conditions of water/sediment testing; maximum values of occurrence

Component	Label	Maximum occurrence (% AR)			System
		Water	Sediment	Total[(a)]	
Fenoxaprop-P-acid (AE F088406)	Phenoxy	73.8 (d 1)	22.8 (d 8)	**81.4 (d 1)**	River
	Chlorophenyl	84.1 (d 1)	27.6 (d 8)	**94.5 (d 1)**	River
	Phenoxy	83.6 (d 1)	24.9 (d 14)	**92.8 (d 1)**	Pond
	Chlorophenyl	85.1 (d 1)	28.1 (d 14)	**94.8 (d 1)**	Pond

(a) Not necessarily the sum of maximum fractions in water and sediment at the same sampling interval due to possibility of maximum occurrence at different sampling intervals

Conclusion:

Once applied to water surfaces fenoxaprop-P-ethyl (AE F046360) was rapidly eliminated from the water phase *via* sorption processes to the sediment. The processes were paralleled by a fast microbial induced hydrolysis to result in fenoxaprop-P-acid (AE F088406) as a predominant metabolite in both water/sediment systems (maxima at 87.3 % in water (Ph label, day 1, River system), 28.1 % in sediment (ClPh label, day 14, Pond system) and at 94.8 % in total systems (labels 1 and 2, day 1, each system - River and Pond).

Fenoxaprop residues were further microbially converted *via* formation of HOPP-acid (AE F096918), chlorobenzoxazolone (AE F054014) and numerous minor metabolites to finally result in non-extractable residues (NER) and ^{14}C-carbon dioxide as terminal products of metabolic transformation under conditions of water/sediment testing.

Sorption of fenoxaprop-P-ethyl (AE F046360) and fenoxaprop-P-acid (AE F088406) to the sediment proceeded rapidly in the two water/sediment systems.

Fenoxaprop-P-ethyl (AE F046360) and its residues are thus expected to degrade fast in aquatic systems of the environment.

Comments RMS AT:

- The study follows OECD guideline 308 and is considered reliable.
- Metabolite assignment in the original report (Mamouni, 2008) was wrong. This was corrected in the amendment by Crowe (2018).
- The RMS AT agrees with the applicant that sample treatment of the 0.17 and 1 DAT water phase samples applied in case of the phenoxy label may have led to further degradation of fenoxaprop-P-acid (AE F088406) during sample handling. Therefore, residues of fenoxaprop-P-acid (AE F088406) and HOPP-acid (AE F096918) observed in these samples are considered not fully reliable and are omitted from kinetic analysis of fenoxaprop-P-acid (AE F088406). This also implies that residues observed for HOPP-acid in this study are on overall not considered suitable for kinetic evaluation.
- It may be noted that metabolite fraction 'M12' exceeds 5 % AR in the total system of the Pond system (phenoxy label) in one sampling point (27 DAT), albeit not triggering further action in relation to regulation (EU) No 283/2013.
- Residues of fenoxaprop-P-ethyl (AE F046360) and its metabolites were kinetically re-assessed in Herrmann et al. (2016).

Reference:	**Fenoxaprop-P-ethyl and metabolites: Kinetic evaluation of the aerobic aquatic metabolism in water/ sediment systems under laboratory conditions**
Author(s), year:	Herrmann, M., Wiedemann, G., Boiselle, N. (2016)
Report/Doc. Number:	EnSa-15-0387, M-555143-01-1
Guideline(s):	FOCUS (2006): Guidance Document on Estimating Trigger 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 (2014): Generic guidance for Estimating Trigger and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration, Version 1.1, 18th of December, 2014
GLP:	Yes
Validity:	Partly (refer to comment section)
Status:	**New submission**

Executive Summary:

For fenoxaprop-P-ethyl (AE F046360) the kinetics of degradation and dissipation in water/sediment systems was evaluated for twelve data sets in total originating from four studies (Tarara, 2001; Fitzmaurice, 2004; Xu, 2012; and Mamouni, 2008). Each study was performed with two differing water/sediment systems. Following application of the active substance in the form of ^{14}C-labelled test item (UL-chlorophenyl- or UL-phenoxy-label) the systems were incubated at 20 °C. The kinetic evaluation followed actual FOCUS guidance.

Degradation in total systems
Degradation rates in total sediment/water systems were derived for use as modelling endpoints in aquatic exposure assessments.

Analysis was performed at Level I for total systems with results summarised for the active substance and metabolites fenoxaprop-P-acid (AE F088406) and HOPP-acid (AE F096918) in the table below. No acceptable parameters were derived at Level II.

Following the flowcharts set by FOCUS the use of the SFO or DFOP kinetic models resulted in acceptable fits to measured data for the active substance. For metabolite fenoxaprop-P-acid the evaluation resulted in acceptable fits as described by the SFO model. Finally, acceptable fits were derived for metabolite HOPP-acid from use of SFO and the FOMC kinetic model.

The evaluation resulted in geometric mean values in total systems of the *DegT50* of 0.164 days for fenoxaprop-P-ethyl, 18.0 days for fenoxaprop-P-acid and 62.1 days for HOPP-acid (AE F096918) for use as modelling endpoints.

Table B.8.2.2.3-35 Total system *DegT50* values for fenoxaprop-P-ethyl (AE F046360), fenoxaprop-P-acid (AE F088406) and HOPP-acid (AE F096918) according to FOCUS Level I

Compound	Total system *DegT50* (geomean, days)
Fenoxaprop-P-ethyl (AE F046360)	0.164
Fenoxaprop-P-acid (AE F088406)	18.0
HOPP-acid (AE F096918)	62.1

Dissipation from water phase
Dissipation rates from water were derived for use as modelling endpoints in aquatic exposure assessments.

Analysis was performed at Level I for water phases with results summarised for the active substance and metabolites fenoxaprop-P-acid (AE F088406) and HOPP-acid (AE F096918) in the table below. No acceptable parameters were derived at Level II.

Following the flowcharts set by FOCUS the use of the SFO or FOMC kinetic models resulted in acceptable fits to measured data for the active substance. For metabolite fenoxaprop-P-acid the evaluation resulted in acceptable fits as described by the SFO and DFOP model. Finally, acceptable fits were derived for metabolite HOPP-acid from use of SFO and the FOMC kinetic model.

The evaluation resulted in geometric mean values for the dissipation from water (*DisT50*) of 0.164 days for fenoxaprop-P-ethyl, 11.6 days for fenoxaprop-P-acid and 22.6 days for HOPP-acid (AE F096918) for use as modelling endpoints.

Table B.8.2.2.3-36 Values of the *DisT50* from water for fenoxaprop-P-ethyl (AE F046360), fenoxaprop-P-acid (AE F088406) and HOPP-acid (AE F096918) according to FOCUS Level I

Compound	Water phase *DisT50* (geomean, days)
Fenoxaprop-P-ethyl (AE F046360)	0.164
Fenoxaprop-P-acid (AE F088406)	11.6
HOPP-acid (AE F096918)	22.6

Dissipation from sediment phase

Dissipation rates from sediment were derived for use as modelling endpoints in aquatic exposure assessments. Analysis was performed at Level I for sediment phases with results summarised for the active substance and metabolites fenoxaprop-P-acid (AE F088406) and HOPP-acid (AE F096918) in the table below. No acceptable parameters were derived at Level II.

Following the flowcharts set by FOCUS the use of the SFO kinetic model resulted in acceptable fits to measured data for the active substance and for metabolite fenoxaprop-P-acid. Finally, no acceptable fits were derived for metabolite HOPP-acid from use of any of the kinetic models available.

The evaluation resulted in geometric mean values for the dissipation from sediment (*DisT50*) of 52.8 days for fenoxaprop-P-ethyl, 40.7 days for fenoxaprop-P-acid and 1000 days for HOPP-acid (AE F096918) for use as modelling endpoints.

Table B.8.2.2.3-37 Values of the *DisT50* from sediment for fenoxaprop-P-ethyl (AE F046360), fenoxaprop-P-acid (AE F088406) and HOPP-acid (AE F096918) according to FOCUS Level I

Compound	Sediment *DisT50* (geomean, days)
Fenoxaprop-P-ethyl (AE F046360)	52.8
Fenoxaprop-P-acid (AE F088406)	40.7
HOPP-acid (AE F096918)	1000

Material and Methods:

The kinetic evaluation was based on data of four water/sediment studies (Tarara, 2001; Fitzmaurice, 2004; Xu, 2012; and Mamouni, 2008) each conducted with two different water/sediment systems. UL-Chlorophenyl-^{14}C-fenoxaprop-P-ethyl was applied to six water/sediment systems and their associated water in total. UL-phenoxy-^{14}C-labeled active substance was applied to the same total number of water/sediment systems. The incubation was performed at 20 °C in the dark for a maximum period of 199 days (UL-chlorophenyl-label) or 118 days (UL-phenoxy-label).

Data pre-processing

Generally, replicates were taken into account separately. The data were checked for consistency and clear outliers. Data for non-extractable residues (NER) and CO_2 were not fitted within the evaluation (open system).

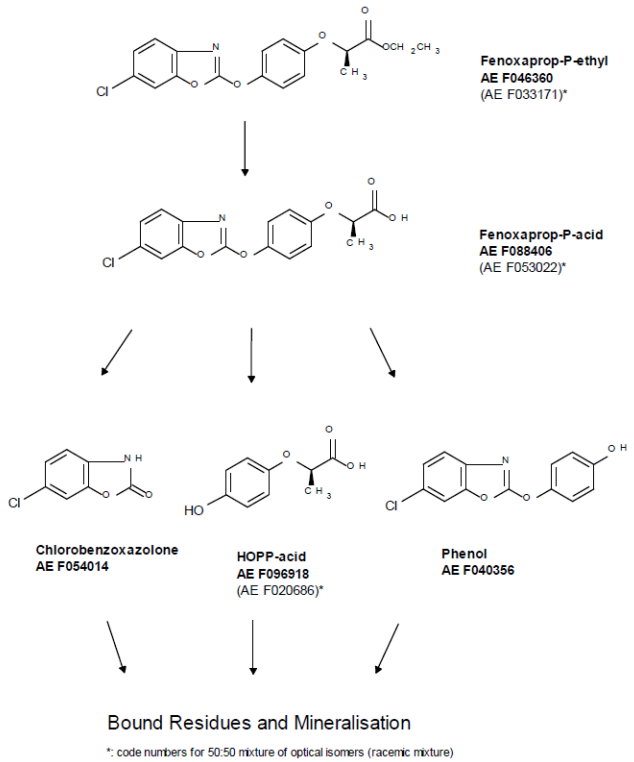
For the residues in the water the following procedure was applied:

- For data processing of day zero samples, radioactivity assigned to metabolites, non-extractable residues (NER) and CO_2 was added to the parent compound and thus metabolite concentrations were set to 0 %. Parent compound was attributed to the water phase only thus resulting in a value of zero for the sediment phase, since the test substance was applied to the water phase.
- Residue values below the limit of detection (LOD = 0.1 % of AR) were set to 0.5 times the LOD or NA for the first non-detect at the end of the curve. The curve could be cut at this time point in case of no later detects.

Kinetic models

The inferring of kinetic degradation parameters followed the proposed metabolic pathway as given in the figure below.

Figure B.8.2.2.3-1: Degradation scheme applied for kinetic analysis.



Following the recommended procedure for determining modelling endpoints [FOCUS, 2006, 2011], all datasets were evaluated using SFO kinetics with free optimisation of parameters, along with FOMC, DFOP and HS kinetics where appropriate.

Each compound was represented by one compartment as the total of measured occurrences in water and sediment with no values associated with a sink compartment. Between compartments transformation reactions were assumed to proceed only one-way. The initial amount of the parent compound was free fitted and the initial amount for metabolites was fixed to a value of zero. All data were weighted equally thus corresponding to an absolute error model.

At least four kinetic models consisting of single first-order (SFO), first-order multiple-compartment (FOMC, Gustafson-Holden), double first-order in parallel (DFOP), and the hockey-stick (HS) model were available, in principle, according to the set of models proposed by FOCUS.

While best-fits should be taken to derive trigger or persistence endpoints SFO should be used to derive modelling input parameters if an acceptable fit can be obtained.

Before a use of bi-phasic kinetic models FOMC, DFOP and HS the following major cases were taken into account:

1. A check whether a degradation or dissipation to 10 % of the initial amount M_0 was reached within experimental period, then the estimation of the *DT50* could be simplified according to the relation $DT50 = DT90/(\ln(10)/\ln(2))$. By this method the equivalent SFO-curve meets the bi-phasic curve at the time $DT90_{\text{bi-phasic}}$ and consequently the residue values at earlier times are over-predicted.
2. In case a value of 10 % for M_0 was not reached within the runtime of the study, however, FOMC should not be used to derive modelling endpoints.
3. In case a value of 10 % for M_0 was not reached within the runtime of the study, the *DT50* could be derived for DFOP and HS models from the slower part of the bi-phasic curve using the relation $DT50 = \ln(2)/k_2$.

The kinetic evaluations were performed according to the respective decision flowcharts for the determination modelling endpoints for parent (Level P-1) and metabolites and to result in dissipation kinetics in water and sediment. Evaluations according to Level II were performed, however, did not result in statistically acceptable fits. Anyway, for lower-tier calculations or the comparison with persistence triggers a Level I evaluation of the dissipation is mostly regarded as appropriate.

Statistical evaluation

The identification of the most appropriate kinetic model for the description of experimental data according to FOCUS is mainly based on the three criteria of visual assessment of fits of calculated transformation curves to experimental data, the value of error of Chi-square (χ^2) test and a single-sided significance t-test.

The choice of the appropriate kinetic model was primarily based on visual assessment of the fit and the χ^2 error.

Within the current evaluation, single first-order (SFO) kinetics had been tested first, since SFO is being used as the simplest kinetic model almost exclusively in environmental exposure models. In case the SFO fit should not be visually acceptable or in case of a significant exceedance of value for χ^2-error of 15 %, bi-phasic models were tested. Finally the model was chosen which was visually acceptable and provided a significantly better fit in terms of the χ^2-error.

The approach avoided the use of over-parameterised models simply and only being chosen on the basis of a marginally better fit. Finally it should be noted that a value of χ^2-error below 15 % should only be considered as guidance and not as an absolute cut-off criterion. This is true, in particular, for the modelling of metabolite data with errors for χ^2 being higher, but with fits still representing a reasonable description of their formation and degradation behaviour.

The kinetic evaluations and the statistical calculations were conducted with KinGUI (v2.0) using iteratively re-weighted least-squares (IRLS) optimisation.

Results and Discussion:

The kinetic evaluation of water-sediment data was performed according to FOCUS Level I and the flowcharts given to result in degradation kinetics in total systems and in dissipation kinetics in water and sediment. Evaluations according to Level II were performed, however, did not result in statistically acceptable parameters.

In case bi-phasic kinetic models such as FOMC or DFOP resulted in an improvement, a conservative approach was taken by was back-calculation from the slow phase of the corresponding kinetic model to derive the corresponding *DegT50* or *DisT50*.

Degradation of the active substance in total systems

Table B.8.2.2.3-38 Fenoxaprop-P-ethyl (AE F046360): Values of the *DegT50* in total system according to FOCUS Level I

Sediment system	Label position[(a)]	*DegT50* (days)	χ^2 error (%)	t-test (p)	VA[(b)]	Kinetic model
Clayton Pond (Study 1)	1	0.172	8.14	< 0.01	+	SFO
Roding River (Study 1)	1	0.382	3.40	< 0.01	O	SFO
Rhine River (Study 2)	2	0.218[(c)]	4.36	k_1 = 0.09, k_2 = 0.04	++	DFOP
Nidda River (Study 2)	2	0.162[(c)]	5.09	k_1 < 0.01, k_2 < 0.01	++	DFOP
Goose River (Study 3)	2	0.110	2.77	< 0.01	+	SFO
Goose River (Study 3)	1	0.106	3.02	< 0.01	+	SFO
Lawrence Pond (Study 3)	2	0.085[(c)]	7.97	k_1 < 0.01, k_2 < 0.01	+	DFOP
Lawrence Pond (Study 3)	1	0.069	4.87	< 0.01	+	SFO
Geometric mean		**0.164**				

Study 1: Fitzmaurice, 2004; Study 2: Tarara, 2000; Study 3: Xu, 2012
(a) Label position: 1 = UL-phenoxy-^{14}C, 2 = chlorophenyl-^{14}C
(b) VA: Visual assessment: + = good, o = acceptable, - = inacceptable
(c) Back-calculated by dividing *DT90*-value from DFOP fit by 3.32

Degradation of metabolites in total systems

Table B.8.2.2.3-39 Fenoxaprop-P-acid (AE F088406): Values of the *DegT50* in total system according to FOCUS Level I

Sediment system	Label position[(a)]	*DegT50* (days)	χ^2 error (%)	t-test (p)	VA[(b)]	Kinetic model
Clayton Pond (Study 1)	1	39.6[(c)]	12.39	< 0.01	+	SFO
Roding River (Study 1)	1	41.9[(c)]	14.75	< 0.01	+	SFO
Rhine River (Study 2)	2	13.5[(d)]	8.59	< 0.01	O	SFO
Nidda River (Study 2)	2	7.65[(d)]	11.38	< 0.01	+	SFO
Goose River (Study 3)	2	17.2[(e)]	4.05	< 0.01	++	SFO
Goose River (Study 3)	1	17.4[(e)]	2.84	< 0.01	+	SFO
Lawrence Pond (Study 3)	2	17.9[(d)]	7.14	< 0.01	O	SFO
Lawrence Pond (Study 3)	1	15.3[(e)]	8.25	< 0.01	O	SFO
Rhine River (Study 4)	2	14.1[(f)]	6.75	< 0.01	+	SFO
Rhine River (Study 4)	1	13.8[(f)]	15.57	< 0.01	+	SFO
Fröschweiher Pond (Study 4)	2	15.8[(f)]	17.74	< 0.01	O	SFO
Fröschweiher Pond (Study 4)	1	16.9[(f)]	11.69	< 0.01	+	SFO
Geometric mean		**18.0**				

Study 1: Fitzmaurice, 2004; Study 2: Tarara, 2000; Study 3: Xu, 2012; Study 4: Mamouni, 2008
(a) Label position: 1 = UL-phenoxy-^{14}C, 2 = chlorophenyl-^{14}C
(b) VA: Visual assessment: + = good, o = acceptable, - = inacceptable
(c) Combined all SFO fit with active substance and metabolite HOPP-acid (AE F096918)
(d) Combined DFOP fit with active substance and SFO fit for fenoxaprop-P-acid (AE F088406)
(e) Combined SFO fit with active substance
(f) Decline fit

Table B.8.2.2.3-40 HOPP-acid (AE F096918): Values of the *DegT50* in total system according to FOCUS Level I

Sediment system	Label position[(a)]	*DegT50* (days)	χ^2 (%)	t-test (p)	VA[(b)]	Kinetic model
Clayton Pond (Study 1)	1	9.82	2.80	0.02	++	SFO
Roding River (Study 1)	1	393[(c)]	6.54	α = 0.41 β = 0.47	+	FOMC
Geometric mean		**62.1**				

