

European Commission



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

ETHOFUMESATE

Volume 3 – B.8 (AS)

Rapporteur Member State: Austria

Co-Rapporteur Member State: Denmark

Version History

| When | What |
|---------|------------------|
| 1998 | Initial DAR |
| 2000/5 | Addendum 2 and 3 |
| 2000/12 | Addendum 8 |
| 2015/01 | DRAR |

Table of contents

| | |
|---|------------|
| RAPPORTER MEMBER STATE : AUSTRIA | 1 |
| B.8. ENVIRONMENTAL FATE AND BEHAVIOUR | 5 |
| B.8.1. FATE AND BEHAVIOUR IN SOIL | 7 |
| B.8.1.1. Route and rate of degradation in soil | 7 |
| B.8.1.1.1. Route of Degradation in Soil | 7 |
| B.8.1.1.1.1. Aerobic degradation (IIA 7.1.1; IIIA 9.1.1) | 7 |
| B.8.1.1.1.2. Anaerobic degradation of the active substance..... | 68 |
| B.8.1.1.1.3. Soil photolysis | 72 |
| B.8.1.1.2. Rate of degradation..... | 88 |
| B.8.1.1.2.1. Laboratory studies | 88 |
| B.8.1.1.2.1.1. Aerobic degradation of the active substance | 88 |
| B.8.1.1.2.1.2. Aerobic degradation of metabolites, breakdown and reaction products | 104 |
| B.8.1.1.2.1.3. Anaerobic degradation of the active substance..... | 156 |
| B.8.1.1.2.2. Field studies..... | 157 |
| B.8.1.1.2.2.1. Soil dissipation studies | 157 |
| B.8.1.1.2.2.2. Soil accumulation studies | 231 |
| B.8.1.1.3. Summary: soil studies..... | 233 |
| B.8.1.2. Adsorption and desorption in soil..... | 236 |
| B.8.1.2.1. Adsorption and desorption..... | 236 |
| B.8.1.2.1.1. Adsorption and desorption of the active substance..... | 236 |
| B.8.1.2.1.2. Adsorption and desorption of metabolites, breakdown and reaction products | 247 |
| B.8.1.2.2. Aged sorption | 256 |
| B.8.1.2.3. Summary: adsorption and desorption in soil | 257 |
| B.8.1.3. Mobility in soil | 257 |
| B.8.1.3.1. Column leaching studies..... | 257 |
| B.8.1.3.1.1. Column leaching of the active substance..... | 257 |
| B.8.1.3.1.2. Column leaching of metabolites, breakdown or reaction products..... | 267 |
| B.8.1.3.2. Lysimeter studies..... | 270 |
| B.8.1.3.3. Summary: mobility in soil | 301 |
| B.8.2. FATE AND BEHAVIOUR IN WATER AND SEDIMENT | 302 |
| B.8.2.1. Route and rate of degradation in aquatic systems (chemical and photochemical degradation)..... | 302 |
| B.8.2.2. Hydrolytic degradation | 302 |
| B.8.2.2.1. Direct photochemical degradation | 305 |
| B.8.2.2.2. Indirect photochemical degradation | 319 |
| B.8.2.3. Route and rate of biological degradation in aquatic systems..... | 322 |

| | |
|---|------------|
| B.8.2.3.1. “Ready biodegradability” | 322 |
| B.8.2.3.2. Aerobic mineralisation in surface water | 325 |
| B.8.2.3.3. Water/sediment study | 336 |
| B.8.2.3.4. Irradiated water/sediment study..... | 396 |
| B.8.2.4. Degradation in the saturated zone..... | 396 |
| B.8.2.5. Summary: fate and behaviour in water and sediment | 396 |
| B.8.3. FATE AND BEHAVIOUR IN AIR | 397 |
| B.8.3.1. Route and rate of degradation in air | 397 |
| B.8.3.2. Transport via air | 399 |
| B.8.3.3. Local and global effects..... | 399 |
| B.8.3.4. Summary: fate and behavior in air..... | 399 |
| B.8.4. DEFINITION OF THE RESIDUE..... | 399 |
| B.8.4.1. Definition of the residue for risk assessment..... | 399 |
| B.8.4.2. Definition of the residue for monitoring..... | 400 |
| B.8.5. MONITORING DATA CONCERNING FATE AND BEHAVIOUR OF THE ACTIVE SUBSTANCE, METABOLITES, DEGRADATION AND REACTION PRODUCTS | 400 |
| B.8.5.1. Summary monitoring data | 423 |
| B.8.6. REFERENCES RELIED ON..... | 424 |

B.8. ENVIRONMENTAL FATE AND BEHAVIOUR

Ethofumesate is an herbicidal active substance and was included into Annex I of Directive 91/414/EEC in 2002 (Directive 2002/37/EC, 3rd May 2002). Directive 91/414/EEC has been repealed by Regulation (EC) no 1107/2009 of 21 October 2009 concerning the placing of plant protection products on the market. Accordingly ethofumesate is deemed to have been approved under Regulation (EC) no 1107/2009, as set out in Part A of the Annex of Commission Implementing Regulation (EC) no 540/2011 as regards the list of approved substances (entry no. 29).

For the renewal of the approval of ethofumesate, two notifiers, TaskForce Ethofumesate (Bayer CropScience and Adama Deutschland GmbH (former Feinchemie Schwebda)) and UPL (United Phosphorus Limited), submitted complete dossiers by the deadline of January 31, 2014. The dossiers for the renewal contain new studies, for instance due to new triggers in soil and water/sediment studies, new guidance on the evaluation of laboratory and field degradation studies, and new data requirements such as the aerobic surface water mineralisation study.

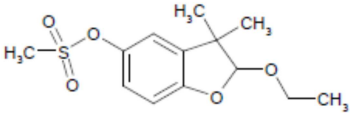
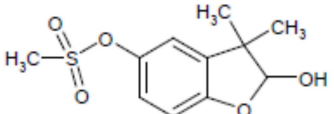
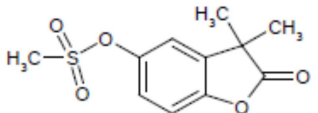
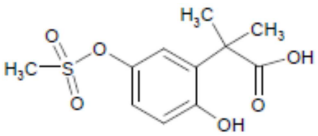
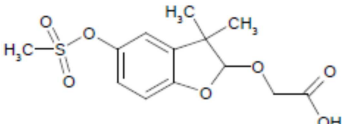
In this renewal assessment report (DRAR), all studies, which were already submitted for the Annex I inclusion under Directive 91/414/EEC, were re-evaluated according to the current valid test guidelines and were summarised in the RAR. The study evaluations originally provided in the DAR (RMS Sweden) were mostly re-worded and additional information was included in DRAR where considered necessary. Where study summaries from the previous DAR were of sufficient quality, they were taken over and only slightly adapted. Where significant information was missing, it was amended. Finally, the validity of studies in view of updated OECD guidelines was proven.

Ethofumesate is a racemic mixture of two enantiomers. In degradation studies (non-guideline lysimeter study and in a water sediment study) no significant changes in the ratio of the racemate (1:1) were observed, indicating that the degradation and distribution of both enantiomers is the same in the environment. Therefore it was considered adequate that all studies on the active substance were performed using the racemic mixture.

Search of the scientific peer reviewed open literature was conducted by both notifiers, covering a period from 2003 to 2013. Both notifiers stated that their literature search was conducted according to EFSA Guidance “Submission of scientific peer-reviewed open literature for the approval of pesticide active substances under Regulation (EC) No 1107/2009” (EFSA Journal 2011;9(2):2092. [49 pp.]). However, the literature search conducted by notifier UPL was not in line with this Guidance. Several relevant (and in part also reliable) sources were missed. In case where reliable and adequate literature was found during the literature search, summaries are integrated in the respective sections of the RAR.

The different synonyms and codes for the active substance ethofumesate and its metabolites used in the RAR are summarised in the table B.8-1.

Table 8-1: Substances and metabolites (structure, synonyms and codes)

| Codes and synonyms | Description (IUPAC) | Structure |
|--|--|---|
| Ethofumesate Synonym: ai a.s. NC 8438, AE B049913 | 2,3-dihydro-2-hydroxy-3,3-dimethylbenzofuran-5-yl methane-sulfonate |  |
| Ethofumesate-2-hydroxy Synonym: NC 8493, AE C508493, BCS-BB94377 2-hydroxy-ethofumesate HDBM | 2,3-dihydro-2-hydroxy-3,3-dimethylbenzofuran-5-yl methane-sulfonate |  |
| Ethofumesate-lactone Synonym: NC 9607, AE C509607 2-keto-Ethofumesate Ethofumesate-2-keto Oxo-derivative 2-oxo Ethofumesate | 2,3-dihydro-3,3-dimethyl-2-oxo-benzofuran-5-yl methanesulfonate |  |
| Ethofumesate-carboxylic acid Synonym: NC 20645, AE C520645, BCS-AV65501 ----- AE C639175 (potassium salt) BCS-CU88901 (sodium salt) HDS | 2-(2-hydroxy-5-methanesulfoxyphenyl)-2-methyl propionic acid |  |
| Ethofumesate-acetic acid Synonym: BCS-CW35117 | ({3,3-dimethyl-5-[(methylsulfonyl)oxy]-2,3-dihydro-1-benzofuran-2-yl}oxy)acetic acid |  |

B.8.1. FATE AND BEHAVIOUR IN SOIL

B.8.1.1. Route and rate of degradation in soil

B.8.1.1.1. Route of Degradation in Soil

B.8.1.1.1.1. Aerobic degradation

| | |
|---------------------|---|
| Reference: | The soil degradation of radiolabelled NC 8438 |
| Notifier: | Taskforce |
| Author(s), year: | Adcock, J. W.; Challis, I. R.; Warner, P. A.; (1974); Amended: 1975-05-01 |
| Report/Doc. number: | A83266 / W 10/2 / M-155706-02-1 |
| Guideline(s): | None |
| GLP: | No |
| Deviations: | Not specified |
| Validity: | Not valid |
| Status: | Previous evaluation in DAR for original approval / baseline dossier. |

Study summary based on previous draft assessment report

Materials and Methods

The transformation of benzene-(random ring-)¹⁴C and ³⁵S- labelled ethofumesate (NC8438) in a 20% EC formulation (Nortron) under sterile, aerobic, and anaerobic was investigated in a sandy loam from a garden in Essex (UK).

Table 8-2: Soil characteristics

| Soil | OC (%) | pH | sand (%) | silt (%) | clay (%) | MHC (%) | CEC (meq/ 100 g) |
|---------------|--------|-----|-------------|-------------|-------------|------------|---------------------|
| UK sandy loam | 2.5 | 7.6 | 64 | 18 | 21 | 35 | n.r |

n.r = not reported

The soils were treated with the formulated NC8438 at a dose of 3 mg as/kg (corresponding to 3.36 kg as/ha) and incubated in the dark at 20±2°C and 65% of its field moisture capacity. In the anaerobic, and in samples for later timepoints in the aerobic and sterile soils, ¹⁴CO₂ and other volatile compounds were trapped in methanol/ethanolamine (1:1). In the aerobic studies, triplicate samples were taken for analysis at various intervals up to 316 days after application. In the anaerobic studies, samples were taken 0 and 30 days after application (prior to induction of anaerobic conditions), and 60 and 90 days after application (after induction of anaerobiosis). In the sterile study, samples were taken after 0, 15, 30, 45, 60, 90 and 120 days. The soil samples were extracted with methanol/water (9:1). In the aerobic studies, the soil samples taken at day 45 were further

extracted with 6M HCl, 2M NaOH, 10M NaOH, N,N-dimethyl formamide, acetic acid or acetic anhydride. The radioactivity was quantified by LSC and characterised by TLC.

Results

The material balances of the applied radioactivity at termination of the aerobic studies are given in the table below.

Table 8-3: Material balance of applied ^{14}C -ethofumesate and ^{35}S -ethofumesate (within brackets) and residues after aerobic incubation in two sandy loam soils. The figures represent % of applied radioactivity.

| Soil | Days after application | NC8438 (%) | $^{14}\text{CO}_2$ (%) | Unextractable (%) | Total recovery (%) |
|------|------------------------|------------|------------------------|-------------------|--------------------|
| UK | 316 (316) | 9.7 (10) | 38 | 51 (90) | 99 |

No $^{35}\text{SO}_2$ or other transformation products were detected. In the anaerobic study, 90 % of the ^{14}C -labelled parent compound present after 30 days of aerobic conditions remained unaltered 60 days after induction of anaerobiosis. Under sterile conditions, 92 and 91% of applied ^{14}C - and ^{35}S -labelled ethofumesate, respectively, remained unaltered after 120 days.

Comments RMS

The aerobic and anaerobic transformation of benzene-(random ring-) ^{14}C - and ^{35}S - labelled ethofumesate 20% EC formulation was investigated in a non-guideline study sandy loam soil from a garden in Essex, UK. The purity of the active substance was not reported. After being air-dried and sieved, the soils were treated with formulated ethofumesate at a dose of 3 mg as/kg (corresponding to 3.36 kg as/ha) and incubated in the dark at $20\pm 2^\circ\text{C}$ and 65% of their field moisture capacity. No pre-incubation period is reported. The soil samples were extracted with methanol/water (9:1), the radioactivity was quantified by LSC and characterised by TLC.

The experiment was conducted with the formulated product; however, the effect of the formulation on microbial biomass and/or activity was not tested. Moreover, the microbial biomass of the soils was not determined. This is especially critical, since – according to the study protocol – the soil was air-dried and sieved and then immediately spiked with the test solution without any pre-incubation of the soil. Therefore, it is highly probable that its microbiology was not comparable to fresh or properly stored soils as it could not recover from the dry phase. Therefore results of the study appear not reliable.

Soil samples were incubated in screw-cap jars. Lids were lightly placed on all jars, except the 230 and 300 day groups, to prevent excessive moisture loss. The lids were occasionally removed to allow aeration of the soil. Therefore, volatiles and $^{14}\text{CO}_2$ might have been lost and the mass balance is highly questionable.

In the aerobic study, recoveries range between 94.2 % AR (227 DAT) and 101.5% AR (45 DAT). At day zero no extraction was performed, therefore no recoveries were determined for study beginning. No transformation products were detected, no unknown radioactivity is reported. Neither the limit of detection, nor the limit of quantification is reported.

Regarding the anaerobic study, the recoveries during the anaerobic phase were claimed to be in the same range as those during the aerobic phase preceding anaerobiosis. However, this cannot be verified since no detailed measured values for the anaerobic and sterile study are reported.

In view of these deficiencies, the study cannot be considered valid.

| | |
|---------------------|--|
| Reference: | Degradation in soil under aerobic conditions 14C Ethofumesate |
| Notifier: | Taskforce |
| Author(s), year: | Hall, B. E., Cameron, B. D.; Phillips, M.; (1991) |
| Report/Doc. number: | A87600 / W 500 / M-161526-01-1 |
| Guideline(s): | BBA: IV, Section 4.1 (1986). |
| GLP: | Yes |
| Deviations: | Not specified |
| Validity: | Not valid |
| Status: | Previous evaluation in DAR for original approval / baseline dossier. |

Study summary based on previous draft assessment report.

Materials and Methods

The aerobic transformation of U-phenyl-¹⁴C-labelled ethofumesate (radiochemical purity 100%) was investigated in Speyer Standard Soil 2.2 and three freshly collected soils in accordance with BBA Guidelines IV-4.1, 1986.

Table 8-4: Soil characteristics

| Soil | OC (%) | pH | sand (%) | silt (%) | clay (%) | MWHC (%) | CEC meq/ 100 g |
|-----------------------|-----------|-----|-------------|-------------|-------------|-------------|-------------------|
| Speyer 2.2 silty sand | 2.6 | 5.0 | 85 | 11 | 4.2 | n.r | 13 |
| Sandy loam | 2.2 | 5.5 | 60 | 28 | 12 | n.r | 9.2 |
| Silty clay loam | 2.9 | 6.7 | 15 | 53 | 32 | n.r | 10 |
| Clay loam | 3.3 | 7.4 | 33 | 47 | 20 | n.r | 33 |

The soils were treated with 3.1 mg a.s./kg dw, dissolved in methanol and applied evenly to the surface of each soil sample. The samples were incubated in the dark at ca. 21±2°C and 40% of their maximum water holding capacity. ¹⁴CO₂ and organic volatiles were trapped in ethanediol and ethanolamine. Duplicate samples were

taken for analysis at 0, 1, 2, 4, 8, 16, 32, 64 and 100 days after application. The soil samples were extracted with acetonitrile. The radioactivity was quantified by LSC and characterised by TLC.

Results

The material balance at the end of the incubation is given in the table below.

Table 8-5: Material balance of applied ^{14}C -ethofumesate after 100 days of incubation in soils maintained in the dark at $21\pm 2^\circ\text{C}$.

| Soil | NC8438 (%) | CO_2 (%) | Unextractable (%) | Total (%) |
|-----------------|---------------|----------------------|----------------------|--------------|
| Speyer 2.2 | 33 | 13 | 34 | 85 |
| Sandy loam | 48 | 8.7 | 31 | 93 |
| Silty clay loam | 50 | 4.8 | 34 | 94 |
| Clay loam | 44 | 12 | 29 | 90 |

No transformation products were identified in the soils throughout the study, and no unknown fraction accounted for more than 3% of applied radioactivity. The half-life of ethofumesate was determined to 61, 99, 113 and 84 days ($r^2=0.98$) in Speyer 2.2, sandy loam, silty clay loam and clay loam, respectively, assuming first order kinetics by a Timme model.

The microbial respiration levels were determined to 6.7, 5.5, 11 and 5.4 $\text{mg CO}_2/12 \text{ h } \hat{100} \text{ g soil}$ pre-application, and 10, 9.7, 14 and 13 $\text{mg CO}_2/12 \text{ h } \hat{100} \text{ g soil}$ after incubation under test conditions for 104 days in Speyer 2.2, sandy loam, silty clay loam and clay loam, respectively.

Table 8-6: Proportions of Applied Radioactivity Recovered as (^{14}C)-Ethofumesate

| Sampling interval (days) | Mean Proportion (%) of Applied Dose Recovered as (^{14}C)-Ethofumesate | | | |
|--------------------------|---|------------|-----------------|-----------|
| | Standard Soil 2.2 | Sandy Loam | Silty Clay Loam | Clay Loam |
| 0 | 96.55 | 95.1 | 94.36 | 95.49 |
| 1 | 97.31 | 91.79 | 92.85 | 95.22 |
| 2 | 95.18 | 92.69 | 93.83 | 93.24 |
| 4 | 95.05 | 92.89 | 92.44 | 92.94 |
| 8 | 90.68 | 90.53 | 91.17 | 89.35 |
| 16 | 84.48 | 83.49 | 83.7 | 81.64 |
| 32 | 67.53 | 72.13 | 75.32 | 74.33 |
| 64 | 44.6 | 56.75 | 66.93 | 53.15 |
| 100 | 32.65 | 47.92 | 50.22 | 43.91 |

Comments RMS

The aerobic transformation of U-phenyl-14C-labelled ethofumesate was investigated in Speyer Standard Soil 2.2 and three freshly collected soils (sandy loam, silty clay loam, clay loam). The soils were dosed with ethofumesate at a rate of 3.1 mg/kg, dissolved in methanol and applied evenly to the surface of each soil sample. The samples were incubated in the dark at ca. 21±2°C and 40% of their maximum water holding capacity.

No pre-incubation period is mentioned. The soil samples (50g) were extracted with acetonitrile (2 x 100mL). Where extractability was less than 90%, the extraction procedure was conducted one further time. The radioactivity was quantified by LSC and characterised by TLC.

The microbial activity was higher at the end of the incubation than at start in all soils. However, the determination of microbial activity was performed in untreated soil, and therefore cannot be used to explain any potential influence of ethofumesate on soil respiration.

Sampling depths were recorded only for three out of four soils. None of these sampling depths matches the requirements of OECD 307 as they were sampled at 10-40 cm, 10-35 cm, 5-35 cm. In addition, the history of the field sites where samples were taken is not reported. According to the study report, soils were stored at 30% WHC in the dark at ambient temperature prior analysis. This is not in line with OECD 307 and might have affected the microbial activity of the soils.

Fundamental soil parameters are missing. The water holding capacity of the soils is not reported. In addition, only microbial respiration is given, not the actual microbial biomass. When converting with the factor of 20.6 (Schinner et al., 1993), microbial biomass at study beginning is < 1% of TOC for 3 out of 4 soils (Sandy loam, Silty clay loam, Clay loam).

Generally, during the study the recoveries are acceptable, although in the Speyer 2.2 soil at study end the recovered radioactivity drops below 90%. The study duration is 100 d, but at study end in all studies between 33% and 50% AR were still present as ethofumesate. As described in the OECD 307 guideline, aerobic studies might be terminated much before 120 days provided that ultimate transformation pathway and ultimate mineralisation are clearly reached at that time. Termination of the test would be possible after 120 days, or when at least 90% of the test substance is transformed, but only if at least 5% CO₂ is formed. This was not the case in this study and the termination of the test with up to 50% of the test substance still present is not deemed acceptable.

Fundamental information on the analytical procedures is missing. The limit of quantification is not mentioned and the limit of determination is specified as 30 d.p.m. above background. No further quantification (LOD in % AR or mg kg⁻¹) is provided.

In view of the above mentioned pitfalls, the study cannot be considered as valid.

| | |
|---------------------|---|
| Reference: | [14C]-Ethofumesate: aerobic metabolism in two soils at two moisture contents |
| Notifier: | Taskforce |
| Author(s), year: | Waring, A.R.; (1992) |
| Report/Doc. number: | A83385 / W 129 / M-155653-01-1 |
| Guideline(s): | USEPA (=EPA): subdiv.N, 162-1; Deviation not specified |
| GLP: | Yes |
| Deviations: | |
| Validity: | Valid |
| Status: | Previous evaluation in DAR for original approval / baseline dossier. |

Adapted study summary based on previous draft assessment report

I. MATERIALS AND METHODS

A. Materials

- Test Material (reference):** [¹⁴C]- Ethofumesate
Code: NC 8438
Radiochemical purity: >98%;
Specific radioactivity: 3.00 MBq / mg (80.99 µCi/mg)
CAS No.: 26225-79-6
- Test Material (reference):** Ethofumesate
Code: NC 8438
Purity: 99.9%;
CAS No.: 26225-79-6
- Test Material (reference):** 2,3-dihydro-2-hydroxy-3,3-dimethylbenzofuran-5-yl-Methanesulfonate
Code: NC 8493
Purity: >99%;
CAS No.: not specified
- Test Material (reference):** (±)-2-ethoxy-2,3-dihydro-3,3-dimethyl-5-hydroxybenzofuran
Code: NC 10458
Purity: not specified;
CAS No.: not specified

5. **Test Material (reference):** 2,3-dihydro-3,3-dimethyl-2-oxobenzofuran-5-ylmethanesulfonate
Code: NC 9607
Purity: 99.8%
CAS No.: not specified
6. **Test Material (reference):** 2,3-dihydro-3,3-dimethyl-2,5-dihydroxybenzofuran
Code: NC 17900
Purity: > 99%
CAS No.: not specified
7. **Test Material (reference):** 2-(2-hydroxy-5-methanesulfoxyphenyl)-2-methylpropanoic acid
Code: NC 20645
Purity: not specified;
CAS No.: not specified

8. **Soils:** Two soil types, a sandy loam and a loam/silt loam, sieved through a 2mm mesh were used.

Table 8-7: Physico-chemical properties of the investigated soils Abington and Terling

| Property | Abington | Terling |
|--|------------|----------------|
| Particle size distribution (%): | | |
| Coarse sand 600 um - 2 mm | 3 | 2 |
| Medium sand 212 - 60 0um | 36 | 5 |
| Fine sand 63 - 212 um | 23 | 8 |
| Coarse silt 20 - 63 um | 14 | 38 |
| Fine silt 2 - 20 um | 9 | 21 |
| Clay <2 um | 15 | 26 |
| Textural class (USDA): | Sandy loam | loam/silt loam |
| Organic matter % | 3.5 | 5.1 |
| Cation exchange capacity (meq/100 g): | 14.9 | 24.8 |
| pH (water): | 7.6 | 6.5 |
| pH (CaCl ₂): | 7 | 5.8 |
| Calcium carbonate % | 9 | <0.1 |
| Field moisture capacity at 33 kPa (%): | 17.31 | 28.98 |

Table 8-8: Microbial biomass in the investigated soils Abington and Terling

| Microbial biomass (ug carbon/g soil) | | | |
|---|--------------------------------|-------------------------|-------------------------|
| Soil type/soil moisture content | Temperature of incubation (°C) | Prior to start of study | At termination of study |
| Abington/75% of its water capacity at 33kPa | 25 | 708.18 | 372.53 |
| Terling/75% of its water capacity at 33 kPa | 25 | 848.8 | 605.34 |
| Abington/1.75% w/w | 25 | ND | 433.81 |
| ND = Not determined | | | |

B. STUDY DESIGN

1. Experimental conditions

The aerobic transformation of U-phenyl-¹⁴C-labelled ethofumesate was investigated in duplicate incubations of a sandy loam soil and a loam/silt loam soil. Moistened carbon dioxide free air was drawn through each unit, before being passed through a series of five traps, the first acting as a security trap, the second containing ethanediol (ca 50 ml) to trap polar organic volatiles, the third containing sulphuric acid (0.1 M, ca 50 ml) to trap basic volatiles, and the final two containing ethanolamine (ca, 50 ml) to trap liberated carbon dioxide. Soils were treated with ethofumesate at 4.8 mg/kg (corresponding to 4.8 kg/ha) or ten times this rate (48 mg/kg in four samples of sandy loam soil to facilitate identification of metabolites). The test substance, dissolved in acetonitrile, was applied dropwise onto the soil surfaces, and incubated in the dark at ca. 25°C and 75% of their moisture content at 33 kPa. The transformation of ethofumesate was also investigated in the sandy loam soil maintained at 1.75% moisture content for up to one year. ¹⁴CO₂ and organic volatiles were trapped in ethanediol, sulphuric acid and ethanolamine.