Study 1: Fitzmaurice, 2004
(a) Label position: 1 = UL-phenoxy-^{14}C, 2 = chlorophenyl-^{14}C
(b) VA: Visual assessment: + = good, o = acceptable, - = inacceptable
(c) Decline fit from maximum, *DT50* back-calculated by dividing *DT90* by 3.32

Dissipation of the active substance from water phase

Table B.8.2.2.3-41 Fenoxaprop-P-ethyl (AE F046360): Values of the *DisT50* from water according to FOCUS Level I

Sediment system	Label position[(a)]	*DT50* (days)	χ^2 error (%)	t-test (p)	VA[(b)]	Kinetic model
Clayton Pond (Study 1)	1	0.172	8.14	< 0.01	+	SFO
Roding River (Study 1)	1	0.382	3.40	< 0.01	O	SFO
Rhine River (Study 2)	2	0.113	13.99	< 0.01	+	SFO
Nidda River (Study 2)	2	0.167**	11.15	α = 0.02 β = 0.12	O	FOMC
Goose River (Study 3)	2	0.059	5.37	< 0.01	+	SFO
Goose River (Study 3)	1	0.057	11.12	< 0.01	+	SFO
Lawrence Pond (Study 3)	2	0.069**	7.72	α < 0.01 β = 0.03	+	FOMC
Lawrence Pond (Study 3)	1	0.060	7.61	< 0.01	O	SFO
Geometric mean		**0.164**				

Study 1: Fitzmaurice, 2004; Study 2: Tarara, 2000; Study 3: Xu, 2012
(a) Label position: 1 = UL-phenoxy-^{14}C, 2 = chlorophenyl-^{14}C
(b) VA: Visual assessment: + = good, o = acceptable, - = inacceptable
(c) Back-calculated by dividing DT_{90} value from FOMC fit by 3.32

Dissipation of metabolites from water phase

Table B.8.2.2.3-42 Fenoxaprop-P-acid (AE F088406): Values of the *DisT50* from water according to FOCUS Level I

Sediment system	Label position[(a)]	*DT50* (days)	χ^2 error (%)	t-test (p)	VA[(b)]	Kinetic model
Clayton Pond (Study 1)	1	33.9	9.33	< 0.01	+	SFO
Roding River (Study 1)	1	40.5	9.10	< 0.01	+	SFO
Rhine River (Study 2)	2	10.7	7.09	< 0.01	+	SFO
Nidda River (Study 2)	2	4.31	9.06	< 0.01	O	SFO
Goose River (Study 3)	2	7.17[(c)]	0.44	k_1 < 0.01, k_2 < 0.01	++	DFOP
Goose River (Study 3)	1	6.67	7.02	< 0.01	++	SFO
Lawrence Pond (Study 3)	2	8.41	6.96	< 0.01	+	SFO
Lawrence Pond (Study 3)	1	8.32	7.07	< 0.01	+	SFO
Rhine River (Study 4)	2	7.95	4.02	< 0.01	++	SFO
Rhine River (Study 4)	1	9.71	11.37	< 0.01	+	SFO
Fröschweiher Pond (Study 4)	2	9.79	15.49	< 0.01	+	SFO
Fröschweiher Pond (Study 4)	1	11.0	7.98	< 0.01	+	SFO
Geometric mean		**11.6**				

Study 1: Fitzmaurice, 2004; Study 2: Tarara, 2000; Study 3: Xu, 2012; Study 4: Mamouni, 2008
(a) Label position: 1 = UL-phenoxy-^{14}C, 2 = chlorophenyl-^{14}C
(b) VA: Visual assessment: + = good, o = acceptable, - = inacceptable
(c) Back-calculated by dividing DT_{90} value from DFOP fit by 3.32

Table B.8.2.2.3-43 HOPP-acid (AE F096918): Values of the *DisT50* from water according to FOCUS Level I

Sediment system	Label position[(a)]	*DT50* (days)	χ^2 error (%)	t-test (p)	VA[(b)]	Kinetic model
Clayton Pond (Study 1)	1	9.90	3.52	0.02	+	SFO
Roding River (Study 1)	1	51.7[(c)]	3.25	α = 0.34 β = 0.48	+	FOMC
Geometric mean		**22.6**				

Study 1: Fitzmaurice, 2004
(a) Label position: 1 = UL-phenoxy-^{14}C, 2 = chlorophenyl-^{14}C
(b) VA: Visual assessment: + = good, o = acceptable, - = inacceptable
(c) Decline fit from maximum, DT_{50} back-calculated by dividing DT_{90} by 3.32

Dissipation of the active substance from sediment

Table B.8.2.2.3-44 Fenoxaprop-P-ethyl (AE F046360): Values of the *DisT50* from sediment according to FOCUS Level I

Sediment system	Label position[(a)]	*DT50* (days)	χ^2 error (%)	t-test (p)	VA[(b)]	Kinetic model
Clayton Pond (Study 1)	1	1000	n.a.	n.a.	n.a.	n.a.
Roding River (Study 1)	1	1000	n.a.	n.a.	n.a.	n.a.
Rhine River (Study 2)	2	1000	n.a.	n.a.	n.a.	n.a.
Nidda River (Study 2)	2	0.268	8.90	0.07	+	SFO[(c)]
Goose River (Study 3)	2	0.196	9.55	< 0.01	+	SFO
Goose River (Study 3)	1	0.126	13.28	< 0.01	+	SFO
Lawrence Pond (Study 3)	2	1000	n.a.	n.a.	n.a.	n.a.
Lawrence Pond (Study 3)	1	0.050	12.31	< 0.01	O	SFO
Geometric mean		**52.8**				

Study 1: Fitzmaurice, 2004; Study 2: Tarara, 2000; Study 3: Xu, 2012
(a) Label position: 1 = UL-phenoxy-^{14}C, 2 = chlorophenyl-^{14}C
(b) VA: Visual assessment: + = good, o = acceptable, - = inacceptable; n.a. = not applicable
(c) From modified SFO by fixing M0

Dissipation of metabolites from sediment

Table B.8.2.2.3-45 Fenoxaprop-P-acid (AE F088406): Values of the *DisT50* from the sediment according to FOCUS Level I

Sediment system	Label position[(a)]	*DT50* (days)	χ^2 error (%)	t-test (p)	VA[(b)]	Kinetic model
Clayton Pond (Study 1)	1	1000	n.a.	n.a.	n.a.	n.a.
Roding River (Study 1)	1	1000	n.a.	n.a.	n.a.	n.a.
Rhine River (Study 2)	2	16.8	16.13	< 0.01	+	SFO
Nidda River (Study 2)	2	8.70	10.53	< 0.01	++	SFO
Goose River (Study 3)	2	19.7	6.22	< 0.01	O	SFO
Goose River (Study 3)	1	19.9	3.37	< 0.01	++	SFO
Lawrence Pond (Study 3)	2	9.88	1.04	< 0.01	+	SFO
Lawrence Pond (Study 3)	1	7.65	4.00	< 0.01	+	SFO
Rhine River (Study 4)	2	18.7	13.52	< 0.01	+	SFO
Rhine River (Study 4)	1	16.7	12.24	< 0.01	+	SFO
Fröschweiher Pond (Study 4)	2	14.0	5.27	< 0.01	+	SFO
Fröschweiher Pond (Study 4)	1	19.6	11.00	< 0.01	+	SFO
Geometric mean		**40.7**				

Study 1: Fitzmaurice, 2004; Study 2: Tarara, 2000; Study 3: Xu, 2012; Study 4: Mamouni, 2008
(a) Label position: 1 = UL-phenoxy-^{14}C, 2 = chlorophenyl-^{14}C
(b) VA: Visual assessment: + = good, o = acceptable, - = inacceptable; n.a. = not applicable

Table B.8.2.2.3-46 <u>HOPP-acid (AE F096918)</u>: Values of the *DisT50* from the sediment according to FOCUS Level I

Sediment system	Label position[(a)]	*DT50* (days)	χ^2 error (%)	t-test (p)	VA[(b)]	Kinetic model
Clayton Pond (Study 1)	1	1000	n.a.	n.a.	n.a.	n.a.
Roding River (Study 1)	1	1000	n.a.	n.a.	n.a.	n.a.
Geometric mean		**1000**				

Study 1: Fitzmaurice, 2004
(a) Label position: 1 = UL-phenoxy-^{14}C, 2 = chlorophenyl-^{14}C
(b) VA: Visual assessment: + = good, o = acceptable, - = inacceptable; n.a. = not applicable

<u>Conclusion:</u>

Kinetic evaluation of degradation in total systems as modelling endpoint
The evaluation resulted in geometric mean values in total systems of the *DegT50* of 0.164 days for fenoxaprop-P-ethyl, 18.0 days for fenoxaprop-P-acid and 62.1 days for HOPP-acid (AE F096918) for use as modelling endpoints.

Kinetic evaluation of dissipation from water phase as modelling endpoint
The evaluation resulted in geometric mean values for the dissipation from water (*DisT50*) of 0.164 days for fenoxaprop-P-ethyl, 11.6 days for fenoxaprop-P-acid and 22.6 days for HOPP-acid (AE F096918) for use as modelling endpoints.

Kinetic evaluation of dissipation from the sediment as modelling endpoint
The evaluation resulted in geometric mean values for the dissipation from sediment (*DisT50*) of 52.8 days for fenoxaprop-P-ethyl, 40.7 days for fenoxaprop-P-acid and 1000 days for HOPP-acid (AE F096918) for use as modelling endpoints.

The results were considered for use as input parameters for modelling in environmental risk assessments.

<u>Comments RMS AT:</u>

- In view of extremely fast degradation of fenoxaprop-P-ethyl (AE F046360) in the total system, the RMS AT considers applying biphasic kinetics (FOMC, DFOP or HS) in case of fenoxaprop-P-ethyl (AE F046360) overly complex and proposes to stay with SFO kinetics for both, trigger and modelling endpoints, in the water phase as well as in the total system. As demonstrated in the tables and figures below, SFO gives sufficiently reliable fits for fenoxaprop-P-ethyl (AE F046360) even if the χ^2 error is above 15 % in rare cases.

- In general, pathway fits ($P_{SFO} \rightarrow M_{SFO}$) linking fenoxaprop-P-acid (AE F0880406) to fenoxaprop-P-

ethyl (AE F046360) are considered reliable at all. As no reliable fit could be obtained for fenoxaprop-P-ethyl (AE F046360) in Mamouni (2008) owing to insufficient number of samples, decline fits for fenoxaprop-P-acid (AE F088406) are considered acceptable in this study as well.

- Based on pathway fitting results from residues observed in Xu (2012), both chlorobenzoxazolone (AE F054014) as well as the phenol metabolite (AE F040356) can be considered stable in the total system (default *DegT50* of 1000 days to be used in the exposure modelling).

- The applicant assessed different labels within Xu (2012) and Mamouni (2008) independently. In principle, the RMS AT considers combing both labels for kinetic assessment more reliable (and more in line with pertinent guidance) but accepts the approach done here as the impact on the overall assessment is considered to be small. Nevertheless, in case of averaging endpoints from different water/sediment systems, labels from one system have to be averaged on beforehand in order to avoid bias.

- The RMS AT notes that in case of Mamouni (2008) the kinetic evaluation is based on non-amended residue data for fenoxaprop-P-ethyl (AE F046360) and fenoxaprop-P-acid (AE F088406). Notice that residue data in Mamouni (2008) have been amended by Crowe (2018). This amendment has indeed no impact on the kinetic evaluation results for fenoxaprop-P-ethyl (AE F046360) (*DegT50* in the total system '< 1 day'). However, in case of fenoxaprop-P-acid (AE F088406) 0.17 and 1 DAT samples of the phenoxy label are not considered fully reliable (also refer to Mamouni, 2008). Therefore, the RMS AT re-evaluated residue data for fenoxaprop-P-acid (AE F088406) in Mamouni (2008) on basis of Crow (2019) applying a SFO decline fit, considering both labels as replicates and omitting the 0.17- and 1-DAT sample in case of the phenoxy label.

Table B.8.2.2.3-47 Degradation of fenoxaprop-P-ethyl (AE F046360) in the entire water/sediment system (pathway fits, all SFO) - applicant fits agreed and amended by the RMS AT

Study	System	Label	*DegT50/T90 (d)*	χ^2 error (%)	t-test	VA	Kinetics
Fitzmaurice, 2004	Clayton Pond	Ph	0.17 / 0.58	18.3	< 0.01	+	SFO[a]
	Roding River	Ph	0.38 / 1.2	17.5	< 0.01	o	SFO[a]
Tarara, 2000	Rhine river	ClPh	0.12 / 0.40[b]	8.1	< 0.01	+	SFO[a]
	Nidda river	ClPh	0.11 / 0.36[b]	3.4	< 0.01	+	SFO[a]
Xu, 2012	Goose River	Ph	0.11 / 0.35	3.0	< 0.01	+	SFO[a]
		ClPh	0.11 / 0.38	3.2	< 0.01	+	SFO[a]
	Lawrence Pond	Ph	0.07 / 0.23	5.0	< 0.01	+	SFO[a]
		ClPh	0.05 / 0.18[b]	18.6	< 0.01	+	SFO[a]
Mamouni, 2008	Rhine River	Ph	< 1[c]	n.a.	n.a.	n.a.	n.a.
		ClPh	< 1[c]	n.a.	n.a.	n.a.	n.a.
	Fröschweiher Pond	Ph	< 1[c]	n.a.	n.a.	n.a.	n.a.
		ClPh	< 1[c]	n.a.	n.a.	n.a.	n.a.

(a) All pathway fits (for details refer to next table)
(b) Re-assessed by RMS AT (see comment section and additional figures)
(c) No reliable fit possible owing to limited number of data points

Table B.8.2.2.3-48 Degradation of fenoxaprop-P-acid (AE F088406) in the entire water/sediment system (pathway fits, all SFO) - applicant fits agreed and amended by the RMS AT

Study	System	Label	*DegT50/T90 (d)*	ff	χ^2 error (%)	t-test	VA	Kinetics
Fitzmaurice, 2004	Clayton Pond	Ph	39.6 / 132	0.96	12.4	< 0.01	+	$P_{SFO} \rightarrow M1_{SFO} \rightarrow M2_{SFO}$[a]
	Roding River	Ph	41.9 / 139	1.00	14.8	< 0.01	+	$P_{SFO} \rightarrow M1_{SFO} \rightarrow M2_{SFO}$[a]
Tarara, 2000	Rhine river	ClPh	13.9 / 46.2[b]	1.00	12.6	< 0.01	o	$P_{SFO} \rightarrow M1_{SFO}$[c]
	Nidda river	ClPh	8.0 / 26.5[b]	0.99	15.0	< 0.01	+	$P_{SFO} \rightarrow M1_{SFO}$[c]
Xu, 2012	Goose River	Ph	17.4 / 57.8	0.97	2.8	< 0.01	+	$P_{SFO} \rightarrow M1_{SFO} \rightarrow M2_{SFO}$[a]
		ClPh	17.2 / 57.0	0.88	4.1	< 0.01	++	$P_{SFO} \rightarrow M1_{SFO} \rightarrow M2_{SFO}/M3_{SFO}$[d]
	Lawrence Pond	Ph	15.3 / 50.9	1.00	8.3	< 0.01	+	$P_{SFO} \rightarrow M1_{SFO}$[c]
		ClPh	18.6 / 62.0[b]	0.98	8.4	< 0.01	o	$P_{SFO} \rightarrow M1_{SFO}$[c]

Mamouni, 2008	Rhine River	Ph & ClPh	13.5 / 44.7[(b)]	na	11.2	< 0.01	+	SFO[(e)]
	Fröschweiher Pond	Ph & ClPh	15.6 / 51.9[(b)]	na	11.4	< 0.01	+	SFO[(e)]

(a) Pathway fit with M1 = fenoxaprop-P-acid (AE F088406), M2 = HOPP-acid (AE F096918); fit results for M2 not considered reliable
(b) Re-assessed by RMS AT (see comment section and additional figures)
(c) Pathway fit with M1 = fenoxaprop-P-acid (AE F088406)
(d) Pathway fit with M1 = fenoxaprop-P-acid (AE F088406), M2 = chlorobenzoxazolone (AE F054014), M3 = phenol metabolite (AE F040356); fit results for M2 and M3 not considered reliable
(e) Decline fit

Table B.8.2.2.3-49 Degradation of fenoxaprop-P-ethyl (AE F046360) in the entire water/sediment system - applicant fits agreed by RMS AT

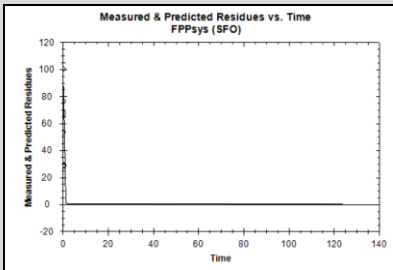
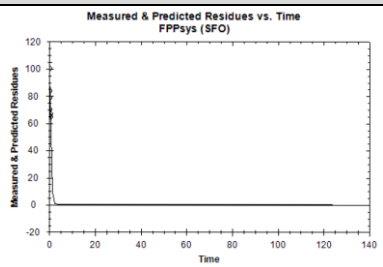
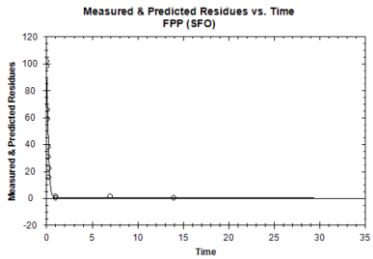
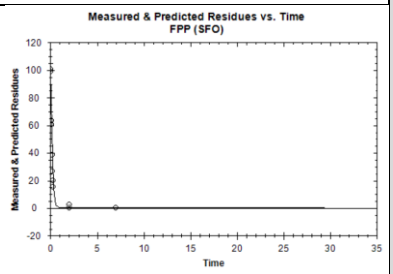
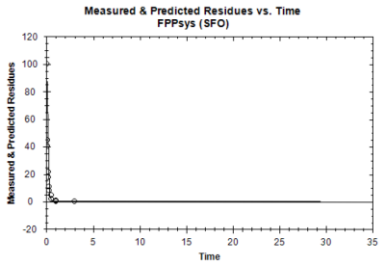
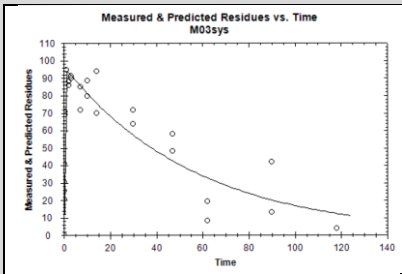
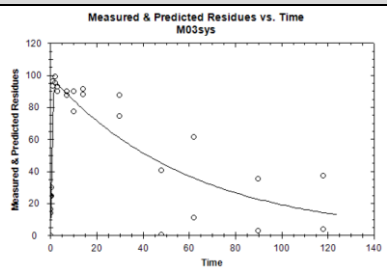
 **Fitzmaurice, 2004, Clayton Pond - SFO**	 **Fitzmaurice, 2004, Roding River - SFO**	Replaced by RMS AT fit (SFO), see below **Tarara, 2000, Rhine River**
Replaced by RMS AT fit (SFO), see below **Tarara, 2000, Nidda River**	 **Xu, 2012, Goose River, ClPh - SFO**	 **Xu, 2012, Goose River, Ph - SFO**
 **Xu, 2012, Lawrence Pond, Ph - SFO**	Replaced by RMS AT fit (SFO), see below **Xu, 2012, Lawrence Pond, ClPh**	

Table B.8.2.2.3-50 Degradation of fenoxaprop-P-acid (AE F088406) in the entire water/sediment system - applicant fits agreed by RMS AT

 **Fitzmaurice, 2004, Clayton Pond - P_{SFO} → M_{SFO}**	 **Fitzmaurice, 2004, Roding River - P_{SFO} → M_{SFO}**	Replaced by RMS AT fit (P_{SFO}→M_{SFO}), see below **Tarara, 2000, Rhine River - P_{SFO} → M_{SFO}**

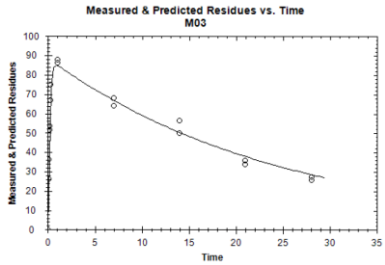
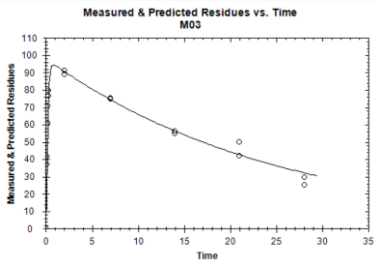
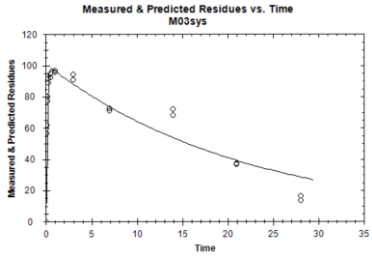
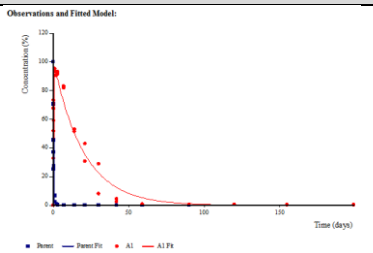
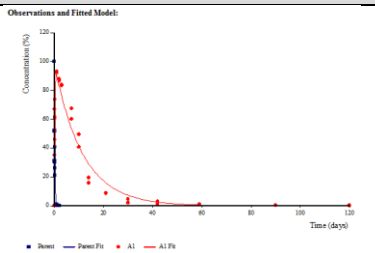
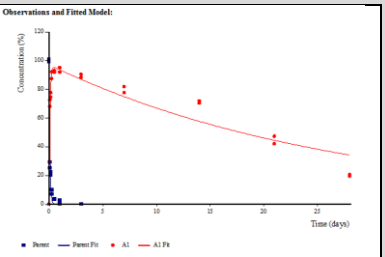
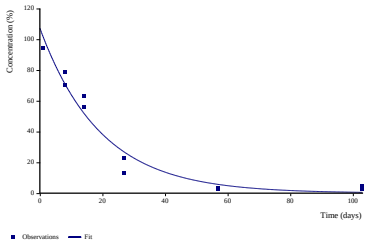
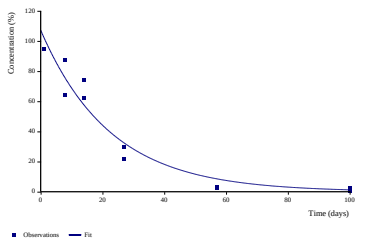
Replaced by RMS AT fit (P_{SFO}→M_{SFO}), see below **Tarara, 2000, Nidda River**	 **Xu, 2012, Goose River, ClPh - P_{SFO} → M_{SFO}**	 **Xu, 2012, Goose River, Ph - P_{SFO} → M_{SFO}**
 **Xu, 2012, Lawrence Pond, Ph - P_{SFO} → M_{SFO}**	Replaced by RMS AT fit (P_{SFO}→M_{SFO}), see below **Xu, 2012, Lawrence Pond, ClPh**	Replaced by RMS AT fit on basis of the amendment by Crowe (2018) considering both labels as replicates, see below **Mamouni, 2008, Rhine, ClPh - P_{SFO} → M_{SFO}**
Replaced by RMS AT fit on basis of the amendment by Crowe (2018) considering both labels as replicates, see below **Mamouni, 2008, Rhine, Ph - P_{SFO} → M_{SFO}**	Replaced by RMS AT fit on basis of the amendment by Crowe (2018) considering both labels as replicates, see below **Mamouni, 2008, Fröschweiher, ClPh - P_{SFO} → M_{SFO}**	Replaced by RMS AT fit on basis of the amendment by Crowe (2018) considering both labels as replicates, see below **Mamouni, 2008, Fröschweiher, Ph - P_{SFO} → M_{SFO}**

Table B.8.2.2.3-51 Degradation of <u>fenoxaprop-P-ethyl (AE F046360)</u> and <u>fenoxaprop-P-acid (AE F088406)</u> in the entire water/sediment system - <u>additional RMS-AT assessment</u> (all P_{SFO}→M_{SFO} pathway fit)

 **Tarara, 2000, Rhine River - P_{SFO} → M_{SFO}**	 **Tarara, 2000, Nidda River - P_{SFO} → M_{SFO}**	 **Xu, 2012, Lawrence Pond, ClPh - P_{SFO} → M_{SFO}**
 **Mamouni, 2008, Rhine, ClPh & Ph - M_{SFO} (Decline fit)**	 **Mamouni, 2008, Fröschweiher, ClPh & Ph - M_{SFO} (Decline fit)**	

- Similar to degradation in the total system, the RMS AT recommends sticking to SFO kinetics for fenoxaprop-P-ethyl (AE F046360) also in case of dissipation in the water phase (sufficient fits in any case). Agreed dissipation values in the water phase are given in the table below.

Table B.8.2.2.3-52 Dissipation of fenoxaprop-P-ethyl (AE F046360) in the water phase - applicant fits agreed and amended by the RMS AT

Study	System	Label	*DegT50 / T90 (d)*	χ^2 error (%)	t-test	VA	Kinetics
Fitzmaurice, 2004	Clayton Pond	Ph	0.17 / 0.57	8.1	< 0.01	+	SFO
	Roding River	Ph	0.38 / 1.3	3.4	< 0.01	o	SFO
Tarara, 2000	Rhine river	ClPh	0.11 / 0.38	14.0	< 0.01	+	SFO
	Nidda river	ClPh	0.09 / 0.29[(a)]	18.0	< 0.01	+	SFO
Xu, 2012	Goose River	Ph	0.06 / 0.19	11.1	< 0.01	+	SFO
		ClPh	0.06 / 0.20	5.4	< 0.01	+	SFO
	Lawrence Pond	Ph	0.06 / 0.20	7.6	< 0.01	+	SFO
		ClPh	0.04 / 0.14[(a)]	18.3	< 0.01	+	SFO
Mamouni, 2008	Rhine River	Ph	< 1[(b)]	n.a.	n.a.	n.a.	n.a.
		ClPh	< 1[(b)]	n.a.	n.a.	n.a.	n.a.
	Fröschweiher Pond	Ph	< 1[(b)]	n.a.	n.a.	n.a.	n.a.
		ClPh	< 1[(b)]	n.a.	n.a.	n.a.	n.a.

(a) Re-assessed by RMS AT applying SFO kinetics for the parent as well (refer to text above, figures not shown)
(b) No reliable fit possible owing to limited number of data points

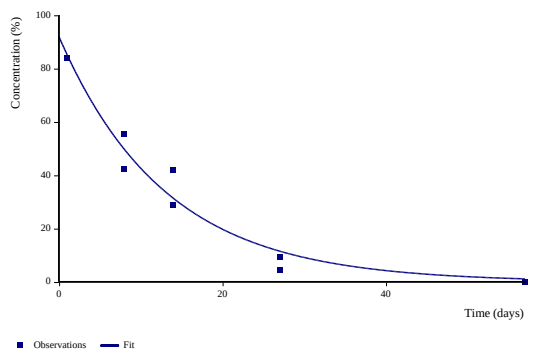
- Dissipation of fenoxaprop-P-ethyl (AE F088406) in the sediment phase as well as dissipation of fenoxaprop-P-acid (AE F088406) in the water and in the sediment phase as presented by the applicant (all SFO with one exception) is accepted by the RMS AT. However, as indicated above, residue data for fenoxaprop-P-acid (AE F088406) at 0.17 and 1 DAT for the phenoxy label in Mamouni (2008, amended by Crowe, 2019) are not considered fully reliable. Dissipation of fenoxaprop-P-acid (AE F088406) in Rhine River and Fröschweiher Pond were therefore re-evaluated by the RMS AT on basis of the amendment by Crowe (2018) considering both labels as replicates and omitting 0.17 and 1 DAT samples in case of the phenoxy label.

Table B.8.2.2.3-53 Fenoxaprop-P-acid (AE F088406): Values of the *DisT50* from water according to FOCUS Level I - Additional RMS assessment

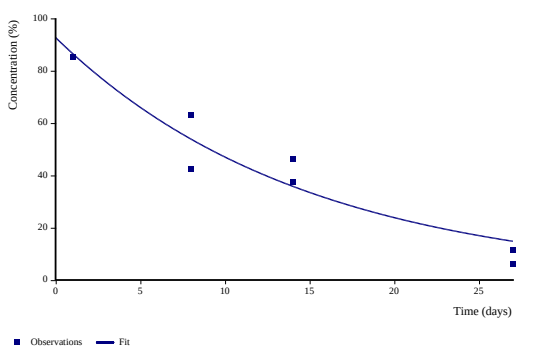
Sediment system	Label	*DT50* (days)	χ^2 error (%)	t-test (p)	VA	Kinetic model
Rhine River (Study 4)	ClPh & Ph	9.0	6.6	< 0.01	+	SFO
Fröschweiher Pond (Study 4)	ClPh & Ph	10.2	7.5	< 0.01	+	SFO

4: Mamouni, 2008

Table B.8.2.2.3-54 Fenoxaprop-P-acid (AE F088406): Fits for the *DisT50* from water according to FOCUS Level I - Additional RMS assessment



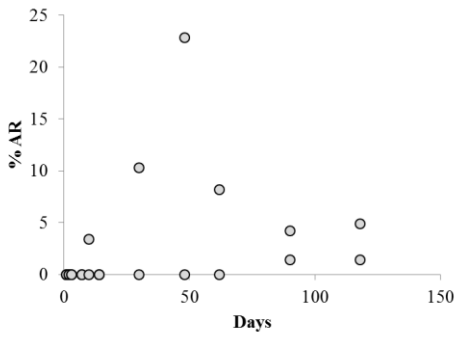
Mamouni, 2008, Rhine, ClPh & Ph - M_{SFO} (Decline fit)



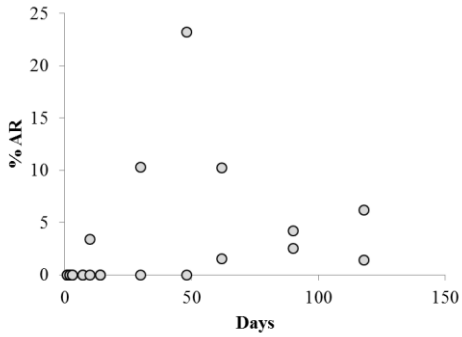
Mamouni, 2008, Fröschweiher, ClPh & Ph - M_{SFO} (Decline fit)

- The RMS AT considers residue data of HOPP-acid (AE F096918) in the Roding River (Fitzmaurice, 2004) not sufficiently robust for kinetic evaluation due to distinct data scatter. Results for HOPP-acid (AE F096918) from this test system are therefore not considered further.

Table B.8.2.2.3-55 Residue data of HOPP-acid (AE F096918) in the Roding River (Fitzmaurice, 2004) (left: water phase, right: total system)



Water phase



Total system

B.8.2.2.4. Irradiated water/sediment study

This point is regarded as a new optional data requirement in the EU. The degradation of fenoxaprop-P-ethyl (AE F046360) is well understood under standard conditions of water/sediment testing. Consequently the conduct of an irradiated water/sediment study would not result in a significantly better understanding of the behaviour of fenoxaprop-P-ethyl (AE F046360) and its residues in the aquatic environment. An irradiated water/sediment study was therefore not performed or regarded as necessary.

B.8.2.3. Degradation in the saturated zone

The evaluation revealed that the results of risk assessment in ground water demonstrated no significant risk for a contamination of sub-soils or the saturated zone by the active substance and its metabolites, when being applied according to good agricultural practice (also refer to Volume 3CP). Therefore, separate investigations on the degradation in the saturated zone are not regarded as necessary.

B.8.2.3.1. Summary on fate and behaviour in water and sediment

Abiotic hydrolysis of fenoxaprop-P-ethyl (AE F046360) was studies in several studies. Although test conditions are highly standardized (following OECD guideline 111), hydrolysis rates obtained and metabolite formation observed were somehow different in these studies, particularly at *p*H 7. On overall, fenoxaprop-P-ethyl (AE F046360) shows significant degradation under conditions of abiotic hydrolysis depending on the *p*H and, probably, on the buffer used in the hydrolysis experiment. As already noted in OECD guideline 111, the buffer system used may influence the rate of hydrolysis. At *p*H 4 and 25 °C, hydrolysis half-life of fenoxaprop-P-ethyl (AE F046360) was in a range from 2.1 - 4.3 days (three studies). At *p*H 5 and 25 °C hydrolysis half-life was in a range from 19.1 - 34.0 days (two studies). At *p*H 9 and 25 °C hydrolysis half-life of fenoxaprop-P-ethyl (AE F046360) was in a range from 0.5 - 0.9 days (three studies). At *p*H 7, however, results on hydrolysis are quite inconsistent with half-lives in a range from 8.6 - 111 days (three studies applying either phosphate or TRIS buffer). On request by the RMS AT, the notifier could not give a sound explanation for inconsistent results obtained under conditions of hydrolysis, particularly at *p*H 7.

In a dedicated hydrolysis study with unlabelled fenoxaprop-P-acid (AE F088406) half-lives at 25 °C were 27.4, 189 and 35 days at *p*H 5, 7 and 9, respectively (interpolated from experiments conducted at 50, 55 and 65 °C). Additional hydrolysis half-lives of fenoxaprop-P-acid (AE F088406) obtained in parent dosed studies (pathway fits) conducted at 25 °C were 2.5 days at *p*H 4 and 143 days at *p*H 9 (chlorophenyl label only).

At *p*H 4 (25 °C), hydrolysis of fenoxaprop-P-ethyl (AE F046360) is considered to be mainly driven by cleavage of the parent molecule at the central ether bond releasing chlorobenzoxazolone (AE F054014, max. 102.4 % AR) and its counterpart AE F029062 (max. 101.2 % AR). HOPP-acid (AE F029062, max. 1.4 % AR), the de-alkylated form of AE F029062, was hardly formed at this *p*H value. In one of the three hydrolysis studies fenoxaprop-P-acid (AE F088406) was found in significant amounts as well (max. 22.2 % AR) indicating that de-alkylation of fenoxaprop-P-ethyl (AE F046360) may also occur at this *p*H value under certain test conditions.

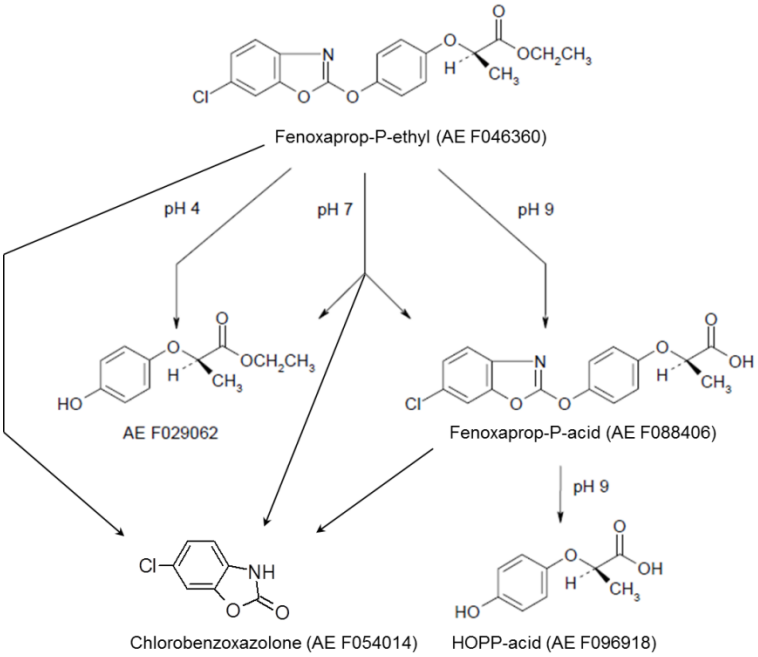
At *p*H 7 (25 °C), hydrolysis of fenoxaprop-P-ethyl (AE F046360) is considered to be governed by both, de-alkylation of the parent releasing fenoxaprop-P-acid (AE F0488406, max. 84.4 % AR) and by cleavage of the parent at the central ether bond releasing chlorobenzoxazolone (AE F054014, max. 27.9 % AR) and AE F029062 (max. 3.2 % AR). HOPP-acid (AE F096918) was not detected at this *p*H value indicating that fenoxaprop-P-acid (AE F088406) and AE F029062 are fairly stable under conditions of abiotic hydrolysis at *p*H 7.

At *p*H 9 (25 °C), de-alkylation of fenoxaprop-P-ethyl (AE F046360) releasing fenoxaprop-P-acid (AE F088406, max. 95.9 % AR) is considered the main driving force for hydrolysis. Fenoxaprop-P-acid (AE F088406) is further degraded by cleavage at the central ether bond to release chlorobenzoxazolone (AE F054014, max. 24.5 % AR) and HOPP-acid (AE F096918, max. 14.2 % AR). Formation of AE F029062 (max. 2.1 % AR) was insignificant at *p*H 9.

In two dedicated studies chlorobenzoxazolone (AE F054014) was shown to be stable at conditions of abiotic hydrolysis at *p*H 5, 7 and 9.

Metabolite AE F029062, a cleavage product of fenoxaprop-P-ethyl (AE F046360) under conditions of abiotic hydrolysis observed in significant amounts at *p*H 4 and *p*H 7 was neither observed in aerobic degradation studies in surface water nor in water/sediment studies. Thus, metabolite AE F029062 is considered not to occur in biotic aquatic systems.