2. Sampling

Samples were taken for analysis at various intervals up to 365 days after application.

3. Description of analytical procedures

The soil samples were extracted with toluene followed by acetonitrile:water (4:1v/v). The radioactivity was quantified by LSC and characterised by TLC/autoradiography. Unextractable soil residues were determined by LSC after combustion. The LOD was 0.47 % AR.

C. RESULTS AND DISCUSSION

In the soils incubated at 75% WHC microbial biomass decreased during the study. In the Abington sandy loam, microbial biomass decreased from 2 % of OC at study beginning to 1.1 % at study end. In the Terling loam/silt loam microbial biomass decreased from 1.7 % of OC at study beginning to 1.2% at study end.

Initially >97% of the radioactivity was recovered in both soils at the two moisture contents described. For all incubated soils, a reduction in total radioactivity recovered was observed throughout the study period. In the sandy loam maintained at 75% WHC, recoveries remained consistently above 90% with one exception at day 180 (89.93% AR). In the loam/silt loam maintained at 75% WHC, recoveries were below 90% at 4 out of 12 sampling days (min. 87.04% AR). In the sandy loam maintained at 1.75% w/w moisture content, recoveries were consistently above 90%. Mineralization to carbon dioxide (CO₂), occurred over the duration of the study reaching 22% and 25% of applied, for moist sandy loam and loam/silt loam respectively, by 365 days. In contrast only 12% of the radioactivity was evolved as CO₂ from the dry sandy loam soil. The amount of

unextractable radioactivity ('bound residue') increased with time reaching 55% and 57% respectively for the moist sandy loam and loam/silt loam after 365 days. Unextracted radioactivity accounted for 41% of the applied radioactivity after 365 days, for the dry sandy loam soil.

Table 8-9: Percentage of applied radioactivity characterised as ethofumesate and its degradates in Terling loam/silt loam soil maintained 25°C and 75% of its water capacity at 33kPa.

| Time point | Replicate | Ethofumesate | NC20645 | NC8493 | NC9607 | NER | CO ₂ | Volatiles | Total |
|---|-----------|--------------|---------|--------|--------|-------|-----------------|-----------|--------|
| 0 Day | A | 95.01 | ND | ND | ND | 0.18 | NA | NA | 98.28 |
| | B | 100.43 | ND | ND | ND | 0.11 | NA | NA | 102.71 |
| | Mean | 97.72 | ND | ND | ND | 0.15 | NA | NA | 100.5 |
| 3 Day | A | 90.32 | ND | ND | ND | 3.04 | 0.17 | ND | 96.13 |
| | B | 89.79 | ND | ND | ND | 2.58 | 0.11 | ND | 95.39 |
| | Mean | 90.06 | ND | ND | ND | 2.81 | 0.14 | ND | 95.76 |
| 10 Day | A | 85.55 | ND | ND | ND | 5.9 | 0.59 | ND | 95.19 |
| | B | 86.62 | ND | ND | ND | 4.58 | 0.35 | ND | 93.4 |
| | Mean | 86.08 | ND | ND | ND | 5.24 | 0.47 | ND | 94.29 |
| 17 Day | A | 81.17 | ND | ND | ND | 10.07 | 0.96 | ND | 94.73 |
| | B | 78.81 | ND | ND | ND | 10.59 | 1.55 | ND | 95.44 |
| | Mean | 79.99 | ND | ND | ND | 10.33 | 1.26 | ND | 95.08 |
| 24 Day | A | 73.33 | 0.28 | ND | 0.44 | 15.09 | 1.98 | ND | 94.78 |
| | B | 80.29 | 0.31 | ND | 0.28 | 5.73 | 1.5 | ND | 90.81 |
| | Mean | 76.81 | 0.29 | ND | 0.36 | 10.41 | 1.74 | ND | 92.8 |
| 45 Day | A | 59.02 | 0.27 | ND | 0.38 | 25.94 | 3.13 | 0.01 | 93.56 |
| | B | 63.01 | 0.17 | ND | 0.39 | 24.05 | 3.31 | ND | 94.27 |
| | Mean | 61.01 | 0.22 | ND | 0.38 | 25 | 3.22 | 0.01 | 93.92 |
| 66 Day | A | 53.87 | 0.38 | ND | ND | 28.4 | 4.54 | ND | 90.24 |
| | B | 39.83 | 0.23 | ND | ND | 39.81 | 5.18 | ND | 88.44 |
| | Mean | 46.85 | 0.3 | ND | ND | 34.11 | 4.86 | ND | 89.34 |
| 90 Day | A | 33.29 | 0.19 | 0.12 | ND | 42.09 | 11.94 | 0.13 | 89.35 |
| | B | 42.43 | ND | 0.03 | ND | 36.61 | 6.37 | 0.01 | 85.84 |
| | Mean | 37.86 | 0.1 | 0.08 | ND | 39.35 | 9.16 | 0.07 | 87.6 |
| 120 Day | A | 24.78 | 0.35 | ND | 0.18 | 50.25 | 12.84 | ND | 91.09 |
| | B | 30.87 | 0.43 | ND | 0.25 | 45.71 | 11.6 | ND | 91.35 |
| | Mean | 27.82 | 0.39 | ND | 0.22 | 47.98 | 12.22 | ND | 91.22 |
| 180 Day | A | 21.88 | 0.27 | 1.01 | ND | 47.13 | 13.89 | ND | 86.09 |
| | B | 8.19 | 0.09 | 0.21 | ND | 54.99 | 22.78 | ND | 87.98 |
| | Mean | 15.03 | 0.18 | 0.61 | ND | 51.06 | 18.34 | ND | 87.04 |
| 270 Day | A | 14.71 | 0.25 | 0.06 | ND | 55.21 | 20.53 | ND | 92.05 |
| | B | 6.76 | 0.31 | 0.15 | ND | 43.96 | 31.27 | ND | 84.6 |
| | Mean | 10.74 | 0.28 | 0.1 | ND | 49.59 | 25.9 | ND | 88.33 |
| 365 Day | A | 5.01 | 0.29 | 0.29 | 0.08 | 57.55 | 23.86 | ND | 88.47 |
| | B | 4.37 | 0.95 | 0.3 | 0.14 | 57.04 | 25.7 | ND | 92.88 |
| | Mean | 4.69 | 0.62 | 0.3 | 0.11 | 57.3 | 24.78 | ND | 90.68 |
| NA = Not Applicable | | | | | | | | | |
| ND = Not Detected (<0.01% of applied radioactivity) | | | | | | | | | |

Table 8-10: Percentage of applied radioactivity characterised as ethofumesate and its degradates in Abington sandy loam soil maintained 25°C and 75% of its water capacity at 33kPa.

| Timepoint | Replicate | Ethofumesate | NC20645 | NC8493 | NC9607 | NER | CO ₂ | Volatiles | Total |
|---|-----------|--------------|---------|--------|--------|-------|-----------------|-----------|--------|
| 0 Day | A | 97.18 | ND | ND | ND | 0.18 | NA | NA | 98.44 |
| | B | 94.93 | ND | ND | ND | 0.17 | NA | NA | 97.2 |
| | Mean | 96.06 | ND | ND | ND | 0.18 | NA | NA | 97.82 |
| 3 Day | A | 90.81 | ND | ND | ND | 2.11 | ND | ND | 95.52 |
| | B | 90.06 | ND | ND | ND | 1.89 | 0.11 | ND | 94.76 |
| | Mean | 90.43 | ND | ND | ND | 2 | 0.06 | ND | 95.14 |
| 10 Day | A | 88.85 | ND | ND | ND | 3.43 | 0.23 | ND | 94.83 |
| | B | 91.41 | ND | ND | ND | 2.72 | 0.23 | ND | 95.3 |
| | Mean | 90.13 | ND | ND | ND | 3.08 | 0.23 | ND | 95.3 |
| 17 Day | A | 79.57 | ND | ND | ND | 7.96 | 1.2 | ND | 93.61 |
| | B | 84.88 | ND | ND | ND | 3.89 | 0.82 | ND | 92.55 |
| | Mean | 82.23 | ND | ND | ND | 5.93 | 1.01 | ND | 93.08 |
| 24 Day | A | 84.8 | 0.49 | 0.18 | 0.61 | 5.07 | 0.62 | ND | 95.81 |
| | B | 84.4 | 0.56 | 0.29 | 0.29 | 12.78 | 0.71 | ND | 103.64 |
| | Mean | 84.6 | 0.52 | 0.23 | 0.45 | 8.93 | 0.67 | ND | 99.73 |
| 45 Day | A | 69.87 | 1.58 | ND | 0.66 | 12.71 | 1.45 | ND | 93.52 |
| | B | 61.55 | 1.01 | ND | 0.72 | 21.4 | 3.85 | ND | 92.19 |
| | Mean | 65.71 | 1.29 | ND | 0.69 | 17.06 | 2.65 | ND | 92.86 |
| 66 Day | A | 67.22 | 0.86 | 0.22 | 0.24 | 17.42 | 1.81 | ND | 91.82 |
| | B | 66.38 | 0.68 | 0.21 | 0.22 | 18.53 | 2.35 | ND | 92.76 |
| | Mean | 66.8 | 0.77 | 0.21 | 0.23 | 17.98 | 2.08 | ND | 92.29 |
| 90 Day | A | 43.1 | 0.65 | 0.15 | 0.36 | 32.99 | 7.47 | ND | 90.42 |
| | B | 77.62 | 0.35 | ND | 1.26 | 9.52 | 1.04 | ND | 93.82 |
| | Mean | 60.36 | 0.5 | 0.07 | 0.81 | 21.2 | 4.26 | ND | 92.12 |
| 120 Day | A | 66.86 | 2.22 | ND | 0.25 | 18.52 | 0.52 | ND | 91.33 |
| | B | 52.3 | 1.42 | ND | 0 | 29.09 | 4.83 | ND | 90.24 |
| | Mean | 59.58 | 1.82 | ND | 0.13 | 23.81 | 2.68 | ND | 90.79 |
| 180 Day | A | 31.31 | 0.82 | ND | ND | 40.42 | 13.28 | ND | 89.21 |
| | B | 49.64 | 1.87 | ND | ND | 28.68 | 5.48 | ND | 90.45 |
| | Mean | 40.48 | 1.35 | ND | ND | 34.55 | 9.38 | ND | 89.83 |
| 270 Day | A | 13.61 | 0.13 | 0.18 | ND | 52.41 | 22.36 | ND | 90.83 |
| | B | 18 | 0.59 | 0.16 | ND | 51.26 | 18 | ND | 91.06 |
| | Mean | 15.8 | 0.36 | 0.17 | ND | 51.84 | 20.18 | ND | 90.95 |
| 365 Day | A | 13.28 | 0.31 | ND | 0.13 | 54.97 | 23.73 | ND | 93.63 |
| | B | 14.57 | 0.42 | ND | 0.12 | 54.21 | 20.17 | ND | 91.98 |
| | Mean | 13.93 | 0.36 | ND | 0.12 | 54.59 | 21.95 | ND | 92.81 |
| NA = Not Applicable | | | | | | | | | |
| ND = Not Detected (<0.01% of applied radioactivity) | | | | | | | | | |

Comments RMS

The aerobic transformation of U-phenyl-14C-labelled ethofumesate was investigated in duplicate incubations of a sandy loam soil and a loam/silt loam soil. Soils were freshly sampled and pre-incubated upon arrival at 25°C. The microbial biomass decreased over time, but was still > 1% TOC at study end.