Figure B.8.2.3.1-1: Proposed route of degradation of fenoxaprop-P-ethyl (AE F046360) under conditions of abiotic hydrolysis



Under conditions of **direct photochemical degradation** conducted in sterile buffer solutions at *p*H 5 (chlorophenyl label) and *p*H 7 (chlorophenyl and phenoxy label) fenoxaprop-P-ethyl (AE F046360) degraded into numerous metabolite fractions, none of them exceeding 10 % AR with the exception of fenoxaprop-P-ethyl-dechloro-hydroxy (BCS-CY11271) observed at max. 17.7 % AR at *p*H 7 in one study only. Metabolites observed at low levels at *p*H 7 were fenoxaprop-P-acid (AE F088406, max. 2.4 % AR), chlorobenzoxazolone (AE F054014, max. 1.8 % AR), HOPP-acid (AE F096918, max. 2.1 % AR), phenol metabolite (AE F040356, max. 5.9 % AR), AE F029062 (max. 3.3 % AR) and AE F031886 (max. 1.4 % AR). Metabolites identified at *p*H 5 were chlorobenzoxazolone (AE F054014, max. 6.4 % AR), phenol metabolite (AE F040356, max. 4.2 % AR) and hydroxybenzoxazolone (AE 0316854, max. 5.5 % AR). It is believed that unidentified, highly polar metabolite fractions formed under conditions of direct photochemical degradation mainly consist of short-chain aliphatic carboxylic acids, two of them definitely identified as malonic acid and succinic acid. Amounts of CO_2 formed at study end were 6.2 % AR (chlorophenyl label, 7 days) at *p*H 5, and 6.6 % AR (phenoxy label, 1.66 days) and 0.8 % AR (chlorophenyl label, 7 days) at *p*H 7, respectively.

Experimental net photolysis half-lives of fenoxaprop-P-ethyl (AE F046360) obtained were 14.6 days at *p*H 5, and 0.3 and 17.8 days, respectively, for the phenoxy and chlorophenyl labelled parent at *p*H 7. On request by the RMS AT, the notifier could not give a sound explanation for the deviating photolysis results of the two labels observed at *p*H 7 in two separate studies (and different laboratories). Related to natural sunlight conditions this gives a photolytic half-life of 85.7 days at *p*H 5 in Schwab (1993), and 0.7 and 17.8 days, respectively, at *p*H 7 (Fitzmaurice, 2008; Fletcher & Gilbert, 2008). Keeping in mind the overall fast degradation of fenoxaprop-P-ethyl (AE F046360) in non-irritated aquatic systems, photolysis is considered of minor importance in the overall dissipation of fenoxaprop-P-ethyl (AE F046360) in the aquatic environment.

Two photolysis studies (both *p*H 7) were also conducted with chlorobenzoxazolone (AE F054014). Numerous unknown metabolites were observed in both studies at significant amounts, beside CO_2 (max. 38.0 % AR at study end) and hydroxybenzoxazolone (AE 0316854, max. 26.6 % AR), considered to at least partly comprise short-chain aliphatic carboxylic compounds. Experimental photolysis half-lives values of chlorobenzoxazolone (AE F054014) obtained in these two studies were 1.3 and 0.11 days, corresponding to 7.0 days in summer (40 °N) in one study and 0.25 days of natural sunlight at 30 - 40 °N in the other study. Direct photolysis processes may therefore contribute to the elimination of chlorobenzoxazolone (AE F054014) from the aquatic environment (chlorobenzoxazolone (AE F054014) is considered rather persistent in aquatic systems under non-irradiated conditions).

The quantum yield (Φ) of fenoxaprop-P-ethyl (AE F046360) was determined in two studies at two different *p*H values, with 5.11×10^{-6} at a *p*H 5 in the first study (Schwab, 1993) and 0.04 at a *p*H 7 in the second study (Fletcher & Gilbert, 2008). It may be noted that in Fletcher & Gilbert (2008) no actinometer was applied, instead the quantum yield was directly calculated on basis of the absorbance (extinction coefficient) measured from 290 to 800 nm (as described in OECD guideline 316).

The quantum yield of the metabolite chlorobenzoxazolone (AE F054014) was determined in two studies as well (both studies conducted at *p*H 7), with Φ = 0.00565 in the first (Burgener, 1999) and 0.151 in the second study (Adam, 2008). There is no obvious reason for the difference observed, except that the actinometer used in both studies was different.

Indirect photochemical degradation of fenoxaprop-P-ethyl (AE F046360) was investigated in one study in irradiated non-sterile surface water (*p*H 9, chlorophenyl label). Major metabolites observed were fenoxaprop-P-acid (AE F088406, max. 56.6 % AR) and highly polar peaks accounting for max. 41.5 % AR in total, likely consisting of short-chain aliphatic carboxylic acids. As no dedicated experiment/analysis was performed to further elucidate these polar fractions, it remains unclear whether individual substances covered by these polar fractions exceed 10 % of AR on individual basis. Chlorobenzoxazolone (AE F054014) and the phenol metabolite (AE F040356) were observed at 3.5 and 4.3 % AR, respectively. CO_2 at study end (144 hrs) accounted for 6.8 % AR. Experimental *DT50* of fenoxaprop-P-ethyl (AE F046360) under conditions of indirect photolysis in surface water (*p*H 9) was 0.7 days. The impact of indirect photochemical degradation on the dissipation of fenoxaprop-P-ethyl (AE F046360) at *p*H 9 is considered negligible as hydrolysis *DT50* in non-irradiated (dark samples) was already 0.3 days.

Fenoxaprop-P-ethyl (AE F046360) is considered **not ready biodegradable** under the conditions of a CO_2 evolution (Modified Sturm) test.

In two **aerobic mineralisation studies in surface water** (chlorophenyl and phenoxy label, *p*H 8.0 and 9.2, two dose levels) fenoxaprop-P-ethyl (AE F046360) was instantaneously de-alkylated to form fenoxaprop-P-acid (AE F088406, max. 101.4 % AR, low dose). Fenoxaprop-P-acid (AE F088406) was further degraded by cleavage at the central ether bond to release chlorobenzoxazolone (AE F054014, max. 36.8 % AR) and HOPP-acid (AE 096918, max. 21.0 % AR). No other metabolite fractions were found above 5 % AR. Obtained *DT50* values (low dose) for fenoxaprop-P-ethyl (AE F046360) under conditions of the test system were 0.4 and 0.2 days at *p*H 8.0 (chlorophenyl label) and *p*H 9.2 (phenoxy label), respectively. *DT50* values (low dose) for fenoxaprop-P-acid (AE F088406) were 107 days at *p*H 8 and 39.4 days at *p*H 9.2. Amounts of CO_2 formed at study end (62 days, low dose) were negligible in case of the chlorophenyl label but 14.1 % AR for the phenoxy label.

The fate and behaviour of fenoxaprop-P-ethyl (AE F046360) in **aerobic water/sediment** was investigated in total eight water/sediment systems (four studies) partly applying both chlorophenyl and phenoxy labelled parent (*p*H in water from 6.6 - 8.3, in the sediment ($CaCl_2$) from 4.4 - 7.9). Similar to observations made in the aerobic mineralisation studies in surface water, fenoxaprop-P-ethyl (AE F046360) was rapidly de-alkylated in water/sediment systems to release fenoxaprop-P-acid (AE F088406, max. 97.2 % in the total system), which was further degraded by cleavage of the central ether bond to release chlorobenzoxazolone (AE F054014, max. 8.5 %) and HOPP-acid (AE F096918, max. 26.3 % AR). In addition, the phenol metabolite (AE F040356) was formed at maximum levels of 13.1 % AR. In Tarara (2000), an unknown metabolite fraction called 'U-1' exceeded 5 % of AR in more than two consecutive sampling points (maximum 6.0 % AR), thus formally triggering identification and exposure assessment according to Regulation (EU) No 283/2013. However, due to its distinct polar character in chromatography, 'U-1' is not regarded as one single compound. No other metabolite fraction exceeded 5 % AR in the total system at more than one sampling point in any of the studies. Formation of CO_2 was depending on the label investigated and was in the range from 13.8 - 67.9 % AR in studies covering approx. 120 days (three studies) and in the range from 0.9 - 36.6 % AR in one study investigating a 28-days period only. As already observed in soil degradation studies formation of non-extractable residues after application of fenoxaprop-P-ethyl (AE F046360) in water/sediment systems was significant as well reaching max. 67.7 % AR in the 120-days studies and max. 66.1 % AR in the 28-days study. Similar to formation of CO_2, formation of NER depends on the label applied (higher amounts of NER observed with the chlorophenyl label).

The overall degradation pathway of fenoxaprop-P-ethyl (AE F046360) observed in one **anaerobic water/sediment** system at 20 and 7 °C (Voelkel, 2004) was similar to that observed under aerobic conditions. Fenoxaprop-P-ethyl (AE F046360) rapidly degraded under anaerobic conditions as well releasing fenoxaprop-P-acid (AE F088406, max. 100.9 % AR at 20 °C), which further degraded to chlorobenzoxazolone (AE F054014,

max. 2.8 % AR at 20 °C), the phenol metabolite (AE F040256, max. 5.5 % AR) and HOPP-acid (AE F096918, max. 42.0 % AR). It is noted that amounts of HOPP-acid (AE F096918) in this study refer to racemic HOPP-acid (AE F020686) measured after application of racemic fenoxaprop-ethyl (AE F033171). Due to anaerobic conditions applied this study is considered as supplemental information only.

Figure B.8.2.3.1-2: Proposed route of degradation of fenoxaprop-P-ethyl (AE F046360) in aquatic systems

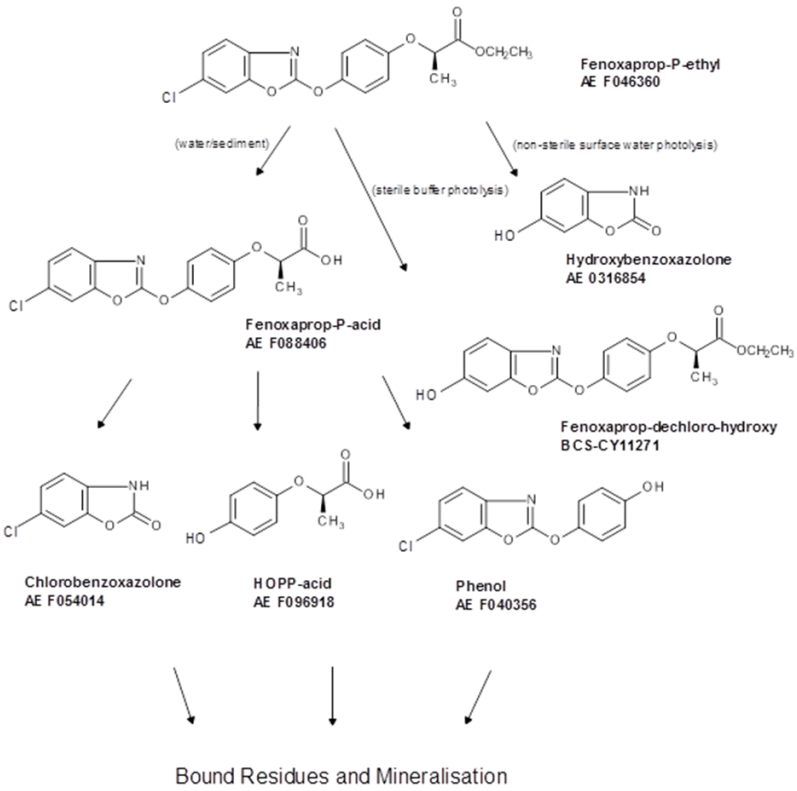


Table B.8.2.3.1-1: Summary on maximum occurrence (% AR) of identified and non-identified (unknown) metabolites in aquatic laboratory studies conducted with fenoxaprop-P-ethyl (AE F046360) (metabolites shaded in grey require an exposure assessment in surface water)

Compound	Aquatic hydrolysis (20-25 °C)	Direct photolytic degra-dation	Indirect photolytic degra-dation	Aerobic minera-lisation in surface water (low dose)	Water/sediment		
					Water phase	Sed. phase	Total system
Fenoxaprop-P-ethyl (AE F046360)	na	na	na	na	na	34.3[(a)]	na
Fenoxaprop-P-acid (AE F088406)	95.9	2.4	56.6	101.4	97.2	47.9[(a)]	97.2
Chlorobenzoxazolone (AE F054014)	102.4	7.1	3.5	36.8	6.7	8.5	8.5
Phenol metabolite (AE F040356)	-	5.9	4.3	-	-	13.1	13.1
HOPP acid (AE F096918)	14.2	2.1	-	21.0	22.9	3.4	26.3[(b)]
Fenoxaprop-P-ethyl-dechloro-hydroxy (BCS-CY11271)	-	17.7	-	-	-	-	-
Hydroxybenzoxazolone (AE 0316854)	-	5.5	-	-	-	-	-
AE F029062	101.2	3.3	-	-	-	-	-
AE F031886	-	1.4	-	-	-	-	-
AE F064124	1.0	-	-	-	-	-	-
Unknowns	8.9	11.4[(c)]	41.5[(d)]	4.8	ni	ni	6.0[(e)]

ni denotes not investigated by the RMS AT
(a) Arithmetic mean of Ph and ClPh label applied to the same water/sediment system
(b) 42.0 % AR in an anaerobic water/sediment study (measured as racemic HOPP-acid (AE F020686) following application of racemic fenoxaprop-ethyl (AE F033171))

(c) Highly polar fraction M1 observed in buffer solution (*p*H 5) considered to mainly comprising aliphatic short chain carboxylic acids (< 10 % on individual basis)
(d) Sum of highly polar fractions 'M1' (18.6 % AR) and 'M2' (22.9 % AR) observed in irradiated surface water (*p*H 9) considered to mainly comprising aliphatic short chain carboxylic acids. Maximum amounts on individual basis unknown.
(e) Unknown metabolite fraction 'U-1' (above 5 % AR at two consecutive sampling points), considered to represent multiple polar components; refer to text above

The rate of degradation/dissipation of fenoxaprop-P-ethyl (AE F046360) and its metabolites in laboratory aquatic systems is summarised in the tables below.

Table B.8.2.3.1-2: Summary on degradation of fenoxaprop-P-ethyl (AE F046360) under conditions of abiotic aquatic hydrolysis at 25 °C

*p*H	Label	Buffer	*DT50* (d)	*DT90* (d)	χ^2 error (%)	Kinetic model	Reference
4	ClPh	Citrate	2.8	9.4	5.0	SFO	Van der Gaauw, 2002
	Ph	Acetate	4.3	14.3	2.3	SFO	Fitzmaurice, 2008
	ClPh	Citrate	2.1	6.8	ns	SFO	Adam, 2008
5	ClPh	Acetate	34.0	113	0.8	SFO	Schwab, 1993[(a)]
	ClPh	Phthalate	19.1	63.5	2.1	SFO	Van der Gaauw, 2002
7	ClPh	Phosphate	23.8	79.1	1.7	SFO	Van der Gaauw, 2002
	Ph	TRIS	111	368	1.3	SFO	Fitzmaurice, 2008
	ClPh	Phosphate	8.6	28.6	ns	SFO	Adam, 2008
9	ClPh	Borate	0.6	1.9	6.1	SFO	Van der Gaauw, 2002
	Ph	Borate	0.9	2.8	3.5	SFO	Fitzmaurice, 2008
	ClPh	Borate	0.7	2.2	ns	SFO	Adam, 2008

(a) Dark control in an aquatic photolysis experiment
ns denotes not stated in the report

Table B.8.2.3.1-3: Summary on degradation of fenoxaprop-P-ethyl (AE F046360) under conditions of abiotic aquatic hydrolysis at 40 °C

*p*H	Label	Buffer	*DT50* (d)	*DT90* (d)	χ^2 error (%)	Kinetic model	Reference
4	ClPh	Citrate	0.8	2.7	2.7	SFO	Van der Gaauw, 2002
	Ph	Acetate	1.2	4.1	5.3	SFO	Fitzmaurice, 2008
	ClPh	Citrate	0.7	2.3	ns	SFO	Adam, 2008
5	ClPh	Phthalate	6.6	21.8	3.2	SFO	Van der Gaauw, 2002
7	ClPh	Phosphate	5.1	16.8	2.3	SFO	Van der Gaauw, 2002
	Ph	TRIS	37.0	123	1.7	SFO	Fitzmaurice, 2008
	ClPh	Phosphate	6.5	21.7	ns	SFO	Adam, 2008
9	ClPh	Borate	0.2	0.5	2.2	SFO	Van der Gaauw, 2002
	Ph	Borate	0.2	0.6	2.3	SFO	Fitzmaurice, 2008
	ClPh	Borate	0.1	0.4	ns	SFO	Adam, 2008

ns denotes not stated in the report

Table B.8.2.3.1-4: Summary on degradation of fenoxaprop-P-acid (AE F088406) under conditions of aquatic hydrolysis at 25 °C

*p*H	Label	Buffer	*DT50* (d)	*DT90* (d)	χ^2 error (%)	Kinetic model	Reference
4	ClPh	Citrate	2.5	8.2	ns	SFO	Adam, 2008
5	None	Citrate	27.4[(a)]	90.8[(a)]	na	SFO	Schollmeier & Eyrich, 1993
7	None	Phosphate	189[(a)]	627[(a)]	na	SFO	Schollmeier & Eyrich, 1993
9	None	Borate	35.0[(a)]	116[(a)]	na	SFO	Schollmeier & Eyrich, 1993
	ClPh	Borate	143	474	ns	SFO	Adam, 2008

na denotes not applicable
ns denotes not stated in the report
(a) Interpolated from 50, 55 and 65 °C study applying the Arrhenius equation

Table B.8.2.3.1-5: Summary on degradation of fenoxaprop-P-acid (AE F088406) under conditions of aquatic hydrolysis at 40 °C

*p*H	Label	Buffer	*DT50* (d)	*DT90* (d)	χ^2 error (%)	Kinetic model	Reference
4	ClPh	Citrate	0.5	1.7	ns	SFO[(a)]	Adam, 2008

5	None	Citrate	6.9[(b)]	22.7[(b)]	na	SFO	Schollmeier & Eyrich, 1993
7	None	Phosphate	38.1[(b)]	127[(b)]	na	SFO	Schollmeier & Eyrich, 1993
	ClPh	Phosphate	24.7	82.1	4.1	SFO[(c)]	Van der Gaauw, 2002
9	None	Borate	5.2[(b)]	17.4[(b)]	na	SFO	Schollmeier & Eyrich, 1993
	ClPh	Borate	12.3	40.8	8.8	SFO[(c)]	Van der Gaauw, 2002
	Ph	Borate	16.9	56.0	1.3	SFO	Fitzmaurice, 2008
	ClPh	Borate	12.7	42.1	ns	SFO[(a)]	Adam, 2008

na denotes not applicable
ns denotes not stated in the report
(a) Decline fit
(a) Interpolated from 50, 55 and 65 °C study applying the Arrhenius equation
(c) $P_{SFO} \rightarrow M_{SFO}$ pathway fit

Table B.8.2.3.1-6: Summary on net degradation of fenoxaprop-P-ethyl (AE F046360) under conditions of direct and indirect aquatic photolysis

Test system	Label	Suntest exposure days[(a)]		Sunlight equivalent days		χ^2 error (%)	Kinetic model	Reference
		DT50 (d)	*DT90* (d)	*DT50* (d)	*DT90* (d)			
*p*H 5 acetate buffer	ClPh	14.6	48.4	85.7[(c)]	-	-	SFO	Schwab, 1993
*p*H 9 surface water[(b)]		0.7	2.2	-	-	-	SFO	
*p*H 7 phosphate buffer	Ph	0.3	1.0	0.7[(d)]	-	-	SFO	Fitzmaurice, 2008
*p*H 7 phosphate buffer	ClPh	17.8	59.0	17.8[(e)]	-	-	SFO	Fletcher & Gilbert, 2008