Soils were treated with ethofumesate at 4.8 mg/kg (corresponding to a field rate of 4.8 kg/ha). The test

substance, dissolved in acetonitrile, was applied dropwise onto the soil surfaces, and incubated in the dark at ca. 25°C and 75% of their moisture content at 33 kPa, which results in gravimetric water contents of the Abington and Terling soil of 13.0 % and 21.7 %, respectively. Maximum water holding capacity was not determined. Taking into account default gravimetric water contents for sandy loams and loams (FOCUS, 2000), this corresponds to 48% and 70 % of the maximum water holding capacity for the Abington and the Terling soil, respectively.

The transformation of ethofumesate was also investigated in the sandy loam soil maintained at 1.75% w/w water content for up to one year. The study is generally in line with the OECD 307 guideline. However, the Abington sandy loam incubated at 1.75% w/w water content cannot be further considered as it is considerably below the moisture content required by OECD 307.

Recoveries differed between the Abington sandy loam and the Terling loam/sandy loam. In the Abington sandy loam, recovery was below 90% only in one out of 24 individual samples, whereas in the Terling loam/sandy loam seven individual samples were below 90%. When considering the replicates' mean values, recovery was below 90% in 4 out of 12 samples in the Terling soil. Therefore, results for the Terling soil were excluded.

Main findings:

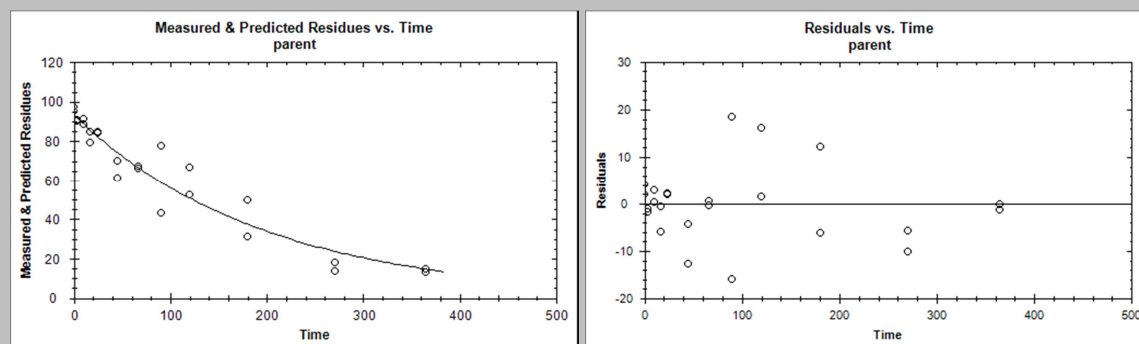
- Metabolites NC20645, NC8493 and NC9607 consistently below 5% AR.
- Bound residue: 54.59% AR (365 DAT)
- Mineralization: 21.95% AR (365 DAT)

The regulatory endpoints are:

| Soil | Model | DT ₅₀ [days] | DT ₉₀ [days] | Chi Squared (χ^2) |
|-----------------------|-------|----------------------------|----------------------------|--------------------------|
| Abington (Sandy loam) | SFO | 137 | 454 | 5.82 |

Degradation kinetics of the Abington sandy loam (re-calculated by RMS with KinGUI 2):

Figure 8-1: Kinetic evaluation Abington sandy loam SFO



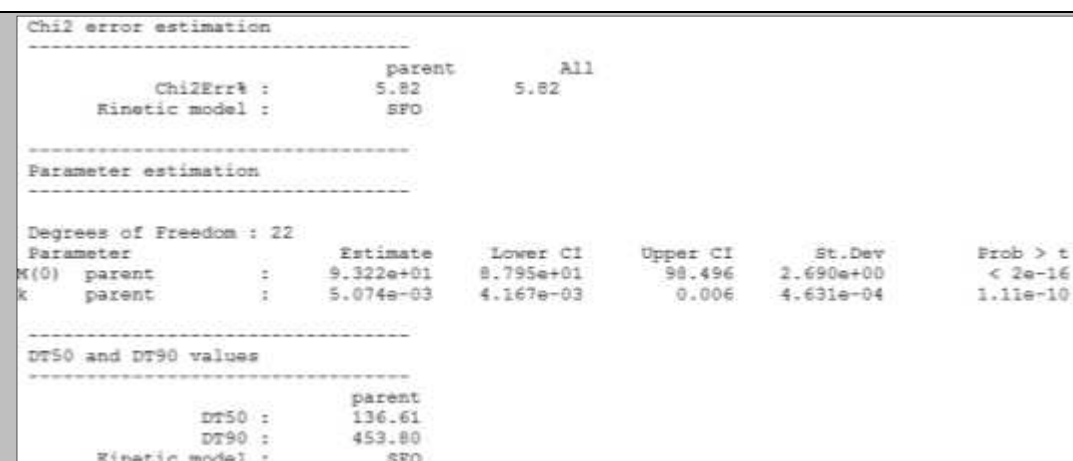


Figure 8-2: Kinetic evaluation Abington sandy loam FOMC

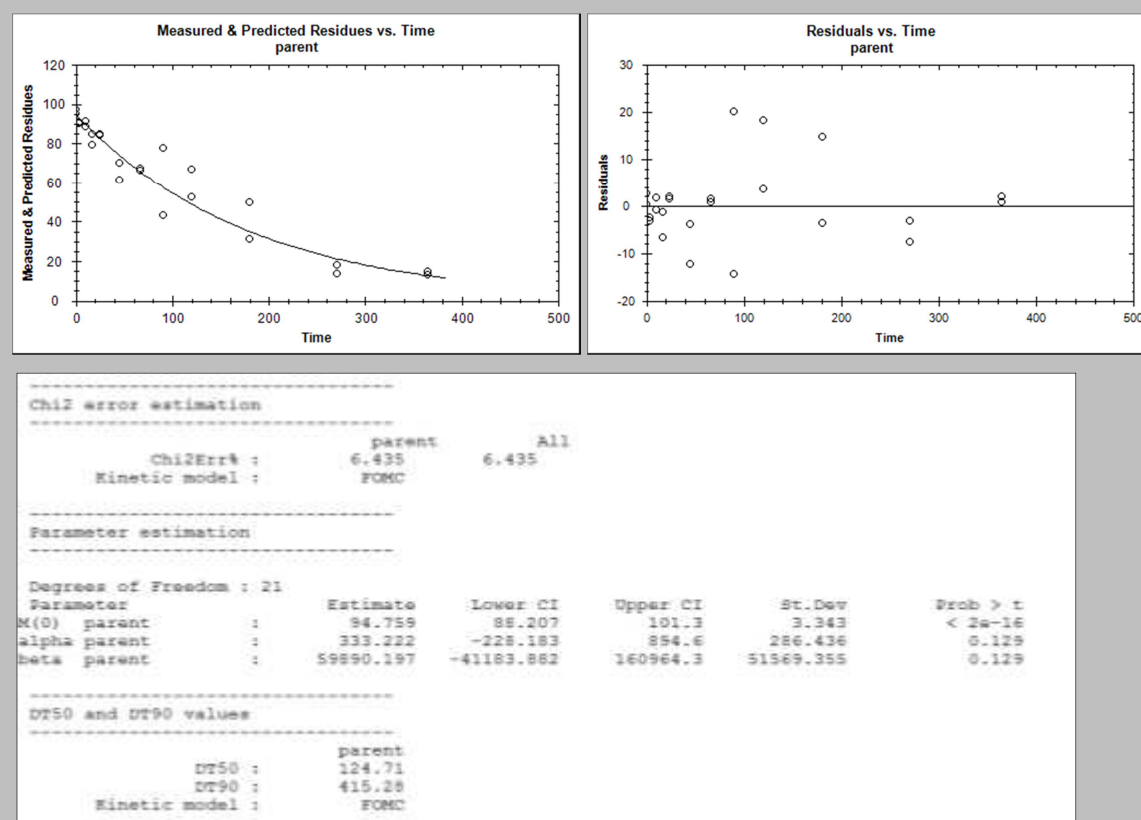
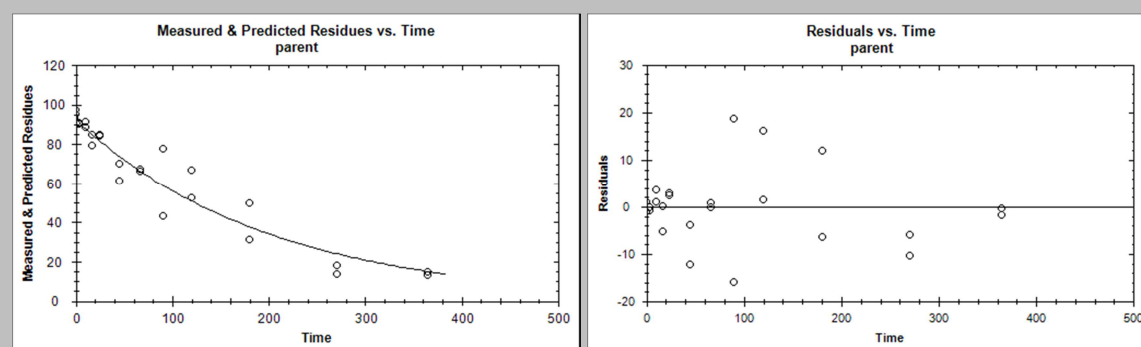


Figure 8-3: Kinetic evaluation Abington sandy loam DFOP



| | | | | | | |
|-------------------------|--------|-----------|------------|----------|-----------|----------|
| Chi2 error estimation | | | | | | |
| ----- | | | | | | |
| Chi2Err% | | parent | All | | | |
| Kinetic model : | | DFOP | 6.176 | | | |
| ----- | | | | | | |
| Parameter estimation | | | | | | |
| ----- | | | | | | |
| Degrees of Freedom : 20 | | | | | | |
| Parameter | | Estimate | Lower CI | Upper CI | St.Dev | Prob > t |
| M(0) | parent | 9.623e+01 | 8.457e+01 | 107.886 | 5.347e+00 | 2.95e-13 |
| k1 | parent | 3.198e+00 | -1.565e+02 | 162.945 | 8.151e+01 | 0.485 |
| k2 | parent | 4.989e-03 | 4.048e-03 | 0.006 | 4.801e-04 | 8.25e-10 |
| g | parent | 4.025e-02 | -8.958e-02 | 0.170 | 6.624e-02 | 0.275 |
| ----- | | | | | | |
| DT50 and DT90 values | | | | | | |
| ----- | | | | | | |
| DT50 : | | parent | 130.69 | | | |
| DT90 : | | parent | 453.26 | | | |
| Kinetic model : | | DFOP | | | | |

| | |
|---------------------|---|
| Reference: | (¹⁴ C)-Ethofumesate: Aerobic metabolism in a standard soil (Speyer 2.2) |
| Notifier: | Taskforce |
| Author(s), year: | Waring, A.R.; (1993) |
| Report/Doc. number: | A83398/ W 156 / M-155666-01-1 |
| Guideline(s): | Biologische Bundesanstalt Guidelines, Part IV, Section 4-1 Stage 1 (December 1986) |
| GLP: | Yes |
| Deviations: | |
| Validity: | Not valid |
| Status: | Previous evaluation in DAR for original approval / baseline dossier. |

Study summary based on previous draft assessment report

Materials and Methods

The aerobic transformation of benzene-¹⁴C-labelled ethofumesate (NC8438, purity >98.6%) was investigated in a loamy sand soil in accordance with BBA Guideline 4-1, 1986.

Table 8-11: Physico-chemical characteristics of the investigated soil.

| Soil | OC (%) | pH | sand (%) | silt (%) | clay (%) | MHC (%) | CEC (meq/100 g) |
|------------|-----------|-----|-------------|-------------|-------------|------------|--------------------|
| Loamy sand | 2.5 | 5.8 | 82 | 13 | 5.1 | 53 | 26 |

The soils were treated with 4.7 mg NC8438/kg (corresponding to 4.7 kg/ha), applied dropwise on top of the soil samples, and incubated in the dark at 20°C and appr. 40% of its maximum water holding capacity. ¹⁴CO₂ and organic volatiles were trapped in ethanediol, sulphuric acid and ethanolamine. Duplicate samples were taken for analysis at 0, 10, 30, 60 and 100 days after application. The soil samples were extracted with toluene followed by

acetonitrile:water (4:1v/v). The radioactivity was quantified by LSC and characterised by TLC followed by autoradiography.

Results

The recovery of applied radioactivity was 92 - 99% throughout the study. Approximately 68% of applied parent compound remained unaltered after 100 days. Evolved $^{14}\text{CO}_2$ accounted for 6%, and unextractable residues for 16% of applied radioactivity at the end of the study. Other identified transformation products were NC20645 (max. 2.9% of applied) and NC9607 (max. 3.7% of applied). The microbial biomass level was determined to 428 mg microbial C/g soil at the start, and 232 mg microbial C/g soil at the end of incubation. The half-life of ethofumesate was determined to 211 days ($r^2 > 0.90$), assuming first order kinetics.