(a) Continuous Suntest irradiation
(b) Indirect photolysis
(c) 52 °N in June
(d) 33.3 °N in June
(e) European summer light

Table B.8.2.3.1-7: Summary on net degradation of chlorobenzoxazolone (AE 054014) under conditions of aquatic photolysis

Test system	Suntest exposure days[(a)]		Sunlight equivalent days		χ^2 error (%)	Kinetic model	Reference
	DT50 (d)	*DT90* (d)	*DT50* (d)	*DT90* (d)			
*p*H 7 phosphate buffer	1.3	4.4	7.0[(b)]	-	-	SFO	Burgener, 1999
*p*H 7 phosphate buffer	0.11	0.37	0.25[(c)]	-	-	SFO	Adam, 2008

ns denotes not stated
(a) Continuous Suntest irradiation
(b) Natural summer sunlight at 40 °N
(c) Natural summer sunlight at 30 - 40 °N

Table B.8.2.3.1-8: Summary on degradation of fenoxaprop-P-ethyl (AE F046360) in aerobic surface water at 20 °C

Water/dose	*p*H	Label	*DegT50* water (d)	*DegT90* water (d)	χ^2 error (%)	Kinetic model	Reference
Wiehltalsperre/low dose	8.0	ClPh	0.4	1.4	5.1	SFO	Telscher & Junge, 2016a
Wiehltalsperre/high dose	8.0	ClPh	0.4	1.2	2.6	SFO	
Wiehltalsperre/low dose	9.2	Ph	0.2	0.6	4.6	SFO	Telscher & Junge, 2016b
Wiehltalsperre/high dose	9.2	Ph	0.2	0.8	3.3	SFO	

Table B.8.2.3.1-9: Summary on degradation of fenoxaprop-P-acid (AE F088406) in aerobic surface water at 20 °C

Water/dose	*p*H	Label	*DegT50* water (d)	*DegT90* water (d)	χ^2 error(%)	Kinetic model	Reference
Wiehltalsperre/low dose	8.0	ClPh	107	354	2.5	SFO[(a)]	Telscher & Junge, 2016a
Wiehltalsperre/high dose	8.0	ClPh	432	> 1000	1.2	SFO[(a)]	
Wiehltalsperre/low dose	9.2	Ph	39.4	131	5.5	SFO[(a)]	Telscher & Junge, 2016b
Wiehltalsperre/high dose	9.2	Ph	134	444	2.4	SFO[(a)]	

(a) Decline fit

Table B.8.2.3.1-10: Summary on degradation and dissipation of fenoxaprop-P-ethyl (AE F046360) in the total water/sediment system as well as in the water and sediment phase (aerobic, 20 °C) - trigger & modelling endpoints

Water / sediment system	*p*H wat. / sed.[a]	Label	*DegT50* system (d)	*DegT90* system (d)	Kinetic model	*DissT50* water (d)	Kinetic model	*DissT50* sed. (d)	Kinetic model	Reference
Rhine River	7.3 / 7.3	ClPh	0.12	0.40	SFO	0.11	SFO	nr	-	Tarara, 2000
Nidda River	6.8 / 5.1	ClPh	0.11	0.36	SFO	0.09	SFO	0.27	SFO	
Clayton Pond	6.6 / 4.4	Ph	0.17	0.58	SFO	0.17	SFO	na	-	Fitzmaurice, 2004
Roding River	8.0 / 7.2	Ph	0.38	1.2	SFO	0.38	SFO	na	-	
Goose River	8.3 / 7.9	ClPh	0.11	0.38	SFO	0.06	SFO	0.20	SFO	Xu, 2012
		Ph	0.11	0.35	SFO	0.06	SFO	0.13	SFO	
Lawrence Pond	7.8 / 7.4	ClPh	0.05	0.18	SFO	0.04	SFO	nr	-	
		Ph	0.07	0.23	SFO	0.06	SFO	0.05	SFO	
Rhine River	8.0 / 7.4[b]	ClPh	< 1	< 1	-	< 1	-	< 1	-	Mamouni, 2008
		Ph	< 1	< 1	-	< 1	-	< 1	-	
Fröschweiher Pond	7.8 / 7.2[b]	ClPh	< 1	< 1	-	< 1	-	< 1	-	
		Ph	< 1	< 1	-	< 1	-	< 1	-	
Geometric mean (n = 8)[c]			**0.13**	**0.44**		**0.11**		**0.14**		

nr denotes no reliable fit
na denotes not applicable (not observed)
(a) Measure in $CaCl_2$
(b) Matrix not specified
(c) Labels in Xu (2012) and Mamouni (2008) averaged (geometric mean) before averaging different water/sediment systems

Table B.8.2.3.1-11: Summary on degradation and dissipation of fenoxaprop-P-acid (AE F088406) in the total water/sediment system as well as in the water and sediment phase (aerobic, 20 °C) - trigger & modelling endpoints

Water / sediment system	*p*H wat. / sed.[a]	Label	*DegT50* system (d)	*DegT90* system (d)	Kinetic model	*ff*	*DissT50* water (d)	Kinetic model	*DissT50* sed. (d)	Kinetic model	Reference
Rhine River	7.3 / 7.3	ClPh	13.9	46.2	SFO[b]	1.0	10.7	SFO[c]	16.8	SFO[c]	Tarara, 2000
Nidda River	6.8 / 5.1	ClPh	8.0	26.5	SFO[b]	0.99	4.3	SFO[c]	8.7	SFO[c]	
Clayton Pond	6.6 / 4.4	Ph	39.6	132	SFO[b]	0.96	33.9	SFO[c]	nr	-	Fitzmaurice, 2004
Roding River	8.0 / 7.2	Ph	41.9	139	SFO[b]	1.0	40.5	SFO[c]	nr	-	
Goose River	8.3 / 7.9	ClPh	17.2	57.0	SFO[b]	0.88	7.2[d]	DFOP[c]	19.7	SFO[c]	Xu, 2012
		Ph	17.4	57.8	SFO[b]	0.97	6.7	SFO[c]	19.9	SFO[c]	
Lawrence Pond	7.8 / 7.4	ClPh	18.6	62.0	SFO[b]	0.98	8.4	SFO[c]	9.9	SFO[c]	
		Ph	15.3	50.9	SFO[b]	1.0	8.3	SFO[c]	7.7	SFO[c]	
Rhine River	8.0 / 7.4[e]	ClPh & Ph	13.5	44.7	SFO[c]	na	9.0	SFO[c]	17.7[h]	SFO[c]	Mamouni, 2008
Fröschweiher Pond	7.8 / 7.2[e]	ClPh & Ph	15.6	51.9	SFO[c]	na	10.2	SFO[c]	16.6[h]	SFO[c]	
Geometric mean (n = 8)[f]			**18.1**	**60.0**		**-**	**11.6**		**14.0**		
Arithmetic mean (n = 6)[g]			**-**	**-**		**0.98**	**-**		**-**		

nr denotes no reliable fit
(a) Measure in $CaCl_2$
(b) $P_{SFO} \rightarrow M_{SFO}$ pathway fit
(c) Decline fit
(d) DFOP *DT90* / 3.32
(e) Matrix not specified
(f) Labels in Xu (2012) averaged (geometric mean) before averaging different water/sediment systems
(g) Labels in Xu (2012) averaged (arithmetic mean) before averaging different water/sediment systems
(h) Geometric mean of individual decline fits for both replicates

Table B.8.2.3.1-12: Summary on degradation and dissipation of HOPP-acid (AE F096918) in the total water/sediment system as well as in the water and sediment phase (aerobic, 20 °C) - trigger & modelling endpoints

Water / sediment	*p*H wat. /	Label	*DegT50* system	*DegT90* system	Kinetic model	*DissT50* water	Kinetic model	*DissT50* sed.	Kinetic model	Reference

system	sed.[(a)]		(d)	(d)		(d)		(d)		
Clayton Pond	6.6 / 5.8	Ph	9.8	32.6	SFO[(b)]	9.9	SFO[(b)]	nr	na	Fitzmaurice, 2004
Roding River	8.0 / 7.7	Ph			No reliable fit (data scatter)					

(a) Measure in $CaCl_2$
(b) Decline fit

Table B.8.2.3.1-13: Summary on degradation and dissipation of fenoxaprop-P-ethyl (AE F046360) in the total water/sediment system (anaerobic, 20 °C) - supplemental information

Water / sediment system	*p*H wat. / sed.	Label	*DegT50* system (d)	*DegT90* system (d)	Kinetic model	*DisT50* water (d)	Kinetic model	*DisT50* sed. (d)	Kinetic model	Reference
Ormalingen	6.8 / 7.5[(a)]	ClPh	0.15	0.51	SFO	nc	nc	nc	nc	Voelkel, 2000

nc denotes not conducted
(a) Matrix not specified

Table B.8.2.3.1-14: Summary on degradation and dissipation of fenoxaprop-P-acid (AE F088406) in the total water/sediment system (anaerobic, 20 °C) - supplemental information

Water / sediment system	*p*H wat. / sed.	Label	*DegT50* system (d)	*DegT90* system (d)	Kinetic model	*DisT50* water (d)	Kinetic model	*DisT50* sed. (d)	Kinetic model	Reference
Ormalingen	6.8 / 7.5[(a)]	ClPh	55.3	184	SFO[(b)]	nc	nc	nc	nc	Voelkel, 2000

nc denotes not conducted
(a) Matrix not specified
(b) $P_{SFO} \rightarrow M_{SFO}$ pathway fit

B.8.3. FATE AND BEHAVIOUR IN AIR

B.8.3.1. Route and rate of degradation in air

No new study was submitted by the Fenoxaprop-P-ethyl Task Force for renewal as studies submitted for first Annex I inclusion are still considered reliable.

Reference:	**Estimation of the reaction with photochemically produced hydroxyl radicals in the atmosphere Code: AE F046360**
Author(s), year:	Buerkle, L. W. (1999)
Report/Doc. Number:	C003258/M-185869-01-1
Guideline(s):	OECD-Test Guideline on Photochemical Oxidative Degradation in the Atmosphere (Draft July 1991)
GLP:	Not applicable
Validity:	Yes
Status:	**Previously submitted**

[The following study report is a copy/paste of the original text in the DAR for Annex I inclusion slightly amended in order to meet editorial settings and to improve readability]

Material and methods:

The degradation of fenoxaprop-P-ethyl (AE F046360) by indirect photolysis (photochemical oxidative degradation) was calculated with the computer program AOPWIN version 1.88 (1999). This atmospheric oxidation program estimates the rate constant for the atmospheric, gas-phase reaction between photochemically produced hydroxyl radicals and organic chemicals. It also estimates the rate constant for the gas-phase reaction between ozone and olefinic/acetylenic compounds (not applicable in this case). The rate constants estimated by the program are then used to calculate atmospheric half-lives based upon average atmospheric concentrations of hydroxyl radicals and ozone.

Results:

The overall OH rate constant for fenoxaprop-P-ethyl (AE F046360) was calculated to be 28.7039×10^{-12} cm^3/molecule/sec. Assuming an OH concentration of 10^6 radicals/cm^3 and 24 hours/day the atmospheric half-life would be 13.4 hours (0.6 days).

Conclusions:

Fenoxaprop-P-ethyl (AE F046360) is rapidly degraded in the atmosphere and a risk for persistence is not given.

Comments RMS AT:

- Re-calculation with AOPWIN version 1.92 revealed an atmospheric half live of only 3.83 hrs (0.16 days; overall OH rate constant of 33.4809×10^{-12} cm^3/molecule/sec).

Reference:	**Calculation of the chemical lifetime of fenoxaprop-P-acid AE F088406 in the troposphere**
Author(s), year:	Hellpointner, E. (2004)
Report/Doc. Number:	C043983/ M-235572-01-1
Guideline(s):	BBA: Part IV, 6-1, (1990)
GLP:	Not applicable
Validity:	Yes
Status:	**Previously submitted**

[The following study report is a copy/paste of the original text in the DAR for Annex I inclusion slightly amended

in order to meet editorial settings and to improve readability]

Material and methods:

The degradation of fenoxaprop-P-acid (AE F088406) by indirect photolysis (photochemical oxidative degradation) was calculated with the computer program AOPWIN version 1.91 (2003), which is based on the estimation method according to structure-activity relationship methods developed by R. Atkinson and co-workers. On account of the molecular structure of fenoxaprop-P-acid (AE F088406) it can be taken for granted with great certainty that mainly reactions with photochemical produced hydroxyl radicals determine its degradation rate and chemical lifetime in air. A value of 1.5×10^6 OH radicals/cm^3 is regarded as the global 12-hours-day-time concentration (excluding the night). The rate constants estimated by the program are used to calculate atmospheric half-lives based upon average atmospheric concentrations of hydroxyl radicals and ozone.

Results:

The overall OH rate constant for fenoxaprop-P-acid (AE F088406) was calculated to be 37.5462×10^{-12} cm^3/molecule/sec. Assuming an OH concentration of 1.5×10^6 radicals/cm^3 and 12 hours/day the atmospheric half-life would be 3.42 hours (0.3 days).

Conclusions:

Fenoxaprop-P-acid (AE F088406) is rapidly degraded in the atmosphere and a risk for persistence is not given.

Comments RMS AT:

- Re-calculation with AOPWIN version 1.92 gave the same result.

B.8.3.2. Transport via air

Being a new potential requirement this had not been addressed in the Dossier submitted or evaluated within the process for Annex I inclusion.

In view of values for vapour pressure measured being below the triggers of 10^{-4} Pa for soil and of 10^{-5} Pa for plants (FOCUS, 2008) no study on transport of the active substance fenoxaprop-P-ethyl (AE F046360) *via* air is regarded as necessary. The combination of a water solubility of 0.43 mg/L with a vapour pressure of 6.5×10^{-6} Pa (at 20 °C) resulted in a low value for the Henry constant (5.5×10^{-3} Pa × m^3 / mol at 20 °C), indicating non-volatility. Once in the air, half-life in the atmosphere (0.16 days according to Atkinson) is low at all. Consequently, fenoxaprop-P-ethyl (AE F046360) is estimated not to be subject to transport via air.

B.8.3.3. Local and global effects

Being a new potential requirement this had not been addressed within the process for Annex I inclusion.

Products containing formulations of fenoxaprop-P-ethyl (AE F046360) are applied as foliar spray to cereals. Following application residues are rapidly degraded. In combination with a low potential for volatility these aspects indicate that residues are not present under outdoor conditions to form a risk for the environment short-term or long-term to set effects at local or global level.

The potential for local effects from use of fenoxaprop-P-ethyl (AE F046360) has been considered in risk assessments performed following its use under field conditions in particular by considering factors like spray drift. The combination of exposure assessments with potential effects measured in soil and surface water do thus cover the environmental compartments of interest. In contrast and since there is no aerial application envisaged, air is not a compartment regarded to be major compartment of potential for fenoxaprop-P-ethyl (AE F046360) occurrence following its intended use in the field.

The setting of global effects like contributions to global warming potential (GWP), ozone depleting potential (OPD), photochemical ozone creation potential (POCP) would require a high probability for the molecule assessed to evaporate and thus occur in the gas phase. This probability can be expressed by the volatility in terms of the vapour pressure and the Henry constant. The very low potential of fenoxaprop-P-ethyl (AE F046360) residues to occur in the atmosphere has been addressed before under B 8.3.2.

Any accumulation in the troposphere would require the combination of persistence in the gas phase, significant volatility and the application of high volumes of active substance. Persistence has been addressed under B 8.3.1 to result in low persistence of fenoxaprop-P-ethyl (AE F046360) residues in the atmosphere.

An acidification potential (AP) would require the generation of acidifying gases like sulphur dioxide or nitrogen oxides in a free form. An eutrophication potential (EP) would require the generation of ammonia or phosphorous compounds acting as nutrients. There were no indications that the degradation of fenoxaprop-P-ethyl (AE F046360) residues in the environment *via* biological of physico-chemical processes would result in products that would have a significant potential for acidification or eutrophication of the environment. Even when this would be the case and to set a potential effect this would require amounts of active substance applied in the field being several orders of magnitude higher in comparison to the seasonal application rates and from use in registered crops.

B.8.4. DEFINITION OF THE RESIDUES

B.8.4.1. Definition of the residue for risk assessment

The residue definitions relevant for risk assessment for each compartment are the following:

Compartment	Residue Definition
Soil	Fenoxaprop-P-ethyl (AE F046360), fenoxaprop-P-acid (AE F088406)[(a)], chlorobenzoxazolone (AE F054014), HOPP-acid (AE F096918)
Groundwater	Fenoxaprop-P-ethyl (AE F046360), fenoxaprop-P-acid (AE F088406)[(a)], chlorobenzoxazolone (AE F054014), HOPP-acid (AE F096918)
Surface Water	Fenoxaprop-P-ethyl (AE F046360), fenoxaprop-P-acid (AE F088406)[(a)], chlorobenzoxazolone (AE F054014), HOPP-acid (AE F096918), phenol metabolite (AE F040356), fenoxaprop-P-ethyl-dechloro-hydroxy (BCS-CY11271)[(b)]
Sediment	Fenoxaprop-P-ethyl (AE F046360), fenoxaprop-P-acid (AE F088406)[(a)], chlorobenzoxazolone (AE F054014), HOPP-acid (AE F096918), phenol metabolite (AE F040356), fenoxaprop-P-ethyl-dechloro-hydroxy (BCS-CY11271)[(b)]
Air	Fenoxaprop-P-ethyl (AE F046360), fenoxaprop-P-acid (AE F088406)[(a)]

(a) Herbicidal active metabolite
(b) Aquatic photolysis

B.8.4.2. Definition of the residue for monitoring

Following risk assessments in soil, ground water and surface water according to the GAP defined, the environmental safety of all components under assessment could be demonstrated according to the requirements set. It is therefore justified to define the active substance fenoxaprop-P-ethyl (AE F046360) and its rapidly formed and relevant (herbicidal active) metabolite fenoxaprop-P-acid (AE F088406) as the relevant residues for monitoring in soil, ground and surface water and air.

B.8.5. MONITORING DATA CONCERNING FATE AND BEHAVIOUR OF THE ACTIVE SUBSTANCE, METABOLITES, DEGRADATION AND REACTION PRODUCTS

The Fenoxaprop-P-ethyl Task Force claims that there are no published data from formal monitoring programs available that would indicate a specific concern or findings of fenoxaprop-P-ethyl (AE F046360) and its residues in remote environmental areas not being subject to the intended use.

Without having these data or reports available the RMS AT considers it difficult to judge on their relevance. **The applicant is therefore asked to provide public monitoring data (ground water and surface water) available in the EU as far as this feasible.** This also includes public report on residues in remote environmental areas which may be available in some of the EU Member States. It may be noted that fenoxaprop-acid (no enantiomer analysis) is regularly included in the public groundwater monitoring at least in Austria (with no concerns here, indeed).