Comments RMS

The study was conducted according to the Biologische Bundesanstalt Guidelines (Part IV, Section 4-1 Stage 1) from December 1986. The aerobic transformation of benzene- ^{14}C -labelled ethofumesate (NC8438, purity >98.6%) was investigated in a loamy sand soil. Apart from the missing bulk density, the soil was well characterized and microbial biomass comprised 0.9 - 1.7% of the total organic carbon during the study. No pre-incubation is reported. Soils were treated with 4.7 mg/kg of ethofumesate (corresponding to a field rate of 4.7 kg/ha), applied dropwise on top of the soil samples, and incubated in the dark at 20°C and approximately 40% of its maximum water holding capacity. The soil samples were extracted with toluene followed by a mixture of acetonitrile and water (4:1v/v). The radioactivity was quantified by LSC and characterised by TLC followed by autoradiography.

The study duration is 100 days and approximately 68% of the initially applied ethofumesate is still present at study end. Therefore, the full degradation pathway of ethofumesate might not have been described in this study and a longer duration would be more appropriate. In addition, sampling took place only at 5 time points (including the time zero sample), which is less than required by OECD 307.

The main pitfall in this study, however, is the storage of the soil. Before the experiment, it was stored outside for 87 days and not – as required by OECD 307 – either freshly processed or kept at 4°C. Such a long storage time might affect the microbial activity of the soils and explain the much longer half-life (211 d) compared to properly processed soils (see Menke (2008), McLaughlin (2012), Hein (2012)).

Therefore, the study is not acceptable.

| | |
|---------------------|--|
| Reference: | Ethofumesate - Fate and behaviour in soil |
| Notifier: | Taskforce |
| Author(s), year: | Fischer, H.; (1994) |
| Report/Doc. number: | OFC00004870 / M-352098-01-1 |
| Guideline(s): | Biologische Bundesanstalt Guidelines, Part IV, Section 4-1 Stage 1 (December 1986) |
| GLP: | Yes |
| Deviations: | |
| Validity: | Not valid |
| Status: | Previous evaluation in DAR for original approval / baseline dossier. |

Study summary based on previous draft assessment report

Materials and Methods

The aerobic transformation of U-phenyl-¹⁴C-labelled ethofumesate (radiochemical purity not reported) was investigated in German Standard Soil 2.2 in accordance with BBA Guidelines IV-4.1, 1986.

Table 8-12: Physico-chemical characteristics of the investigated soil.

| Soil | Org. C (%) | pH | sand (%) | silt (%) | clay (%) | MWHC (%) | CEC (meq/100 g) |
|------|---------------|-----|-------------|-------------|-------------|-------------|--------------------|
| 2.2 | 2.3 | 5.8 | 90 | n.r. | n.r. | 44 | n.r. |

The soils were treated with 1.2 mg as/kg dw, dissolved in methanol and applied evenly to the surface of each soil sample. The samples were incubated in the dark at ca. 20±2°C and 40% of their maximum water holding capacity. ¹⁴CO₂ was trapped in KOH-solution. Duplicate samples were taken for analysis at 0, 8, 15, 32, 63 and 130 days after application. The soil samples were extracted with hexane, methanol and water. The radioactivity was quantified by LSC and characterised by TLC.

Results

The material balance at the end of the incubation is given in the table below.

Table 8-13: Material balance of applied ¹⁴C-ethofumesate after 130 days of incubation in soils maintained in the dark at 21±2°C.

| Soil | Parent compound (%) | CO ₂ (%) | Unextractable (%) | Total (%) |
|------|------------------------|------------------------|----------------------|--------------|
| 2.2 | 30 | 27 | 35 | 93 |

No transformation products were identified in the soil throughout the study, and no unknown fraction accounted for more than 3% of applied radioactivity. The half-life of ethofumesate was determined to 43 days (confidence interval 5 - 82 days) assuming 1.5 order kinetics by a Timme model.

The mean microbial biomass levels were determined to 67 mg C/100 g soil pre-application, and 70 mg C/100 g soil at the end of incubation.

Comments RMS

The aerobic transformation of U-phenyl-¹⁴C-labelled ethofumesate (radiochemical purity not reported) was investigated in German Standard Soil 2.2. The soils were treated with ethofumesate at a rate of 1.2 mg/kg, dissolved in methanol and applied evenly to the surface of each soil sample. The samples were incubated in the dark at ca. 20±2°C and 40% of their maximum water holding capacity. The soil samples were extracted with hexane, methanol and water. The radioactivity was quantified by LSC and characterised by TLC.

Although the study is generally well conducted, fundamental information about the studied soils (field site history, previous pesticide use, sampling depth, storage conditions and pre-incubation) are not reported. Moreover, fundamental details on the analytical procedures employed for active substance and degradation products (purity, limit of quantification, limit of determination) are not reported.

Therefore, the study was excluded from further considerations.

| | |
|---------------------|--|
| Reference: | [Phenyl-UL-¹⁴C]ethofumesate (AE B049913): Time - dependent sorption in soils |
| Notifier: | Taskforce |
| Author(s), year: | Menke, U.; Telscher, M.; 2008 |
| Report/Doc. number: | MEF-08/514 / M-313317-01 |
| Guideline(s): | OECD 106 and 307 |
| GLP: | Yes |
| Deviations: | Not specified |
| Validity: | Valid |
| Status: | New study. |

I. MATERIALS AND METHODS

A. Materials

| | |
|------------------------------|--|
| 1. Test Material: | [Phenyl-UL- ¹⁴ C]Ethofumesate |
| Radiochemical purity: | not specified |

Specific radioactivity: 3.78 MBq mg⁻¹ (102.2 µCi/mg)

2. Soils

The study was carried out using four different soils. These soils are representative for agricultural use areas as required by the guidelines and cover a representative range of physico-chemical properties. All soils were sampled freshly from the fields.

Table 8-14: Characterization of soils

| Parameter | Soil Laacher Hof AXXa (AX) | Dollendorf II (DD) | Laacher Hof Wurmweise (WW) | Hoefchen Am Hohenseh 4a (HF) |
|---|--|-------------------------------|---|---|
| Geographic location - city - state - country | Monheim NRW Germany | Blankenheim NRW Germany | Monheim NRW Germany | Burscheid NRW Germany |
| Side description | Grassland | | | |
| Soil taxonomic classification (USDA) | sandy, mixed, mesic Typic Cambudolls | N/A | loamy, mixed, mesic Typic Argudalfs | loamy, mixed, mesic Typic Argudalfs |
| Texture class (USDA) - sand (50 µm – 2 mm) [%] - silt (2 µm – 50 µm) [%] - clay (< 2 µm) [%] | sandy loam 71 20 9 | clay loam 27 42 31 | sandy loam 55 26 19 | silt loam 31 52 17 |
| pH - in CaCl ₂ (soil/CaCl ₂ 1/2) - in water (soil/water 1/1) - in KCl | 6.1 6.3 5.9 | 7.2 7.4 6.9 | 5.4 5.6 5.1 | 6.5 6.8 6.3 |
| Organic matter ^{a)} [%] | 3.4 | 8.1 | 3.3 | 4.3 |
| Organic carbon [%] | 2.0 | 4.7 | 1.9 | 2.5 |
| Microbial biomass [mg microbial carbon/kg dry soil] - day 0 - day 59 - day 120 | 649 370 266 | 2925 2046 1632 | 352 411 168 | 1295 866 664 |
| CEC [meq/100 g] | 9.0 | 20.6 | 9.6 | 12.8 |
| 55% MWHC [g H ₂ O ad/100 g dry soil] | 27.2 | 43.9 | 33.7 | 33.7 |

a) calculated: % organic matter = % organic carbon × 1.724

CEC cation exchange capacity

MWHC maximum water holding capacity

N/A not applicable or not determined

NRW North Rhine-Westphalia

B. STUDY DESIGN

The test systems were static systems and consisted on 300-mL Erlenmeyer flasks equipped with traps to collect ¹⁴CO₂ and volatile organic compounds.

The objective of the present study was to investigate the changes of the sorption parameter of ethofumesate affected by a preceding aging period under aerobic conditions in four European soils by time-dependent sorption experiments. This test was designed in analogy to the "batch equilibrium" – test. The soils incubated with the test

item were shaken for 24 hours with 0.01 M CaCl_2 solution. After centrifugation, the distribution of the test item between supernatant and soil was determined by means of LSC and HPLC.

In addition, the metabolism and degradation rates of ethofumesate under aerobic conditions in soil were investigated. The concentration of the test item and possible metabolites was determined throughout the study, including the formation of volatile products. Material balances were established at each sampling interval and the DT_{50} and DT_{90} values were calculated for each soil.

1. Experimental conditions

The test vessels were incubated under aerobic conditions in a dark climatic chamber at an average temperature of 20.7 °C for a maximum period of 120 days. The soil moisture was set to about 55% of the maximum water holding capacity at the beginning of the study and maintained by replenishing the lost water. The vessels were closed with trap attachments which allowed absorption of volatile compounds, but which were permeable for oxygen exchange.

2. Sampling

Samples were taken for analysis 0, 1, 3, 7, 14, 30, 45, 59, 91, and 120 days after treatment (DAT).

3. Description of analytical procedures

At each sampling date the soil samples were shaken for 24 hours with 300 mL CaCl_2 solution in order to measure the time-dependent sorption of the test item. Subsequently they were extracted by shaking at ambient temperature and microwave with acetonitrile, three times with acetonitrile/water (80/20 = v/v), once with acetonitrile and once using microwave extraction at about 70 °C with acetonitrile/water (80/20 = v/v). Ethofumesate residues were analyzed and quantified by HPLC. TLC was used as confirmation method. The identity of the test item was confirmed by chromatography using the non-labeled reference item.

C. RESULTS AND DISCUSSION

Mass Balance (Total Recovery) and distribution of radioactivity:

Degradation of product distribution (% of AR) over 120 days aerobic incubation of treated soil (mean of two samples)

| Soil | Compound | Days after application | | | | | | | | | |
|----------------------------------|-------------------------------|------------------------|------|------|------|------|------|------|------|------|------|
| | | 0 | 1 | 3 | 7 | 14 | 30 | 45 | 59 | 91 | 120 |
| Laacher Hof AXXa | Ethofumesate | 95.6 | 95.5 | 92.7 | 86.0 | 71.3 | 42.8 | 29.1 | 22.3 | 16.2 | 12.0 |
| | Region a | 0.3 | 0.5 | 0.2 | 0.2 | 0.6 | 0.4 | n.d. | n.d. | n.d. | n.d. |
| | Sum of not identified peaks | 0.5 | 0.5 | 0.5 | 0.3 | 0.3 | 0.3 | 0.2 | 0.2 | 0.1 | 0.0 |
| | Total extracted radioactivity | 96.4 | 96.5 | 93.4 | 86.5 | 72.3 | 43.5 | 29.3 | 22.5 | 16.3 | 12.1 |
| | ¹⁴ CO ₂ | n.a. | 0.2 | 0.4 | 1.6 | 4.4 | 14.1 | 21.0 | 24.6 | 31.0 | 36.0 |
| | Volatile organics | n.a. | n.d. | n.d. | n.d. | n.d. | n.d. | 0.1 | 0.1 | 0.2 | 0.1 |
| | Non-extractable residues | 1.9 | 2.5 | 4.6 | 9.6 | 18.5 | 36.0 | 44.8 | 45.2 | 48.3 | 47.4 |
| | Total recovery | 98.3 | 99.1 | 98.4 | 97.6 | 95.2 | 93.6 | 95.2 | 92.4 | 95.8 | 95.6 |
| | | | | | | | | | | | |
| Dollendorf II | Ethofumesate | 91.3 | 89.7 | 83.7 | 73.0 | 55.7 | 29.7 | 19.2 | 9.6 | 5.0 | 2.4 |
| | Region a | 2.1 | 2.4 | 2.8 | 3.4 | 2.5 | 2.0 | n.d. | n.d. | n.d. | n.d. |
| | Sum of not identified peaks | 0.4 | 0.4 | 0.5 | 0.4 | 0.8 | 0.2 | 0.1 | 0.1 | n.d. | 1.2 |
| | Total extracted radioactivity | 93.8 | 92.5 | 86.9 | 76.7 | 59.5 | 31.8 | 19.4 | 9.7 | 5.0 | 3.7 |
| | ¹⁴ CO ₂ | n.a. | 0.2 | 0.6 | 2.4 | 7.7 | 18.0 | 26.1 | 31.9 | 41.5 | 43.1 |
| | Volatile organics | n.a. | n.d. | n.d. | n.d. | n.d. | 0.1 | 0.1 | 0.1 | 0.1 | n.d. |
| | Non-extractable residues | 4.4 | 5.1 | 8.5 | 15.0 | 24.8 | 38.9 | 47.7 | 49.6 | 48.9 | 46.9 |
| | Total recovery | 98.2 | 97.8 | 96.0 | 94.2 | 92.0 | 88.8 | 93.3 | 91.3 | 95.5 | 93.7 |
| | | | | | | | | | | | |
| Laacher Hof Wurmwiese | Ethofumesate | 95.2 | 95.2 | 88.0 | 76.8 | 59.8 | 29.9 | 18.7 | 13.3 | 9.8 | 8.2 |
| | Region a | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| | Sum of not identified peaks | 0.4 | 0.5 | 0.4 | 0.4 | 0.3 | 0.2 | 0.1 | 0.1 | 0.1 | 0.1 |
| | Total extracted radioactivity | 95.7 | 95.8 | 88.4 | 77.1 | 60.1 | 30.0 | 18.8 | 13.3 | 9.9 | 8.3 |
| | ¹⁴ CO ₂ | n.a. | 0.3 | 0.8 | 2.7 | 6.9 | 18.7 | 27.6 | 31.9 | 40.6 | 42.6 |
| | Volatile organics | n.a. | n.d. | n.d. | n.d. | 0.1 | 0.1 | 0.1 | 0.1 | n.d. | 0.1 |
| | Non-extractable residues | 2.1 | 3.2 | 6.8 | 14.9 | 24.3 | 42.2 | 47.9 | 46.6 | 42.8 | 44.5 |
| | Total recovery | 97.8 | 99.3 | 96.0 | 94.7 | 91.3 | 91.0 | 94.4 | 91.9 | 93.4 | 95.4 |
| | | | | | | | | | | | |
| Hoefchen Am Hohenseh 4a | Ethofumesate | 91.0 | 91.0 | 85.9 | 76.9 | 59.0 | 31.9 | 16.8 | 9.6 | 4.0 | 2.4 |
| | Region a | 1.9 | 1.8 | 2.0 | 1.5 | 1.9 | 0.9 | n.d. | n.d. | n.d. | n.d. |
| | Sum of not identified peaks | 0.5 | 0.5 | 0.4 | 0.4 | 0.2 | 0.1 | 0.1 | 0.1 | n.d. | 1.0 |
| | Total extracted radioactivity | 93.3 | 93.3 | 88.2 | 78.7 | 61.1 | 32.9 | 16.9 | 9.7 | 4.0 | 3.4 |
| | ¹⁴ CO ₂ | n.a. | 0.2 | 0.6 | 2.1 | 5.9 | 16.8 | 25.5 | 30.0 | 39.8 | 40.9 |

| | | | | | | | | | | | |
|------|--------------------------|------|------|------|------|------|------|------|------|------|------|
| | Volatile organics | n.a. | n.d. | n.d. | 0.1 | 0.1 | n.d. | 0.1 | 0.1 | 0.1 | 0.2 |
| | Non-extractable residues | 3.1 | 3.8 | 6.7 | 13.3 | 23.9 | 41.2 | 50.2 | 51.1 | 49.5 | 48.8 |
| | Total recovery | 96.4 | 97.3 | 95.6 | 94.1 | 91.0 | 90.9 | 92.6 | 90.9 | 93.3 | 92.9 |
| n.d. | not detected | | | | | | | | | | |
| n.a. | not analyzed | | | | | | | | | | |

Non-extractable and Extractable Residues

Non-extractable ^{14}C -residues increased from 1.9, 3.1, 2.1, and 4.4% AR at DAT-0 to a plateau of about 50% from DAT-45 towards the end of the study in the soils AX, HF, WW, and DD, respectively.

Mineralization :

A high amount of ethofumesate was mineralized to $^{14}\text{CO}_2$ indicating the fast and complete degradation of ethofumesate in soil. The mineralization at DAT-120 was in the range of 36.0% (AX) to 43.1% (DD).

Degradation of Test material and Formation of Transformation Products :

The test item was declining from 95.6, 91.0, 95.2 and 91.3% AR at DAT-0 to 12.0, 2.4, 8.2, and 2.4% in soils AX, HF, WW and DD, respectively, at the end of the study at DAT-120.

Besides CO_2 , one minor unidentified transformation product (Reg a) was detected by HPLC. It appeared with maximum concentrations of 3.4% AR (DAT-7) in soil DD. No other transformation product was detected in significant amount. The total of unidentified extracted radioactivity (sum of not identified peaks) did not exceed 1.2% AR.

Kinetic evaluation

Soil AX

Figure 8-4: Kinetic evaluation soil AX (SFO)

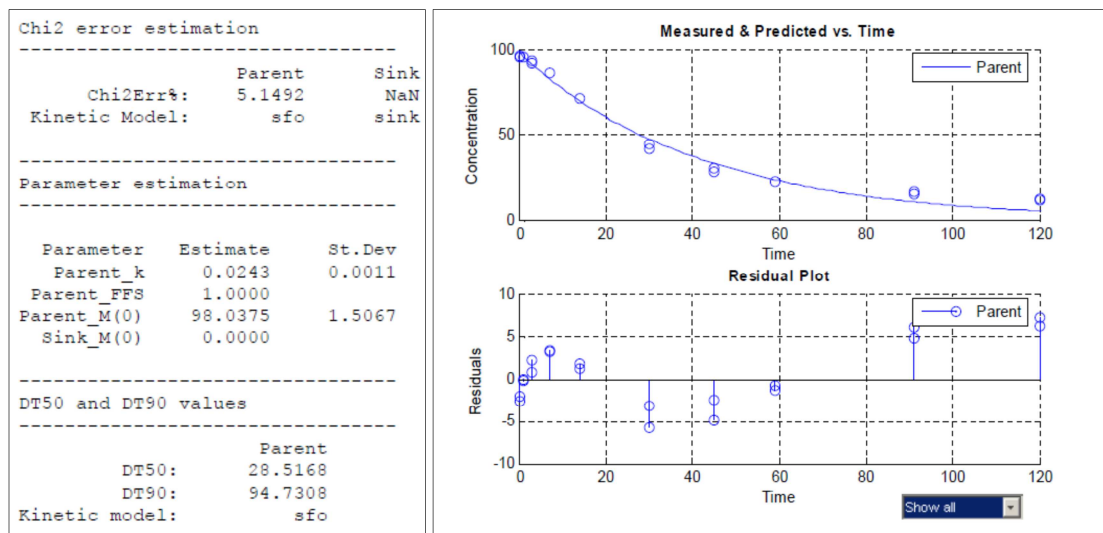


Figure 8-5: Kinetic evaluation soil AX (FOMC)

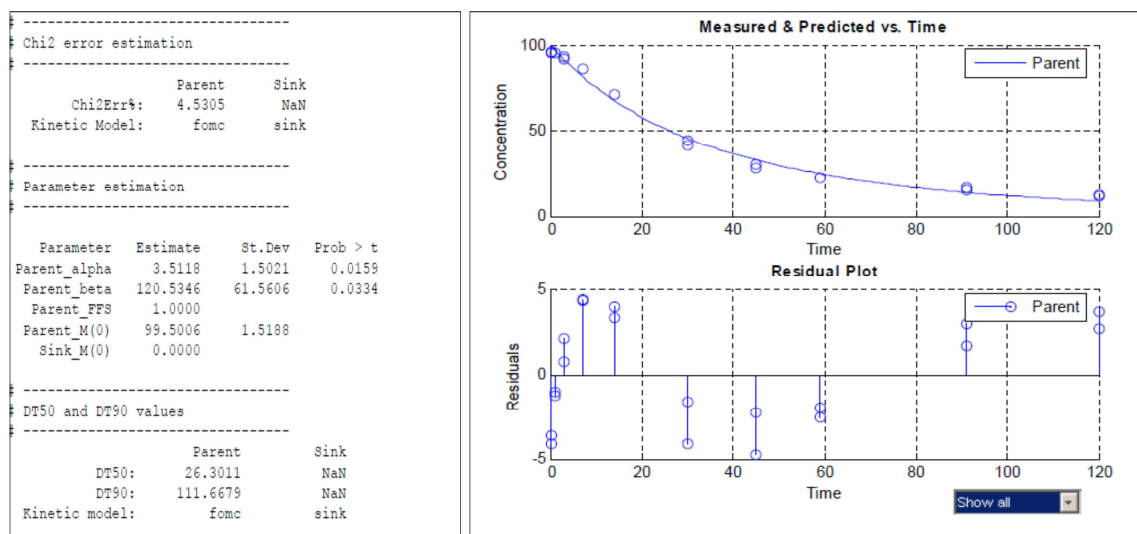


Figure 8-6: Kinetic evaluation soil AX (DFOP)

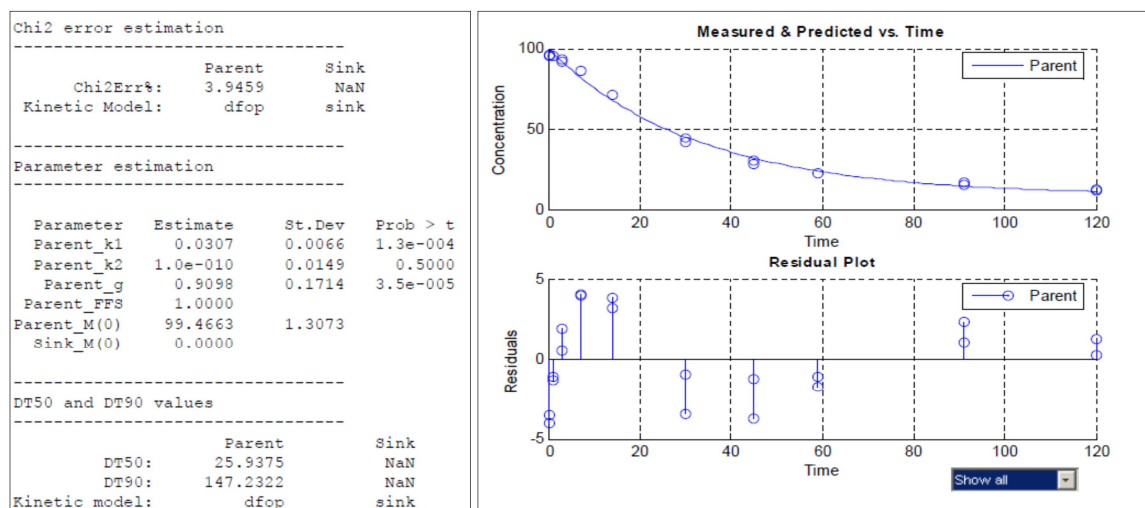


Figure 8-7: Kinetic evaluation soil HF (SFO)

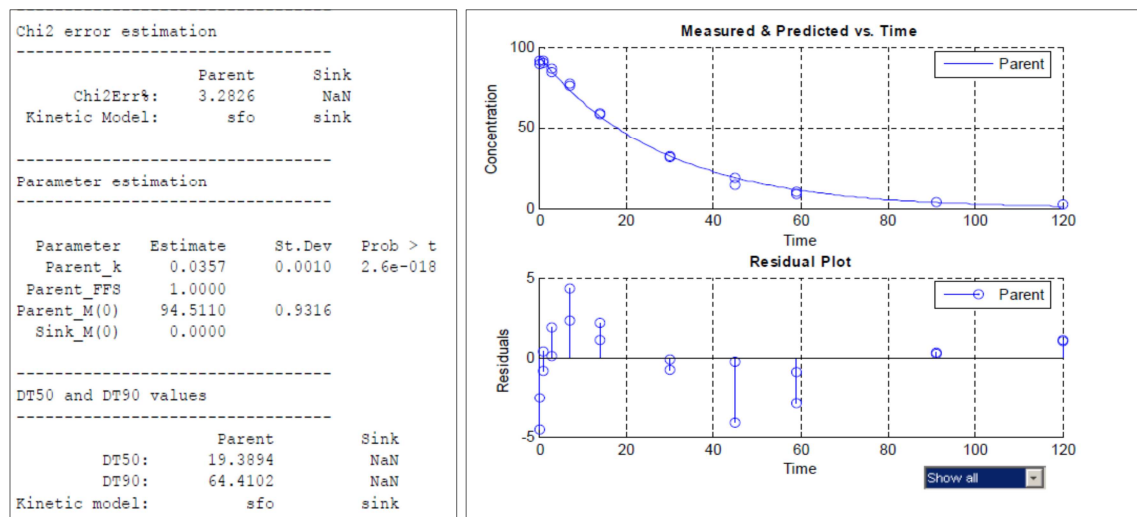


Figure 8-8: Kinetic evaluation soil HF (FOMC)