B.8.6. REFERENCES RELIED ON

For fenoxaprop-P-ethyl (AE F046360), its metabolites and appropriate trade names, searches and reviews of the published literature are presented in the following summary.

Reference:	**Summary of the literature data for Fenoxaprop-P-ethyl**
Author(s), year:	Wolf, R., 2016
Report/Doc. Number:	M-556789-01-1
Guideline(s):	EFSA Journal 2011;9(2):2092
GLP:	Not applicable
Validity:	Yes
Status:	**New submission**

Summary:

For fenoxaprop-P-ethyl (AE F046360) and its relevant metabolites, a total of 1250 references were identified and evaluated for potential relevance. Besides references that were clearly out of the scope of the literature review report (e.g. publications dealing with chemical synthesis, or efficacy reports), the area of environmental fate and ecotoxicology were most represented in the search results. According to EFSA guidance 1135 publications have been excluded from further consideration after the rapid assessment. For 115 publications full-text documents have been obtained and assessed in detail. Ninety-one publications have been considered irrelevant after detailed assessment. In total 24 publications were evaluated as relevant for detailed assessment and has been classified for relevance according to EFSA guidance.

For fenoxaprop-P-ethyl (AE F046360) the publication by Zhang et al. (2010) has been identified as relevant after detailed assessment and classified as case a) according to EFSA Guidance Point 5.4.1. The article assesses the degradation behaviour of the two enantiomers of fenoxaprop-ethyl (AE F046360) in aerobic soil. Based on the results, racemic fenoxaprop-ethyl (AE F033171) can be degraded in soil by enantioselective hydrolysis while enantiomers of fenoxaprop-ethyl esters are configurationally stable. Enantioselective degradation in soil via the R-enantiomer is also observed when the biologically inactive S-form of fenoxaprop-acid is applied, while configurational stability is found when fenoxaprop-P-acid (AE F088406) is applied to soil. The data support the results of two studies on US soils conducted by the Fenoxaprop Task Force, but also provides further information for refining the risk assessment. Thus a detailed summary is provided under B 8.1.1.1.

Beside this, 23 other publications have been identified as studies relevant after detailed assessment and classified in accordance with the EFSA Guidance Point 5.4.1. However, none of these studies was considered to have an impact on an EU-agreed endpoint, or would require any adaptation of the risk assessments presented in the fenoxaprop-P-ethyl (AE F046360) supplementary (Annex I Renewal) dossier.

Search strategy:

A broad collection of relevant databases was used for the literature search (scientific peer-reviewed open literature published between 2005-01-01 and 2016-01-11). STN, a scientific information platform hosted by CAS, itself a division of the American Chemical Society, was selected as the preferred provider[10]. It offers a reliable scientific search service that includes all databases considered relevant to cover the requirements established in the AIR3 renewal regulation and the EFSA Guidance document. Moreover, hosted databases have a defined query language for different sources which facilitates duplicate removal.

The following databases have been included in the literature research: Agricola, last update on 2016-01-05; Biosis, 2016-01-06; CABA, 2016-01-07; Chemical Abstracts, 2016-01-10; Derwent Drug File (DRUGU), 2016-01-08; EMBASE, 2016-01-08; Esbiobase, 2016-01-07; IPA, 2016-01-05; Medline, 2016-01-10; Pascal, 2014-12-22; PQSciTech, 2015-12-22; Registry, 2016-01-08; Scisearch, 2016-01-04; Toxcenter, 2016-01-04 and FSTA, 2015-12-18.

The table below presents the input parameters for the database search on fenoxaprop-P-ethyl (AE F046360) and relevant metabolites. The information used for screening the selected databases to identify all relevant

[10] http://www.cas.org/products/ stnfamily/index.html

publications consists of IUPAC name, CAS name/number, common names, codes and abbreviations, molecular structure, molecular formula, molar mass and other names/codes, as far as available.

Table B.8.6-1: List of input parameters for the database search on fenoxaprop-P-ethyl (AE F046360) and relevant metabolites

i) Fenoxaprop-P-ethyl (AE F046360)	
IUPAC name:	2-(4-(6-chloro-2-benzoxazolyl)oxy)-phenoxy)propanoic acid ethyl ester
CAS number:	66441-23-4, 71283-80-2, 113776-20-8
STN Query	(66441-23-4 OR 82110-72-3 OR 87714-45-2 OR 116573-18-3 OR 71283-80-2 OR 1223013-63-5 OR 113776-20-8 OR FENOXAPROP-ETHYL OR FENOXAPROP P-ETHYL OR HOE 046360 OR HOE 33171 OR (ACCLAIM OR FURORE OR WHIP OR PUMA OR ISOMERO OR OPTION SUPER OR (RAPSODE OR FENOVA OR FOXTROT OR COUGAR OR STARPROP OR OSKAR OR FOXTAIL OR TETRAMOR OR ARSOL OR RUMBA OR NORTON OR CHEETAH OR DOPLER OR DEPON OR FURORE OR GREENEX OR PUMA OR RALON OR RICESTAR OR WHIP OR TRIUMPH OR GREENEX OR DUKE OR ACCLAIM OR DJINN OR OPTION OR HUSSAR OR GAMO OR PROPER OR LISTEN OR BLEDOR OR RUGIR OR BAGHERA OR PRIMERA OR TIGRESS OR CORNICHE OR ATLAS OR FPE)(W)(R OR TM OR RTM) OR "ETHYL-2-(4-(6-CHLORO-2-BENZOXA 1LYL-OXY)-PHENOXY-PROPANOATE " OR "ETHYL (2R)-2-[4-(6-CHLORO-2-BENZOXAZOLYLOXY)PHENOXY]PROPIONATE" OR "ETHYL 2-[4-(6-CHLOROBENZOXAZOLYL-2-OXY)PHENOXY]PROPIONATE" OR "ETHYL 2-[4-(6-CHLORO-2-BENZOXAZOLYLOXY)PHENOXY]PROPIONATE") AND PY>2004 NOT P/DT
ii) Metabolites (tailored to metabolites observed in the environment)	
M01 **Phenol metabolite (AE F040356)**	4-((6-chloro-1,3-benzoxazol-2-yl)oxy)phenol CAS: 70217-01-5 Query: (70217-01-5 OR "4-[(6-CHLORO-2-BENZOXAZOLYL)OXY]PHENOL" OR "6-CHLORO-2-(4-HYDROXYPHENOXY)-BENZOXAZOLE" OR HOE 040356) AND PY>2004 NOT P/DT
M02 **Chlorobenzoxazolone (AE F054014)**	6-chloro-1,3-benzoxazol-2(3H)-one CAS: 19932-84-4 Query: (19932-84-4 OR HOE 054014 OR "6-CHLORO-2(3H)-BENZOXAZOLONE" OR 6-CHLORO-2,3-DIHYDROBENZOXAZOL-2-ONE OR 6-CHLORO-2-BENZOXAZOLINONE OR 6-CHLOROBENZOXAZOLINONE OR 6-CHLORO-2-BENZOXAZOLONE OR 6-CHLOROBENZOXAZOLONE OR NSC 26191 OR NSC 664284) AND PY>2004 NOT P/DT
M03 **Fenoxaprop-P-acid (AE F088406)**	2-(4-(6-chlorobenzoxazolyl-2-yloxy)phenoxy)propanoic acid CAS: 113158-40-0, 95617-09-7, 113776-21-9 Query: (113158-40-0 OR 95617-09-7 OR 73519-55-8 OR 108093-88-5 OR 131776-21-9 OR FENOXAPROP ACID OR HOE 53022 OR HOE 088406 OR "2-[4-[(6-CHLORO-2-BENZOXAZOLYL)OXY]PHENOXY]PROPANOIC ACID" OR FENOXAPROP (NOTW)(P OR ETHYL)) AND PY>2004 NOT P/DT
M04 **HOPP-acid (AE F096918)**	2-(4-hydroxyphenoxy)propanoic acid CAS: 94050-90-5, 67648-61-7, 105118-15-8 Query: (94050-90-5 OR 67648-61-7 OR 95977-31-4 OR 105118-15-8 OR "2-(4-HYDROXYPHENOXY)PROPANOIC ACID" OR "2-(4-HYDROXYPHENOXY)PROPIONIC ACID" OR "2-(P-HYDROXYPHENOXY)PROPIONIC ACID" OR NSC 522955) AND PY>2004 NOT P/DT
M05 **AE F029062**	2-(4-hydroxyphenoxy)propanoic acid ethyl ester CAS: 96478-44-3, 71301-98-9, 65343-67-1 Query: (96478-44-3 OR 71301-98-9 OR 65343-67-1 OR 59012-02-1 OR "2-(4-HYDROXYPHENOXY)PROPIONIC ACID ETHYL ESTER" OR "2-(P-HYDROXYPHENOXY)PROPIONIC ACID ETHYL ESTER" OR "ETHYL 2-(4-HYDROXYPHENOXY)PROPANOATE" OR "ETHYL 2-(4-HYDROXYPHENOXY)PROPIONATE" OR "ETHYL (R)-2-(4-HYDROXYPHENOXY)PROPIONATE") AND PY>2004 NOT P/DT
M06 **Fenoxaprop-P-dechloro-hydroxy (BCS-CY11271)**	2-(4-((6-hydroxy-1,3-benzoxazol-2-yl)oxy)phenoxy)propanoic acid CAS: - Query: ("2-{4-[(6-HYDROXY-1-BENZOXAZOL-2-YL)OXY]PHENOXY}PROPANOIC ACID") AND PY>2004 NOT P/DT

M07 **Hydroxybenzoxazolone (AE 0316854)**	6-hydroxy-1,3-benzoxazol-2(3H)-one CAS: 78213-03-3 Query: (78213-03-3 OR NSC 603719 OR 6-HYDROXY-2,3-DIHYDROBENZOXAZOL-2-ONE OR "6-HYDROXYBENZOXAZOL-2(3H)-ONE") AND PY>2004 NOT P/DT
M08 **AE F064124**	6-chloro-5-hydroxy-1,3-benzoxazol-2(3H)-one CAS: 88412-29-7 Query: (88412-29-7 OR 6-CHLORO-1,3-BENZOXAZOLE-2,5-DIOL OR "6-CHLORO-5-HYDROXY-1,3-BENZOXAZOL-2(3H)-ONE") AND PY>2004 NOT P/DT

Search results:

A total of 642 publications were found for fenoxaprop-P-ethyl and 608 for the metabolites.

No.	Name	Number of hits
a.i.	Fenoxaprop-P-ethyl (AE F046360)	642
M01	4-((6-chloro-1,3-benzoxazol-2-yl)oxy)phenol	4
M02	6-chloro-1,3-benzoxazol-2(3H)-one	23
M03	2-(4-(6-chlorobenzoxazolyl-2-yloxy)phenoxy)propanoic acid	485
M04	2-(4-hydroxyphenoxy)propanoic acid	60
M05	2-(4-hydroxyphenoxy)propanoic acid ethyl ester	16
M06	2-(4-((6-hydroxy-1,3-benzoxazol-2-yl)oxy)phenoxy)propanoic acid	0
M07	6-hydroxy-1,3-benzoxazol-2(3H)-one	18
M08	6-chloro-5-hydroxy-1,3-benzoxazol-2(3H)-one	0
Others	-	2

Based on the abstracts the following topics were used to classify publications as being obviously irrelevant (*rapid assessment*):

- Efficacy
- Analytical method development
- New ways of synthesis
- Studies on a molecular level, which cannot be related to environmental 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

Those publications, which have passed the rapid assessment, have been evaluated based on their full text versions (*detailed assessment*). The assessment criteria are shown below:
Not relevant, because

- 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 a non-relevant route of exposure
- Observations cannot be transferred into an endpoint

The table below gives a statistical overview of the rapid and detailed assessments.

Table B.8.6-2: Results of the study selection process, for each data requirement or group of data requirements searched

Data requirement(s) captured in the search	a.i.	M01	M02	M03	M04	M05	M07
Total number of *summary records* retrieved after *all* searches of peer-reviewed literature[(a)]	642	4	23	485	60	16	18
Number of *summary records* excluded from the search results after rapid assessment for relevance	565	4	21	454	57	15	17
Total number of *full-text documents* assessed in detail[(a)]	**77**	**-**	**2**	**31**	**3**	**1**	**1**
Number of *publications* excluded from further consideration after detailed assessment for relevance	57	-	2	27	3	1	1
Number of *publications* not excluded for relevance after detailed assessment (i.e. relevant studies and studies of unclear relevance)	**20**	**-**	**-**	**4**	**-**	**-**	**-**

(a) Both from bibliographic databases and other sources of peer-reviewed literature

The results of the detailed assessment are shown in the table below.

Table B.8.6-3: Report of all relevant studies and studies of unclear relevance after detailed assessment of full-text documents for relevance: ordered by data requirement (tailored to e-Fate)

KCA- SANCO Data Point	KCP - SANCO Data Point	Author(s)	Year	Title	Source	Classification of study
KCA 7.1.1. Route of degradation in soil		Zhang, Yanfeng; Liu, Donghui; Diao, Jinling; He, Zeying; Zhou, Zhiqiang; Wang, Peng; Li, Xuefeng	2010	Enantioselective environmental behavior of the chiral herbicide fenoxaprop-ethyl and its chiral metabolite fenoxaprop in soil	Journal of agricultural and food chemistry (2010) , Volume 58, Number 24, p. 12878-12884., Electronic ISSN: 0021-8561 Source Note: 2010 Dec. 22, v. 58, no. 24	Case a) In this publication the degradation behaviour of various forms of the active substance fenoxaprop-ethyl and its metabolite fenoxaprop-acid was investigated in three Chinese soils incubated at 25°C and about 60% of the MWHC in the dark for 25 days in maximum. Enantioselective HPLC analysis (chiral column) was performed following incubation of racemic mixtures as well as the separate enantiomers each of fenoxaprop-ethyl and fenoxaprop-acid. A summary is provided under CA 7.1.1.1./09
KCA 7.2.1. Route and rate of degradation in aquatic systems (chemical and photochemical degradation)		Pythoglou, Paschalina; Vryzas, Zisis; Alexoudis, Christos; Senseman, Scott A.; Vassiliou, George.	2012	Influence of biotic and abiotic factors on dissipation of fenoxaprop-P-ethyl in water	Fresenius Environ. Bull., Volume 21, Issue 10a, Page 3012-3017, Publication Year 2012	Case c) The article contains adequate information about the dissipation, distribution, degradation or metabolism of the substance of concern in air, soil, water or sediment over time. Although the dissipation study followed OECD guidelines the described methodology is out of scope for use in environmental risk assessment.
KCA 7.2.1.1. Hydrolytic degradation		Lin, Jing; Chen, Jingwen; Cai, Xiyun; Wang, Ying.	2009	Influential factors and the degradation pathway in hydrolysis of fenoxaprop-P-ethyl in buffer solutions	Anquan Yu Huanjing Xuebao, Volume 9, Issue 1, Page 13-16, Publication Year 2009	Case c) The article contains adequate information about the degradation of the substance of concern in water but is out of scope for use in environmental risk assessment.
KCA 7.2.1.1. Hydrolytic degradation; KCA 8.2.4.1. Acute toxicity to Daphnia		Lin, Jing; Chen, Jingwen; Cai, Xiyun; Qiao, Xianliang; Huang, Liping; Wang, Degao; Wang, Zhuang.	2007	Evolution of toxicity upon hydrolysis of fenoxaprop-P-ethyl	J. Agric. Food Chem., Volume 55, Issue 18, Page 7626-7629, Publication Year 2007	Case c) The article contains adequate information about the dissipation of the substance of water over time; EC_{50} values after 48h exposure to *Daphnia magna* are presented. However the publication is out of scope for use in environmental risk assessment.
KCA 7.2.1.2. Direct photochemical degradation; KCA 8.2.4.1. Acute toxicity to Daphnia		Lin, Jing; Chen, Jingwen; Wang, Ying; Cai, Xiyun; Wei, Xiaoxuan; Qiao, Xianliang.	2008	More toxic and photoresistant products from photodegradation of fenoxaprop-P-ethyl	J. Agric. Food Chem., Volume 56, Issue 17, Page 8226-8230, Publication Year 2008	Case c) The article contains adequate information about the dissipation, distribution, degradation or metabolism of the substance of concern in air, soil, water or sediment; 48h EC_{50} values are presented for additional metabolites. Publication is out of scope for use in environmental risk assessment.

KCA- SANCO Data Point	KCP - SANCO Data Point	Author(s)	Year	Title	Source	Classification of study
KCA 7.5. Monitoring data		Barco-Bonilla, Nieves; Romero-Gonzalez, Roberto; Plaza-Bolanos, Patricia; Frenich, Antonia Garrido; Martinez Vidal, Jose L.; Salas, Juan J.; Martin, Isabel.	2013	Study of the distribution of 204 organic contaminants between the aqueous phase and the suspended particulate matter in treated wastewater for proper environmental control	Desalin. Water Treat., Volume 51, Issue 10-12, Page 2497-2515, Publication Year 2013	Case c) The article reports on the presence of the substance of concern in samples collected from groundwater, soil, surface waters, sediments or air from the European zone. The described method is out of scope for use in environmental risk assessment.
KCA 7.5. Monitoring data		Barco-Bonilla, Nieves; Romero-Gonzalez, Roberto; Plaza-Bolanos, Patricia; Martinez Vidal, Jose L.; Garrido Frenich, Antonia.	2013	Systematic study of the contamination of wastewater treatment plant effluents by organic priority compounds in Almeria province (SE Spain)	Sci. Total Environ., Volume 447, Page 381-389, Publication Year 2013	Case c) This article is out of scope for use in environmental risk assessment in particular representativity of sample collection.
KCA 7.5. Monitoring data		Hurtado-Sanchez, M. C.; Romero-Gonzalez, R.; Rodriguez-Caceres, M. I.; Duran-Meras, I.; Frenich, A. Garrido	2013	Rapid and sensitive on-line solid phase extraction-ultra high performance liquid chromatography-electro-spray-tandem mass spectrometry analysis of pesticides in surface waters	Journal of Chromatography A (2013), 1305, 193-202	Case c) The article reports on the presence of the substance of concern in samples collected from groundwater, soil, surface waters, sediments or air from the European zone. The described analytical method is out of scope for use in environmental risk assessment.
KCA 7.5. Monitoring data		Jansson, Christer; Kreuger, Jenny.	2010	Multiresidue analysis of 95 pesticides at low nanogram/liter levels in surface waters using online preconcentration and high performance liquid chromatography/tandem mass spectrometry	J. AOAC Int., Volume 93, Issue 6, Page 1732-1747, Publication Year 2010	Case c) The article reports on the presence of the substance of concern in samples collected from groundwater, soil, surface waters, sediments or air from the European zone. The descriped method is out of scope for use in environmental risk assessment.
KCA 7.5. Monitoring data		Lindqvist, Bengt-Olov; Hansson, Jan-Bertil; Joensson, Christina; Persson, Kenneth M.	2007	Presence of pesticide residues in groundwaters: monitoring in Simrishamn in 2002-2007	Vatten, Volume 63, Issue 2, Page 159-163, Publication Year 2007	Case c) The article reports on the presence of the substance of concern in samples collected from groundwater, soil, surface waters, sediments or air from the European zone. Out of scope for use in environmental risk assessment..