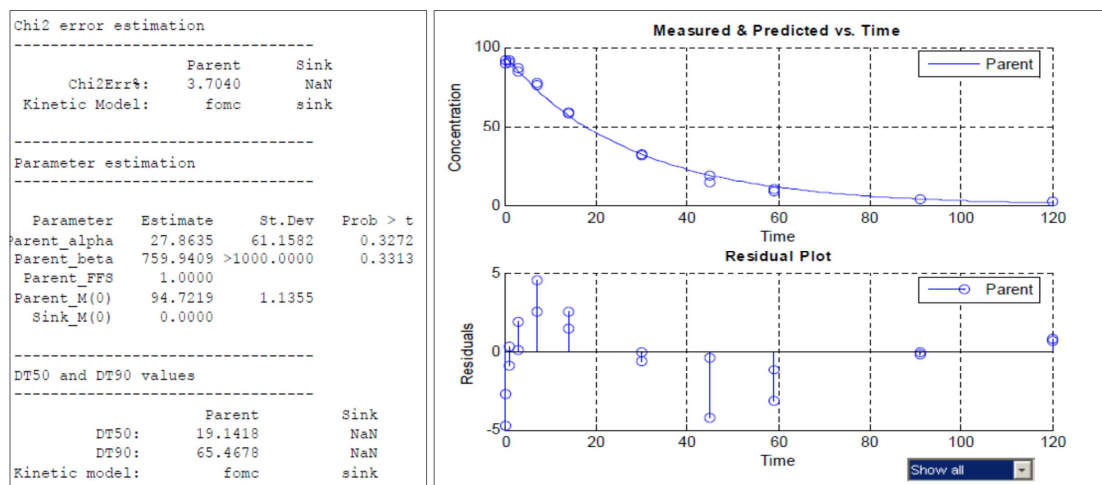


Figure 8-9: Kinetic evaluation soil HF (DFOP)

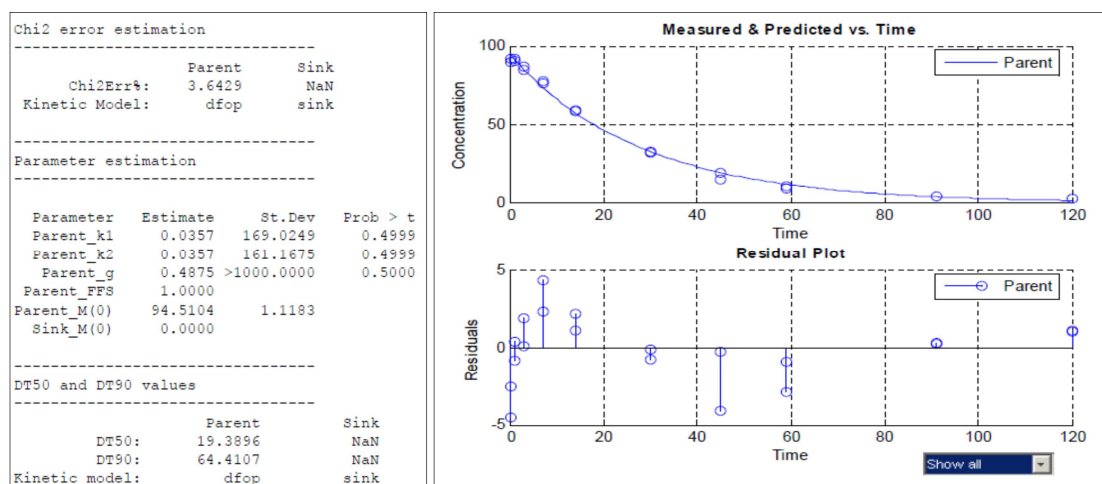


Figure 8-10: Kinetic evaluation soil WW (SFO)

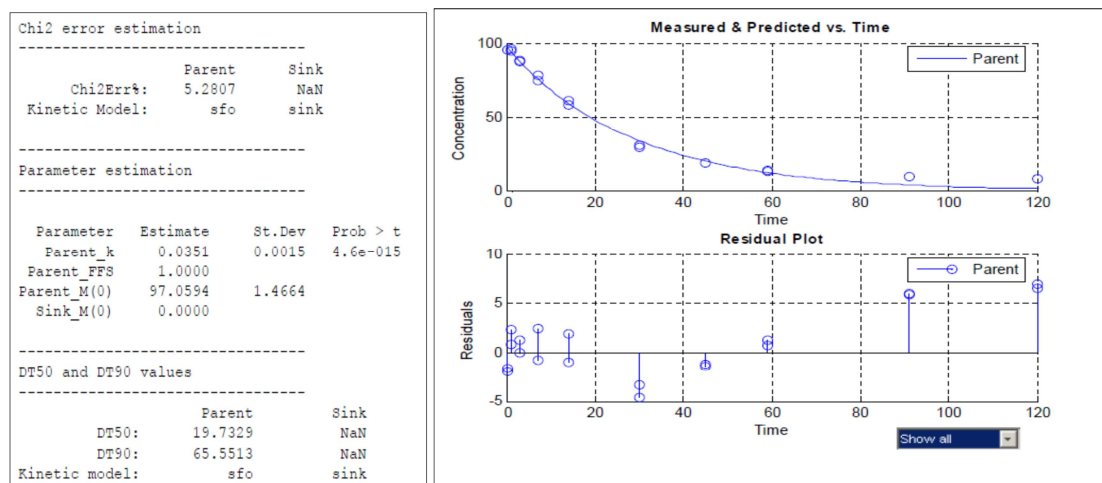


Figure 8-11: Kinetic evaluation soil WW (FOMC)

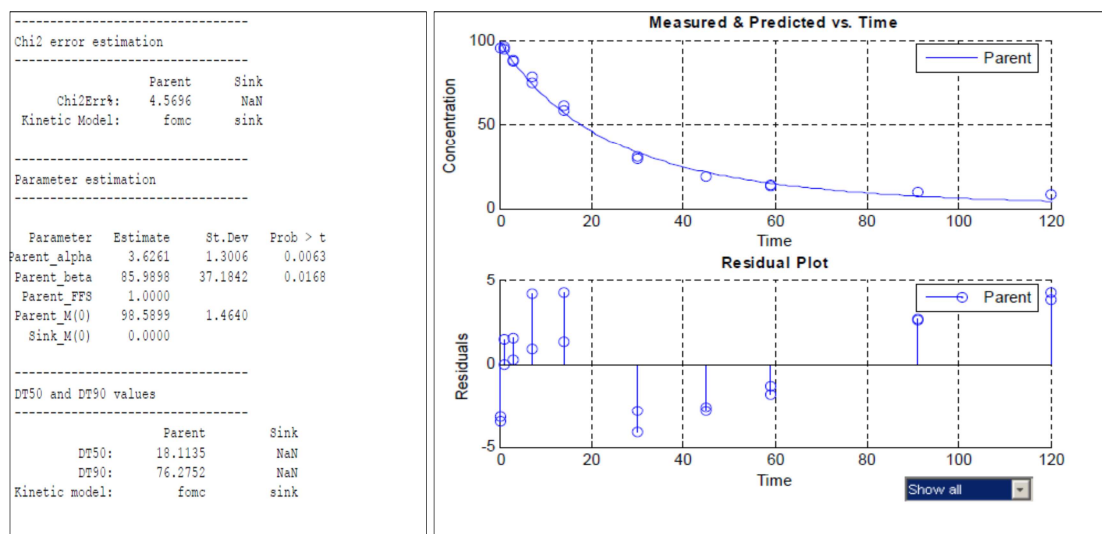


Figure 8-12: Kinetic evaluation soil WW (DFOP)

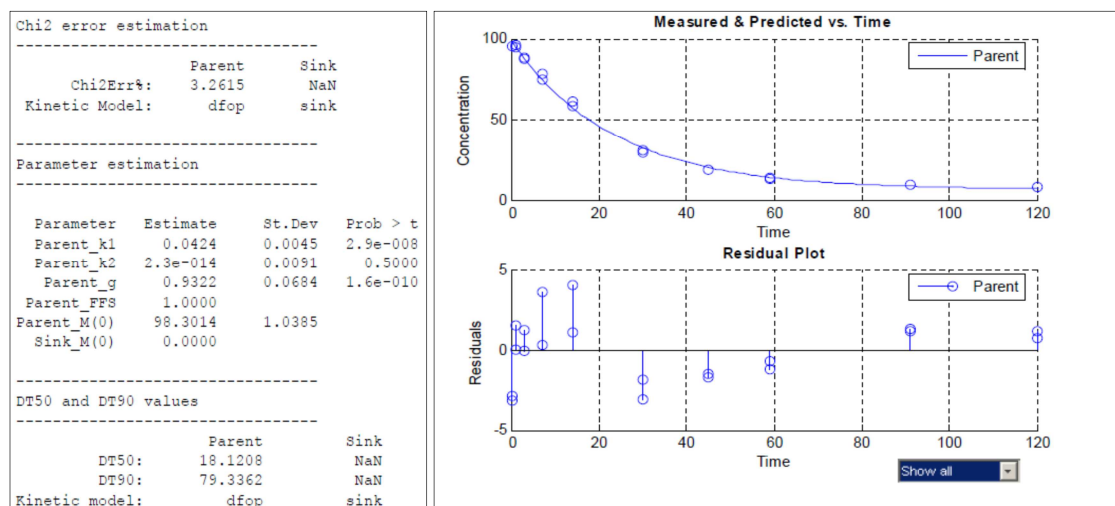


Figure 8-13: Kinetic evaluation soil DD (SFO)

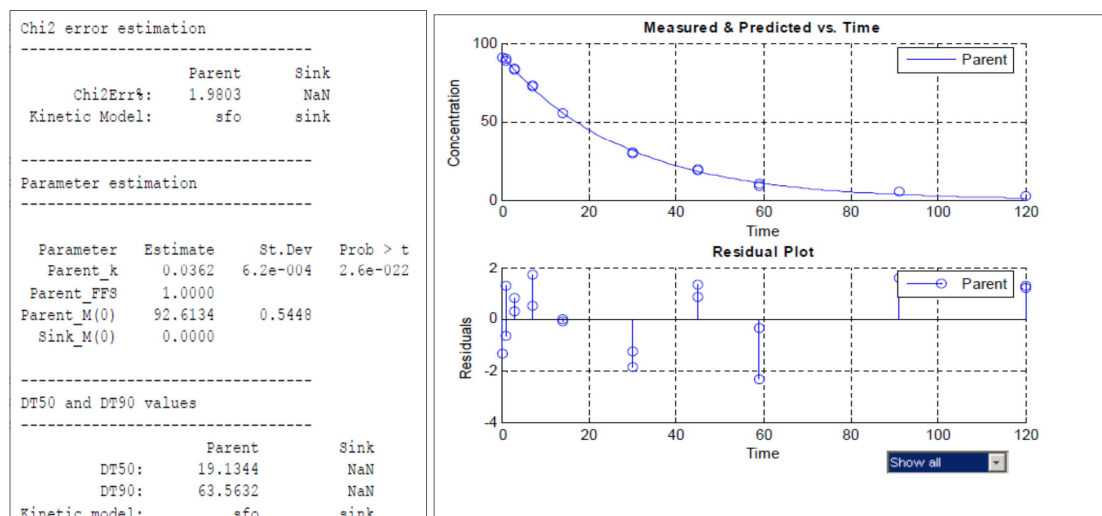


Figure 8-14: Kinetic evaluation soil DD (FOMC)