KCA- SANCO Data Point	KCP - SANCO Data Point	Author(s)	Year	Title	Source	Classification of study
KCA 7.5. Monitoring data		Montoro, Elena Pastor; Gonzalez, Roberto Romero; Frenich, Antonia Garrido; Torres, M. Elena Hernandez; Vidal, Jose Luis Martinez.	2007	Fast determination of herbicides in waters by ultra-performance liquid chromatography/tandem mass spectrometry	Rapid Commun. Mass Spectrom., Volume 21, Issue 22, Page 3585-3592, Publication Year 2007	Case c) The article is out of scope for use in environmental risk assessment in particular representativity of sample collection. No endpoint can be derived.
KCA 7.5. Monitoring data		Raeppel, Caroline; Fabritius, Marie; Nief, Marie; Appenzeller, Brice M. R.; Millet, Maurice	2014	Coupling ASE, silylation and SPME-GC/MS for the analysis of current-used pesticides in atmosphere	Talanta (2014), 121, 24-29	Case c) The article reports on the presence of the substance of concern in samples collected from groundwater, soil, surface waters, sediments or air from the European zone. The described method is out of scope for use in environmental risk assessment
KCA 7.5. Monitoring data		Reemtsma Thorsten; Alder Lutz; Banasiak Ursula	2013	Emerging pesticide metabolites in groundwater and surface water as determined by the application of a multimethod for 150 pesticide metabolites	Water research, (2013 Jun 27). Electronic Publication Date: 27 Jun 2013	Case c) The article reports on the presence of the substance of concern in samples collected from groundwater and surface waters from the European zone. The described method is out of scope for use in environmental risk assessment
KCA 7.5. Monitoring data		Sauret, Nathalie; Wortham, Henri; Putaud, Jean-Philippe; Mirabel, Philippe.	2008	Study of the effects of environmental parameters on the gas/particle partitioning of current-use pesticides in urban air	Atmos. Environ., Volume 42, Issue 3, Page 544-553, Publication Year 2008	Case c) The article reports on the presence of the substance of concern in samples collected from air in urban areas (Strasbourg, France). A new partition equation was defined for the pesticides under study using environmental parameters such as temperature, relative humidity, and organic carbon content of atmospheric aerosols. This assessment is out of scope for use in environmental risk assessment
KCA 7.5. Monitoring data		Sauret-Szczepanski, Nathalie; Mirabel, Philippe; Wortham, Henri.	2005	Development of an SPME-GC-MS/MS method for the determination of pesticides in rainwater: Laboratory and field experiments	Environ. Pollut. (Amsterdam, Neth.), Volume 139, Issue 1, Page 133-142, Publication Year 2005	Case c) In this article the concentrations of fenoxaprop in rain samples from Strassbourg (France) are presented. However the method is outdated and thus out of scope for use in the environmetal risk assessment

KCA- SANCO Data Point	KCP - SANCO Data Point	Author(s)	Year	Title	Source	Classification of study
KCA 7.5. Monitoring data		Tankiewicz, Maciej; Morrison, Calum; Biziuk, Marek	2013	Multi-residue method for the determination of 16 recently used pesticides from various chemical groups in aqueous samples by using DI-SPME coupled with GC-MS	Talanta (2013), 107, 1-10	Case c) The article reports on an analytical method applied to analytes of natural water samples from river, sea, canal and rain. The method is out of scope for use in environmental risk assessment

Conclusion:

For fenoxaprop-P-ethyl (AE F046360) and its metabolites, a total of 1250 references were identified and evaluated for potential relevance. One publication with relevance after detailed assessment has been classified according to EFSA Guidance 5.4.1 as case a). This publication Zhang et al. (2010) provides further information for refining the risk assessment. No further publication has been identified which would indicate that a side-effect on human health, the environment and non-target species may exist, which would then need to be considered in the risk assessment of the supplementary (renewal) dossier.

Comments (RMS AT):

- None

Annex point / reference number	Author(s)	Year	Title Source *(where different from company)* Company name, Report No., Date, GLP status *(where relevant)*, published or not	Vertebrate study Y/N	Data protection claimed Y/N	Justification if data protection is claimed	Owner	Previous evaluation
KCA 7.1.1.1 /01	Stumpf, K.; Dambach, P.	1988	Aerobic soil metabolism Hoe 046360 - chlorophenyl-^{14}C Hoechst AG, Frankfurt am Main, Germany Bayer CropScience, Report No.: A39289, Edition Number: M-120879-01-1 Date: 1988-10-10 GLP/GEP: yes, unpublished	N	N		Bayer CropScience	Y
KCA 7.1.1.1 /02	Buettner, B.; Schweighoefer, U.; Kuenzler, K.	1992	Aerobic soil metabolism study at 11 and 21 C Hoe 046360-chlorophenyl-U-^{14}C Hoechst AG, Frankfurt am Main, Germany Bayer CropScience, Report No.: A47274, Edition Number: M-135697-01-1 EPA MRID No.: 43400602 Date: 1992-01-23 GLP/GEP: yes, unpublished	N	N		Bayer CropScience	Y
KCA 7.1.1.1 /03	Buerkle, W. L.; Schuld, G.; Grundschoettel, P.	1986	Aerobic soil metabolism study Hoe 033171-dioxyphenyl-1-14C Hoechst AG, Frankfurt am Main, Germany Bayer CropScience, Report No.: A32791, Edition Number: M-112654-01-1 EPA MRID No.: 00130347, 00258976, 47123206 Date: 1986-02-19 GLP/GEP: yes, unpublished	N	N		Bayer CropScience	Y
KCA 7.1.1.1 /04	Tarara, G.	1999	Metabolic fate of the 4-hydroxyphenoxypropionic acid moiety and discussion of the radiolabel position Fenoxaprop-P-ethyl Code: AE F046360 Hoechst Schering AgrEvo GmbH, Frankfurt am Main, Germany Bayer CropScience, Report No.: C005529, Edition Number: M-192232-01-1 Date: 1999-09-15 GLP/GEP: n.a., unpublished	N	N		Bayer CropScience	Y

KCA 7.1.1.1 /05	Schwab, W.	1993a	Aerobic soil metabolism (addendum to report CB051/87, A39289) Hoe 046360 - chlorophenyl-^{14}C Hoechst AG, Frankfurt am Main, Germany Bayer CropScience, Report No.: A49512, Edition Number: M-138550-01-1 Date: 1993-01-14 GLP/GEP: no, unpublished	N	N		Bayer CropScience	Y
KCA 7.1.1.1 /06	Schwab, W.	1993b	Aerobic soil metabolism study (addendum to report CB058/85, A32791) Hoe 033171-dioxyphenyl-1-14C Hoechst AG, Frankfurt am Main, Germany Bayer CropScience, Report No.: A49511, Edition Number: M-138549-01-1 EPA MRID No.: 00130347 Date: 1993-01-14 GLP/GEP: no, unpublished	N	N		Bayer CropScience	Y
KCA 7.1.1.1 /07	Tarara, G.	2004a	Identity of volatiles as 14CO2: Hoe 046360-chlorophenyl-14C, Aerobic soil metabolism Generated by: BCS AG, Monheim, Germany Document No: A39289 GLP/GEP: not applicable (statement) Unpublished	N	N		Bayer CropScience	Y
KCA 7.1.1.1 /08	Tarara, G.	2004b	Validity of study: Aerobic soil metabolism study using Hoe 033171-dioxyphenyl-1-14C Generated by: BCS AG, Monheim, Germany Document No: C045288 GLP/GEP: not applicable (statement) Unpublished	N	N		Bayer CropScience	Y
KCA 7.1.1.1 /09	Shepherd, J. J.	2012	[Chlorophenyl-UL-14C]fenoxaprop-P-ethyl: Aerobic soil metabolism in four US soils Bayer CropScience LP, Stilwell, KS, USA TF- BCS-CHA, Report No.: MEFPL006-1, Edition Number: M-424708-02-1 EPA MRID No.: 48757101 Date: 2012-02-10 **...Amended: 2012-02-15** GLP/GEP: yes, unpublished	N	Y	Study done to cover US data requirements	TF- BCS-CHA	N

KCA 7.1.1.1 /10	Shepherd, J. J.; Ripperger, R. J.	2011	[Phenoxy-UL-14C]fenoxaprop-P-ethyl: Aerobic soil metabolism in four US soils Bayer CropScience LP, Stilwell, KS, USA TF- BCS-CHA, Report No.: M-424988-02-1, Edition Number: M-424988-02-1 EPA MRID No.: 48868703 Date: 2011-02-14 **...Amended: 2012-05-16** GLP/GEP: yes, unpublished	N	Y	Study done to cover US data requirements	TF- BCS-CHA	N
KCA 7.1.1.1 /11	Zhang, Y.; Liu, D.; Diao, J.; He, Z.; Zhou, Z.; Wang, P.; Li, X.	2010	Enantioselective Environmental Behavior of the Chiral Herbicide Fenoxaprop - ethyl and Its Chiral Metabolite Fenoxaprop in Soil Journal:Journal of agricultural and food chemistry (2010) , Volume 58, Number 24, p. 12878-12884., Electronic ISSN: 0021-8561 Source Note: 2010 Dec. 22, v. 58, no. 24, Year:2010, Report No.: M-507961-01-1, Edition Number: M-507961-01-1 GLP/GEP: n.a., published	N	N		Public data	N
KCA 7.1.1.2 /01	Voelkel, W.	2001	^{14}C-AE F046360/^{14}C-AE F033171: Anaerobic soil degradation RCC Ltd., Itingen, Switzerland Bayer CropScience, Report No.: C024193, Edition Number: M-227834-01-1 Date: 2001-08-28 GLP/GEP: yes, unpublished	N	N		Bayer CropScience	Y
KCA 7.1.1.2 /02	Adam, A.	2008a	^{14}C-fenoxaprop-P-ethyl - Degradation and metabolism in one soil incubated under anaerobic conditions Harlan Laboratories Ltd., Itingen, Switzerland TF- BCS-CHA, Report No.: 266 FPE, Edition Number: M-548193-01-1 Date: 2008-11-25 GLP/GEP: yes, unpublished	N	Y	Study performed to address data requirements in the EU	TF- BCS-CHA	N

KCA 7.1.1.3 /01	Sarafin, R.; Jordan, H. J.	1989	Photodegradation on soil Hoe 033171-14C (fenoxaprop-ethyl) Hoechst AG, Frankfurt am Main, Germany Bayer CropScience, Report No.: A40297, Edition Number: M-122796-01-1 Date: 1989-01-10 GLP/GEP: yes, unpublished	N	N		Bayer CropScience	Y
KCA 7.1.2.1.1 /01	Stumpf, K.; Dambach, P.	1988	Aerobic soil metabolism Hoe 046360 - chlorophenyl-14C Hoechst AG, Frankfurt am Main, Germany Bayer CropScience, Report No.: A39289, Edition Number: M-120879-01-1 Date: 1988-10-10 GLP/GEP: yes, unpublished	N	N		Bayer CropScience	Y
KCA 7.1.2.1.1 /02	Buettner, B.; Schweighoefer, U.; Kuenzler, K.	1992	Aerobic soil metabolism study at 11 and 21 C Hoe 046360-chlorophenyl-U-14C Hoechst AG, Frankfurt am Main, Germany Bayer CropScience, Report No.: A47274, Edition Number: M-135697-01-1 EPA MRID No.: 43400602 Date: 1992-01-23 GLP/GEP: yes, unpublished	N	N		Bayer CropScience	Y
KCA 7.1.2.1.1 /03	Schwab, W.	1993a	Aerobic soil metabolism (addendum to report CB051/87, A39289) Hoe 046360 - chlorophenyl-14C Hoechst AG, Frankfurt am Main, Germany Bayer CropScience, Report No.: A49512, Edition Number: M-138550-01-1 Date: 1993-01-14 GLP/GEP: no, unpublished	N	N		Bayer CropScience	Y
KCA 7.1.2.1.1 /04	Shepherd, J. J.	2012	[Chlorophenyl-UL-14C]fenoxaprop-P-ethyl: Aerobic soil metabolism in four US soils Bayer CropScience LP, Stilwell, KS, USA TF- BCS-CHA, Report No.: MEFPL006-1, Edition Number: M-424708-02-1 EPA MRID No.: 48757101 Date: 2012-02-10 **...Amended: 2012-02-15** GLP/GEP: yes, unpublished	N	Y	Study done to cover US data requirements	TF- BCS-CHA	N

KCA 7.1.2.1.1 /05	Shepherd, J. J.; Ripperger, R. J.	2011	[Phenoxy-UL-14C]fenoxaprop-P-ethyl: Aerobic soil metabolism in four US soils Bayer CropScience LP, Stilwell, KS, USA TF- BCS-CHA, Report No.: M-424988-02-1, Edition Number: M-424988-02-1 EPA MRID No.: 48868703 Date: 2011-02-14 **...Amended: 2012-05-16** GLP/GEP: yes, unpublished	N	Y	Study done to cover US data requirements	TF- BCS-CHA	N
KCA 7.1.2.1.1 /06	Oberdoerster, C.; Boiselle, N.; Herrmann, M.	2016	Fenoxaprop-P-ethyl and metabolites: Kinetic evaluation of aerobic soil degradation under laboratory conditions TF- BCS-CHA, Report No.: EnSa-15-0391, Edition Number: M-552947-01-1 Date: 2016-04-22 GLP/GEP: no, unpublished	N	N		TF- BCS-CHA	N
KCA 7.1.2.1.2 /01	Stumpf, K.; Dambach, P.	1988	Aerobic soil metabolism Hoe 046360 - chlorophenyl-14C Hoechst AG, Frankfurt am Main, Germany Bayer CropScience, Report No.: A39289, Edition Number: M-120879-01-1 Date: 1988-10-10 GLP/GEP: yes, unpublished	N	N		Bayer CropScience	Y
KCA 7.1.2.1.2 /02	Buettner, B.; Schweighoefer, U.; Kuenzler, K.	1992	Aerobic soil metabolism study at 11 and 21 C Hoe 046360-chlorophenyl-U-14C Hoechst AG, Frankfurt am Main, Germany Bayer CropScience, Report No.: A47274, Edition Number: M-135697-01-1 EPA MRID No.: 43400602 Date: 1992-01-23 GLP/GEP: yes, unpublished	N	N		Bayer CropScience	Y
KCA 7.1.2.1.2 /03	Schwab, W.	1993a	Aerobic soil metabolism (addendum to report CB051/87, A39289) Hoe 046360 - chlorophenyl-14C Hoechst AG, Frankfurt am Main, Germany Bayer CropScience, Report No.: A49512, Edition Number: M-138550-01-1 Date: 1993-01-14 GLP/GEP: no, unpublished	N	N		Bayer CropScience	Y

KCA 7.1.2.1.2 /04	Shepherd, J. J.	2012	[Chlorophenyl-UL-14C]fenoxaprop-P-ethyl: Aerobic soil metabolism in four US soils Bayer CropScience LP, Stilwell, KS, USA TF- BCS-CHA, Report No.: MEFPL006-1, Edition Number: M-424708-02-1 EPA MRID No.: 48757101 Date: 2012-02-10 **...Amended: 2012-02-15** GLP/GEP: yes, unpublished	N	Y	Study done to cover US data requirements	TF- BCS-CHA	N
KCA 7.1.2.1.2 /05	Shepherd, J. J.; Ripperger, R. J.	2011	[Phenoxy-UL-^{14}C]fenoxaprop-P-ethyl: Aerobic soil metabolism in four US soils Bayer CropScience LP, Stilwell, KS, USA TF- BCS-CHA, Report No.: M-424988-02-1, Edition Number: M-424988-02-1 EPA MRID No.: 48868703 Date: 2011-02-14 **...Amended: 2012-05-16** GLP/GEP: yes, unpublished	N	Y	Study done to cover US data requirements	TF- BCS-CHA	N
KCA 7.1.2.1.2 /06	Fitzmaurice, M.	2010	[^{14}C]-HPPA: Rate of degradation under aerobic conditions in three soils at 20 degree Battelle UK Ltd., Chelmsford, Essex, United Kingdom TF- BCS-CHA, Report No.: 315 FPE, Edition Number: M-548269-01-1 Date: 2010-05-14 GLP/GEP: yes, unpublished	N	Y	Study performed to address data requirements in the EU	TF- BCS-CHA	N
KCA 7.1.2.1.2 /07	Stroech, K.; Junge, T.	2014	[phenyl-UL-^{14}C]AE F096918 (HOPP acid): Degradation in four aerobic soils TF- BCS-CHA, Report No.: EnSa-13-0977, Edition Number: M-483333-01-1 Date: 2014-03-28 GLP/GEP: yes, unpublished	N	Y	Study performed to address data requirements in the EU	TF- BCS-CHA	N
KCA 7.1.2.1.2 /08	Oberdoerster, C.; Boiselle, N.; Herrmann, M.	2016	Fenoxaprop-P-ethyl and metabolites: Kinetic evaluation of aerobic soil degradation under laboratory conditions TF- BCS-CHA, Report No.: EnSa-15-0391, Edition Number: M-552947-01-1 Date: 2016-04-22 GLP/GEP: no, unpublished	N	N		TF- BCS-CHA	N

KCA 7.1.2.1.3 /01	Voelkel, W.	2001	^{14}C-AE F046360/^{14}C-AE F033171: Anaerobic soil degradation RCC Ltd., Itingen, Switzerland Bayer CropScience, Report No.: C024193, Edition Number: M-227834-01-1 Date: 2001-08-28 GLP/GEP: yes, unpublished	N	N		Bayer CropScience	Y
KCA 7.1.2.1.3 /02	Adam, A.	2008a	^{14}C-fenoxaprop-P-ethyl - Degradation and metabolism in one soil incubated under anaerobic conditions Harlan Laboratories Ltd., Itingen, Switzerland TF- BCS-CHA, Report No.: 266 FPE, Edition Number: M-548193-01-1 Date: 2008-11-25 GLP/GEP: yes, unpublished	N	Y	Study performed to address data requirements in the EU	TF- BCS-CHA	N
KCA 7.1.2.1.4 /01	Voelkel, W.	2001	^{14}C-AE F046360/^{14}C-AE F033171: Anaerobic soil degradation RCC Ltd., Itingen, Switzerland Bayer CropScience, Report No.: C024193, Edition Number: M-227834-01-1 Date: 2001-08-28 GLP/GEP: yes, unpublished	N	N		Bayer CropScience	Y
KCA 7.1.2.1.4 /02	Adam, A.	2008a	^{14}C-fenoxaprop-P-ethyl - Degradation and metabolism in one soil incubated under anaerobic conditions Harlan Laboratories Ltd., Itingen, Switzerland TF- BCS-CHA, Report No.: 266 FPE, Edition Number: M-548193-01-1 Date: 2008-11-25 GLP/GEP: yes, unpublished	N	Y	Study performed to address data requirements in the EU	TF- BCS-CHA	Y
KCA 7.1.2.2.1 /01	Carringer, R. D.; O'Grodnick, J. S.; Clayton, B.; Parkes, R. L.	1993a	Field dissipation applied to peanuts in North Carolina of Fenoxaprop-P-ethyl Super Whip 0.67EC (Bugle(R) herbicide) American Agricultural Services, Inc., USA Bayer CropScience, Report No.: A51887, Edition Number: M-132786-02-1 Date: 1993-12-17 **...Amended: 1996-10-21** GLP/GEP: yes, unpublished	N	N		Bayer CropScience	Y

KCA 7.1.2.2.1 /02	Carringer, R. D.; O'Grodnick, J. S.; Clayton, B.; Parkes, R. L.	1993b	Field dissipation applied to soybeans in Iowa of Fenoxaprop-P-ethyl Super Whip 0.67EC (Bugle(R) herbicide) American Agricultural Services, Inc., USA Bayer CropScience, Report No.: A51888, Edition Number: M-132787-02-1 Date: 1993-12-17 **...Amended: 1996-10-21** GLP/GEP: yes, unpublished **...also filed: KCA 6.1 /04**	N	N		Bayer CropScience	Y
KCA 7.1.2.2.1 /03	Belyk, M. B.; Gadsby, M. C.	1991a	A comparative field dissipation study of Hoe 046360 (Excel Super) and Hoe 046360 + Hoe 070542 (Puma Super) in a dry-land Saskatchewan soil Hoechst Canada Inc.; Bayer CropScience, Report No.: C000912, Edition Number: M-181455-01-1 Date: 1991-05-01 GLP/GEP: no, unpublished	N	N		Bayer CropScience	Y
KCA 7.1.2.2.1 /04	Belyk, M. B.; Gadsby, M. C.	1991b	Field persistence and dissipation of Hoe 046360 and Hoe 070542 over a one, two and three year period Hoechst Canada Inc.; Bayer CropScience, Report No.: C000913, Edition Number: M-181457-01-1 Date: 1991-04-01 GLP/GEP: no, unpublished	N	N		Bayer CropScience	Y
KCA 7.1.3.1.1 /01	Goerlitz, G.; Rutz, U.	1988	Adsorption in the system soil/water and Hoe 088406 adsorption in the system soil/water - Code: Hoe 088406 Hoechst AG, Frankfurt am Main, Germany Bayer CropScience, Report No.: A38826, Edition Number: M-120443-01-1 EPA MRID No.: 41567705 Date: 1988-08-15 GLP/GEP: yes, unpublished	N	N		Bayer CropScience	Y

KCA 7.1.3.1.1 /02	Reynolds, J. L.	1992	Adsorption and desorption in four soils of 14C-fenoxaprop-P-ethyl in four soils XenoBiotics Laboratories, Inc., Plainsboro, NJ, USA Bayer CropScience, Report No.: M-137847-02-3, Edition Number: M-137847-02-3 Date: 1992-09-17 GLP/GEP: yes, unpublished	N	N		Bayer CropScience	Y
KCA 7.1.3.1.2 /01	Goerlitz, G.; Rutz, U.	1988	Adsorption in the system soil/water and Hoe 088406 adsorption in the system soil/water - Code: Hoe 088406 Hoechst AG, Frankfurt am Main, Germany Bayer CropScience, Report No.: A38826, Edition Number: M-120443-01-1 EPA MRID No.: 41567705 Date: 1988-08-15 GLP/GEP: yes, unpublished	N	N		Bayer CropScience	Y
KCA 7.1.3.1.2 /02	Reynolds, J. L.	1992	Adsorption and desorption in four soils of 14C-fenoxaprop-P-ethyl in four soils XenoBiotics Laboratories, Inc., Plainsboro, NJ, USA Bayer CropScience, Report No.: M-137847-02-3, Edition Number: M-137847-02-3 Date: 1992-09-17 GLP/GEP: yes, unpublished	N	N		Bayer CropScience	Y
KCA 7.1.3.1.2 /03	Rupprecht, J. K.	1999	The adsorption/desorption of (14C)-AE F088406 on six soils and one sediment AgrEvo USA Company, Pikeville, NC, USA Bayer CropScience, Report No.: C000921, Edition Number: M-181475-01-1 EPA MRID No.: 44768101 Date: 1999-02-22 GLP/GEP: yes, unpublished	N	N		Bayer CropScience	Y
KCA 7.1.3.1.2 /04	Allan, J. G.	1999	The adsorption/desorption of (14C)-AE F054014 on Nine Soils and One Sediment AgrEvo USA Company, Pikeville, NC, USA Bayer CropScience, Report No.: B004850, Edition Number: M-181470-02-1 Date: 1999-02-22 **...Amended: 2004-12-02** GLP/GEP: yes, unpublished	N	N		Bayer CropScience	Y

KCA 7.1.3.1.2 /05	Voelkel, W.	2008a	14C-fenoxaprop-P - Adsorption/desorption on soil RCC Ltd., Itingen, Switzerland TF- BCS-CHA, Report No.: 251 FPE, Edition Number: M-548178-01-1 Date: 2008-08-25 GLP/GEP: yes, unpublished	N	Y	Study performed to address data requirements in the EU	TF- BCS-CHA	N
KCA 7.1.3.1.2 /06	Voelkel, W.	2008b	14C-6-chloro-2,3-dihydrobenzoxazol-2-one (Metabolite of fenoxaprop-P-ethyl) - Adsorption/desorption on soil RCC Ltd., Itingen, Switzerland TF- BCS-CHA, Report No.: 250 FPE, Edition Number: M-548174-01-1 Date: 2008-08-25 GLP/GEP: yes, unpublished	N	Y	Study performed to address data requirements in the EU	TF- BCS-CHA	N
KCA 7.1.3.1.2 /07	Mills, E. A. M.	2010	[14C]-HPPA: Adsorption to and desorption from three soils Battelle UK Ltd., Chelmsford, Essex, United Kingdom TF- BCS-CHA, Report No.: 316 FPE, Edition Number: M-548276-01-1 Date: 2010-03-22 GLP/GEP: yes, unpublished	N	Y	Study performed to address data requirements in the EU	TF- BCS-CHA	N
KCA 7.1.4.1.1 /01	Gildemeister, H.; von Fleischbein, I.	1988	Examination of the leaching behaviour in accordance with BBA Guideline IV, 4-2 Code: Hoe 046360 Hoechst AG, Frankfurt am Main, Germany Bayer CropScience, Report No.: A43632, Edition Number: M-119529-01-2 Date: 1988-03-18 GLP/GEP: no, unpublished	N	N		Bayer CropScience	Y
KCA 7.1.4.1.1 /02	Buhl, H. J.; Schwab, W.; Mueller, A.	1993	Leaching behaviour of the formulated non-aged active ingredient in the presence of Hoe 070542 (Hoe 046360 01 EW11 A2) in the LUFA standard soils 2.1, 2.2 and 2.3 and leaching behaviour of the aged active ingredient in the LUFA standard soil 2.1 Hoechst AG, Frankfurt am Main, Germany Bayer CropScience, Report No.: C003248, Edition Number: M-132667-01-2 Date: 1993-11-26 GLP/GEP: yes, unpublished	N	N		Bayer CropScience	Y

KCA 7.1.4.1.1 /03	Tarara, G.	2003	Fenoxaprop-P-ethyl, AE F046360 Environmental fate and behaviour: The influence of the addition of a safener on the leaching behaviour and soil degradation of the active ingredient Statement Bayer CropScience, Report No.: C038236, Edition Number: M-224570-01-1 Date: 2003-11-28 GLP/GEP: n.a., unpublished	N	N		Bayer CropScience	Y
KCA 7.2.1.1 /01	van der Gaauw, A.	2002	(14C)-fenoxaprop-ethyl: Hydrolysis at five different pH values Code: AE F046360 RCC Ltd., Itingen, Switzerland Bayer CropScience, Report No.: C028353, Edition Number: M-215094-01-1 Date: 2002-11-13 GLP/GEP: yes, unpublished	N	N		Bayer CropScience	y
KCA 7.2.1.1 /02	Schollmeier, M.; Eyrich, U.	1993	Determination of the abiotic hydrolysis as a function of pH according to OECD Guideline #111 and EEC Guideline C.7. Hoe 088406 (Fenoxaprop-P) Metabolite of Hoe 046360 (Fenoxaprop-P-ethyl) Code: Hoe 088406 00 ZB88 0001 Hoechst AG, Frankfurt am Main, Germany Bayer CropScience, Report No.: A51145, Edition Number: M-132116-01-1 EPA MRID No.: 44659603 Date: 1993-08-11 GLP/GEP: yes, unpublished	N	N		Bayer CropScience	Y
KCA 7.2.1.1 /03	Burgener, A.	1999a	Hydrolysis of 14C-AE F054014 at different pH values RCC Ltd., Itingen, Switzerland Bayer CropScience, Report No.: C003621, Edition Number: M-186478-01-1 Date: 1999-03-29 GLP/GEP: yes, unpublished	N	N		Bayer CropScience	Y
KCA 7.2.1.1 /04	Fitzmaurice, M.	2008a	[14C]-Fenoxaprop-P-ethyl: Hydrolytic degradation at pH 4, 7 and 9 Battelle UK Ltd., Ongar, Essex, United Kingdom TF- BCS-CHA, Report No.: CX/05/001, Edition Number: M-344546-01-1 Date: 2008-05-13 GLP/GEP: yes, unpublished	N	Y	Study performed to address data requirements in the EU	TF- BCS-CHA	N

KCA 7.2.1.1 /05	Adam, D.	2008	[14C]-fenoxaprop-P-ethyl - Hydrolysis at three different pH values RCC Ltd., Itingen, Switzerland TF- BCS-CHA, Report No.: 244 FPE, Edition Number: M-548135-01-1 Date: 2008-05-28 GLP/GEP: yes, unpublished	N	Y	Study performed to address data requirements in the EU	TF- BCS-CHA	N
KCA 7.2.1.1 /06	Adam, D.	2007	14C-6-chloro-2,3-dihydrobenzoxazol-2-one (Metabolite of fenoxaprop-P-ethyl) - Hydrolysis at three different pH values RCC Ltd., Itingen, Switzerland TF- BCS-CHA, Report No.: 237 FPE, Edition Number: M-548134-01-1 Date: 2007-12-10 GLP/GEP: yes, unpublished	N	Y	Study performed to address data requirements in the EU	TF- BCS-CHA	N
KCA 7.2.1.2 /01	Schwab, W.	1993c	Photodegradation in surface water, sterile buffer and distilled water of Fenoxaprop-P-ethyl Hoe 046360-14C Hoechst AG, Frankfurt am Main, Germany Bayer CropScience, Report No.: A51353, Edition Number: M-132306-02-1 EPA MRID No.: 44664001, 44676401 Date: 1993-09-28 **...Amended: 1993-10-13** GLP/GEP: yes, unpublished	N	N		Bayer CropScience	Y
KCA 7.2.1.2 /02	Burgener, A.	1999b	Aqueous photolysis of 14C-AE F054014 under laboratory conditions RCC Ltd., Itingen, Switzerland Bayer CropScience, Report No.: C006616, Edition Number: M-194301-01-1 Date: 1999-12-20 GLP/GEP: yes, unpublished	N	N		Bayer CropScience	Y
KCA 7.2.1.2 /03	Fitzmaurice, M.	2008	[14C]-Fenoxaprop-P-ethyl: Aqueous photolysis in sterile buffer solution at pH 7 Battelle UK Ltd., Ongar, Essex, United Kingdom TF- BCS-CHA, Report No.: CX/05/031, Edition Number: M-344639-01-1 Date: 2008-11-06 GLP/GEP: yes, unpublished	N	Y	Study performed to address data requirements in the EU	TF- BCS-CHA	N

KCA 7.2.1.2 /04	Tarara, G.	2016	Identification of an unknown photo-transformation product observed in aqueous photolysis in sterile buffer solution at pH 7 - 14C-Fenoxaprop-P-ethyl (BCS-CA37044, AE F046360) TF- BCS-CHA, Report No.: EnSa-16-0323, Edition Number: M-554364-01-1 Date: 2016-05-11 GLP/GEP: yes, unpublished	N	Y	EU- and US-data requirements	TF- BCS-CHA	N
KCA 7.2.1.2 /05	Fletcher, T.; Gilbert, J.	2008	[14C]-fenoxaprop-P-ethyl: Photodegradation and quantum yield in sterile, aqueous solution Covance Laboratories Ltd, North Yorkshire, United Kingdom TF- BCS-CHA, Report No.: 268 FPE, Edition Number: M-548205-01-1 Date: 2008-12-16 GLP/GEP: yes, unpublished	N	Y	Data required for metabolites following the EFSA AGD	TF- BCS-CHA	N
KCA 7.2.1.2 /06	Adam, A.	2008b	14C-6-chloro-2,3-dihydrobenzoxazol-2-one (metabolite of fenoxaprop-P-ethyl) - Aqueous photolysis and determination of the quantum yield Harlan Laboratories Ltd., Itingen, Switzerland TF- BCS-CHA, Report No.: 267 FPE, Edition Number: M-548198-01-1 Date: 2008-11-26 GLP/GEP: yes, unpublished	N	Y	Study performed to address data requirements in the EU	TF- BCS-CHA	N
KCA 7.2.1.3 /01	Schwab, W.	1993c	Photodegradation in surface water, sterile buffer and distilled water of Fenoxaprop-P-ethyl Hoe 046360-14C Hoechst AG, Frankfurt am Main, Germany Bayer CropScience, Report No.: A51353, Edition Number: M-132306-02-1 EPA MRID No.: 44664001, 44676401 Date: 1993-09-28 **...Amended: 1993-10-13** GLP/GEP: yes, unpublished	N	N		Bayer CropScience	Y
KCA 7.2.2.1 /01	Hargreaves, T. L.; Murphy, C. M.	2005	Fenoxaprop-P-ethyl technical: Determination of ready biodegradability by the C02 evolution (modified sturm) test Charles River Laboratories, Tranent, United Kingdom TF- BCS-CHA, Report No.: 151 FPE, Edition Number: M-548090-01-1 Date: 2005-01-18 GLP/GEP: yes, unpublished	N	Y	Study performed to address data requirements in the EU	TF- BCS-CHA	N

KCA 7.2.2.2 /01	Telscher, M.; Junge, T.	2016a	[chlorophenyl-UL-14C]fenoxaprop-P-ethyl: Aerobic mineralisation in surface water TF- BCS-CHA, Report No.: EnSa-15-0163, Edition Number: M-551145-01-1 Date: 2016-03-21 GLP/GEP: yes, unpublished	N	Y	New EU data requirement	TF- BCS-CHA	N
KCA 7.2.2.2 /02	Telscher, M.; Junge, T.	2016b	[phenoxy-UL-14C]fenoxaprop-P-ethyl: Aerobic mineralisation in surface water TF- BCS-CHA, Report No.: EnSa-15-0232, Edition Number: M-553135-01-1 Date: 2016-04-18 GLP/GEP: yes, unpublished	N	Y	New EU data requirement	TF- BCS-CHA	N
KCA 7.2.2.3 /01	Tarara, G.	2000	Degradation in two sediment/water-systems at 20 degrees C under aerobic conditions (U-14C-chlorophenyl)AE F046360 Hoechst Schering AgrEvo GmbH, Frankfurt am Main, Germany Bayer CropScience, Report No.: C007688, Edition Number: M-227806-01-1 Date: 2000-03-16 GLP/GEP: yes, unpublished	N	N		Bayer CropScience	Y
KCA 7.2.2.3 /02	Fitzmaurice, M.	2004	[14C]-Fenoxaprop-P-Ethyl: Degradation and retention in two water/sediment systems Battelle AgriFood Ltd., Ongar, Essex, United Kingdom Bayer CropScience, Report No.: 41428002, Edition Number: M-242393-01-1 EPA MRID No.: 41428002, 41567702 Date: 2004-12-21 GLP/GEP: yes, unpublished	N	N		Bayer CropScience	Y
KCA 7.2.2.3 /03	Voelkel, W.	2000	Degradation and metabolism in an anaerobic aquatic system Code: 14C-AE F046360 / 14C-AE F033171 RCC Ltd., Environmental Chemistry & Pharmanalytics Division, Itingen, Switzerland Bayer CropScience, Report No.: C007381, Edition Number: M-195784-01-1 EPA MRID No.: 45081601 Date: 2000-03-02 GLP/GEP: yes, unpublished	N	N		Bayer CropScience	Y

KCA 7.2.2.3 /04	Xu, T.	2012	[phenoxy-UL-14C] and [chlorophenyl-UL-14C]fenoxaprop-P-ethyl: Aerobic aquatic metabolism in two sediment/water systems Bayer CropScience LP, Stilwell, KS, USA TF- BCS-CHA, Report No.: MEFPL007, Edition Number: M-431724-01-1 EPA MRID No.: 48868701 Date: 2012-05-30 GLP/GEP: yes, unpublished	N	Y	New EU data requirement	TF- BCS-CHA	N
KCA 7.2.2.3 /05	Mamouni, A.	2008	^{14}C-Fenoxaprop-P-ethyl - Route and rate of degradation in aerobic aquatic sediment systems Harlan Laboratories Ltd., Itingen, Switzerland TF- BCS-CHA, Report No.: 265 FPE, Edition Number: M-548188-01-1 Date: 2008-11-28 GLP/GEP: yes, unpublished	N	Y	Study performed to address data requirements in the EU	TF- BCS-CHA	N
KCA 7.2.2.3 /05	Crowe, A.	2018	Report Amendment 1: ^{14}C-Fenoxaprop-P-Ethyl: Route and Rate of Degradation in Aerobic Aquatic Sediment Systems Envigo CRS Limited, Alconbury, Huntingdon, Cambridgeshire, UK Report No.: DR26BS Edition Number: M-548188-02-1 Date: 2018-02-28 GLP/GEP: yes, unpublished	N	Y		TF- BCS-CHA	N
KCA 7.2.2.3 /07	Herrmann, M.; Wiedemann, G.; Boiselle, N.	2016	Fenoxaprop-P-ethyl and metabolites - Kinetic evaluation of the aerobic aquatic metabolism in water/ sediment systems under laboratory conditions TF- BCS-CHA, Report No.: EnSa-15-0387, Edition Number: M-555143-01-1 Date: 2016-05-18 GLP/GEP: no, unpublished	N	N		TF- BCS-CHA	N
KCA 7.3.1 /01	Buerkle, L. W.	1999	Estimation of the reaction with photochemically produced hydroxyl radicals in the atmosphere Code: AE F046360 Hoechst Schering AgrEvo GmbH, Frankfurt am Main, Germany Bayer CropScience, Report No.: C003258, Edition Number: M-185869-01-1 Date: 1999-03-17 GLP/GEP: no, unpublished	N	N		Bayer CropScience	Y

KCA 7.3.1 /02	Hellpointner, E.	2004	Calculation of the chemical lifetime of fenoxaprop-P-acid AE F088406 in the troposphere Bayer CropScience, Report No.: C043983, Report includes Trial Nos.: HPO-276 Edition Number: M-235572-01-1 Date: 2004-09-17 GLP/GEP: no, unpublished	N	N		Bayer CropScience	Y