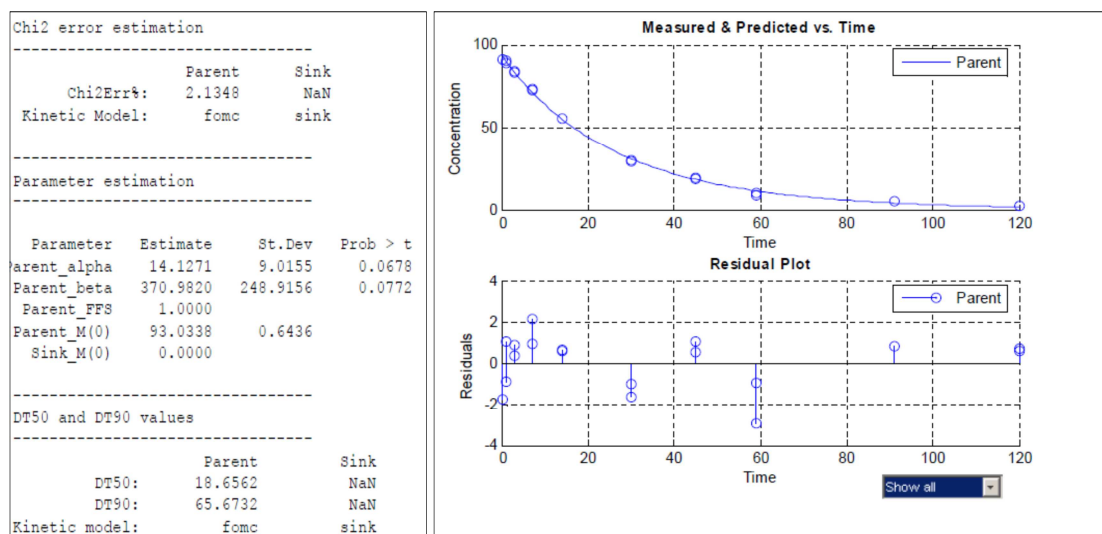
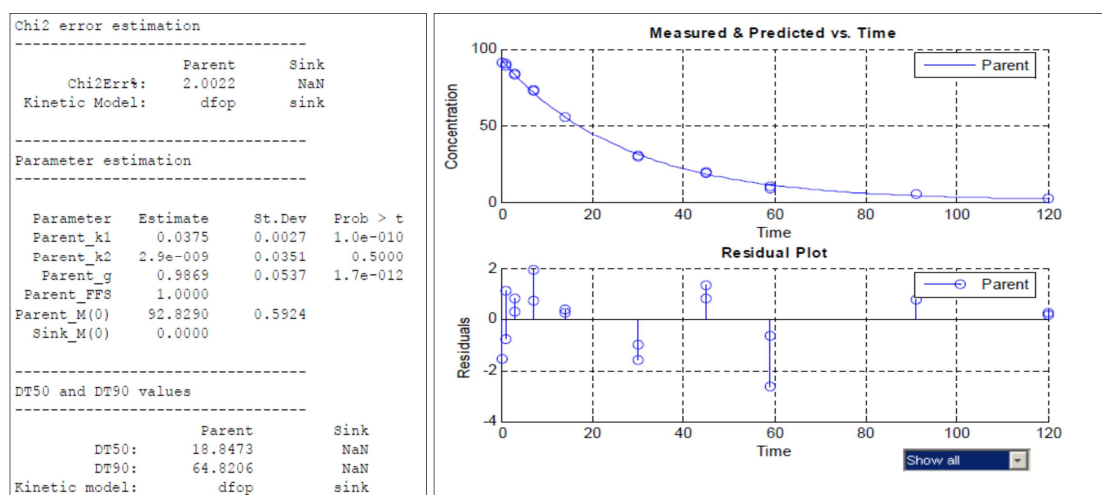


Figure 8-15: Kinetic evaluation soil DD (DFOP)



III. CONCLUSION

Ethofumesate degraded fast in all fresh samples soils. The high amount of mineralization indicated the complete degradation. One minor metabolite with at maximum 3.4% of AR was detected.

Comments RMS

Aerobic degradation of [phenyl-UL-14C] Ethofumesate was studied in two sandy loam soils, a silt loam soil and a clay loam soil for 120 days under aerobic conditions in the dark at 20.7 °C and 55% max. water holding capacity. In this study, which was designed as a time-dependent sorption study, ethofumesate was applied at the nominal rate of 2.680 mg/kg soil. Samples were taken at 0, 1, 3, 7, 14, 30, 45, 59, 91, and 120 days after treatment. At each sampling date the soil samples were shaken for 24 hours with 300 mL CaCl₂ solution in order to measure the time-dependent sorption of the test item. Subsequently they were extracted by shaking at ambient

temperature and microwave with acetonitrile/water mixtures, and the ethofumesate residues were analyzed and quantified by HPLC. TLC was used as confirmation method. The identity of the test item was confirmed by chromatography using the non-labeled reference item. The study is well conducted and fully acceptable as a route and rate of degradation study. No metabolites above 5% AR were detected.

For the AX (sandy loam) and the WW (sandy loam) soil, both the FOMC and DFOP models give a slightly better χ^2 error than the SFO model. Therefore, the notifier considered the bi-phasic model as more appropriate. Nevertheless, the visual fits are very similar for SFO and FOMC and it appears to be justified to use the SFO model both as modelling and persistence endpoint.

The endpoints are:

| Soil | Kinetic model | DT50 [d] | DT90 [d] | Chi2 error [%] |
|------|---------------|-------------|-------------|-------------------|
| AX | SFO | 28.5 | 94.7 | 5.1 |
| HF | SFO | 19.4 | 64.4 | 3.3 |
| WW | SFO | 19.7 | 65.5 | 5.3 |
| DD | SFO | 19.1 | 63.6 | 2.0 |

| | |
|----------------------------|--|
| Reference: | [¹⁴ C]Ethofumesate – Aerobic rate of Degradation in Soil |
| Notifier: | UPL/Agrichem |
| Author(s), year: | Sean P. McLaughlin, M.S. (2012) |
| Report/Doc. number: | Smithers Viscient Study No. 13845.6130 |
| Guideline(s): | OECD Guideline 307 OPPTS Guideline 835.4100 |
| GLP: | Yes Not applicable to kinetic evaluation |
| Deviations: | None |
| Validity: | Valid |
| Status: | New study. |

I. MATERIALS AND METHODS

A. Materials

| | |
|--------------------------------|---|
| 1. Test Material: | [¹⁴ C U-ring]ethofumesate |
| Radiochemical purity: | > 98% (Determined by Smithers Viscient to be > 98.9%) |
| Specific radioactivity: | 55 mCi/mmol (426,476 dpm/μg) |

-
- | | |
|-----------------|----------|
| Lot No.: | 11BLY014 |
|-----------------|----------|
- 2. Test Material:** ethofumesate
- | | |
|-------------------------------------|------------|
| Purity: | 99.5% |
| CAS No.: | 26225-79-6 |
| Lot No.: | SZE6128X |
| Further relevant properties: | None |
- 3. Test Material (reference R):** 2,3-dihydro-2-hydroxy-2,3-dimethylbenzofuran-5-yl methanesulphonate
- | | |
|-------------------------------------|---------------|
| Code: | NC 8493 |
| Purity: | 99.8% |
| CAS No.: | 26322-82-7 |
| Batch No.: | EPP/VMV/ 358A |
| Further relevant properties: | None |
- 4. Soils:** The test soils were from Fislis and Montesquieu (France), Horn and Sevelen (Switzerland). None of the soils had knowingly received pesticide applications in the last 3 years. All soils were collected from the top 20 cm and passed through a 2-mm sieve to assure uniformity. Soil characterisations are presented in the tables below.

Table 8-15: Characterization of soils

| Soil Property | Fislis | Horn | Montesquieu | Sevelen |
|---|-----------|-------|-------------|------------|
| Soil type (USDA) | Silt Loam | Loam | Clay | Sandy Loam |
| | | | | |
| Sand [%] | 11.89 | 41.87 | 16.67 | 54.61 |
| Silt [%] | 62.84 | 34.92 | 38.40 | 37.36 |
| Clay [%] | 25.27 | 23.21 | 44.93 | 8.03 |
| | | | | |
| Bulk density disturbed [kg/dm ³] | 1.39 | 1.41 | 1.57 | 1.37 |
| pH [CaCl ₂] | 6.82 | 7.23 | 7.37 | 7.51 |
| Cation Exchange Capacity [mmol/z//100 g B] | 25.15 | 23.24 | 21.93 | 7.26 |
| Field moisture | | | | |
| pF 1.0 [%] | 62.24 | 60.99 | 57.45 | 47.43 |
| pF 2.0 [%] | 42.56 | 38.72 | 38.39 | 32.76 |
| pF 2.5 [%] | 35.45 | 33.69 | 31.70 | 23.58 |

Table 8-16: Soil microbial biomass

| Interval | Soil microbial biomass [mg C/100 g soil] | Percent soil organic C (SOC) [%] | Microbial biomass [% of SOC] |
|---------------------|---|--|---------------------------------|
| Fislis Soil | | | |
| Post-handling | 36.3 | 2.0 | 1.82 |
| Start of incubation | 27.0 | 2.1 | 1.29 |
| End of incubation | 23.3 | 2.2 | 1.06 |
| Horn Soil | | | |
| Post-handling | 67.9 | 2.7 | 2.52 |
| Start of incubation | 74.8 | 2.7 | 2.77 |
| End of incubation | 87.2 | 2.8 | 3.11 |
| Montesquieu Soil | | | |
| Post-handling | 40.5 | 2.0 | 2.02 |
| Start of incubation | 35.3 | 1.8 | 1.96 |
| End of incubation | 36.9 | 2.3 | 1.61 |
| Sevelen Soil | | | |
| Post-handling | 36.9 | 3.1 | 1.19 |
| Start of incubation | 33.2 | 3.2 | 1.04 |
| End of incubation | 35.9 | 3.2 | 1.12 |

B. STUDY DESIGN

1. Experimental conditions

The aerobic transformation of Ethofumesate in soil was studied with labelled Ethofumesate at the rate of 1.0 mg/kg soil, equivalent to 1.0 kg/ha.

Samples of collected and sieved soil, equivalent to 100 g dry weight of soil, were filled into glass test vessels and adjusted to a pH range of 2.5 with purified reagent water. The test vessels were dosed with the 0.1 mg/mL [¹⁴C]ethofumesate isotopically-diluted stock solution to obtain a soil concentration of approximately 1.0 µg/g. The soils were further well mixed and solvent was given time to evaporate prior to attaching to the test set up. Aerobic test vessels were aerated continuously with hydrated air. The aerobic soil test systems were placed on volatile trapping trains.

Stock solution of the radiolabelled form of the test substance was combined with non-radiolabeled Ethofumesate stock solution and brought to final volume of 100 mL with acetone and water. Samples were incubated in dark environmental chamber at 20 ± 2°C for an incubation period of 62 days.

2. Sampling

Duplicate samples were taken on 0, 3, 7, 14, 28, 40 (or 45) and 62 days. Volatile traps for the [¹⁴C]ethofumesate-treated soils were analysed by LSC at each sampling interval, except on day 0.

3. Description of analytical procedures

The soil samples were processed and analysed immediately after sampling. Samples were extracted with 100 mL of 0.01 M CaCl₂ using a shaker table at approximately 150 rpm for approximately 24 hours. Samples were then extracted by centrifugation and analysed by LSC. The extraction procedure was repeated up to three times with acetonitrile/water 80/20, (v/v, 3 × 100 mL) using shaker table at 200 rpm for 30 min. If < 5% AR was recovered no further extractions were conducted.

The organic extracts were pooled for each sample and a portion concentrated under reduced pressure using a rotary evaporator (using minimal heating). The samples were transferred to graduate centrifuge tubes using acetonitrile/water 1/2 (v/v). Duplicate 0.1 mL aliquots were analysed by LSC. The recovery was, except in one occasion, at least 90% AR. The extract was analysed by HPLC/RAM (Phenomenex Luna C18(2), 250 × 4.6 mm, 5 µm) to quantify [¹⁴C]Ethofumesate and degradation products. The soil-bound residues were analysed by combustion and volatile organic traps were radioassayed directly by LSC. Identification of the transformation products was done by co-chromatography with reference standards and confirmed using TLC.

II. RESULTS AND DISCUSSION

A. MASS BALANCE

Average mass balance ranged from 96.2 to 110.4% AR for the samples tested over the course of the 62-day study.

Table 8-17: Distribution of radioactivity (% AR, average of duplicate samples) following 62 days of incubation in the dark at 20°C under aerobic conditions

| Day | CaCl ₂ | Extractables | Bound | ¹⁴ CO ₂ | VOC | Mass balance |
|-------------------------|-------------------|--------------|-------|-------------------------------|--------|--------------|
| Fislis soil | | | | | | |
| 0 | 16.7 | 84.5 | 9.2 | NA | NA | 110.4 |
| 3 | 11.3 | 74.7 | 17.7 | NA | NA | 104.9 |
| 7 | 9.6 | 66.2 | 27.6 | 4.2 | < 0.01 | 107.6 |
| 14 | 7.4 | 51.1 | 41.0 | 10.0 | ND | 109.5 |
| 28 | 3.4 | 29.3 | 56.7 | 20.7 | < 0.01 | 110.2 |
| 45 | 1.7 | 13.4 | 62.7 | 28.1 | < 0.01 | 106.0 |
| 62 | 1.3 | 8.1 | 63.7 | 31.6 | ND | 104.7 |
| Horn soil | | | | | | |
| 0 | 14.0 | 83.8 | 10.5 | NA | NA | 108.3 |
| 3 | 8.0 | 69.4 | 25.4 | NA | NA | 105.5 |
| 7 | 6.7 | 60.3 | 34.6 | 6.0 | ND | 107.7 |
| 14 | 4.1 | 33.7 | 54.4 | 17.0 | < 0.01 | 109.1 |
| 28 | 1.3 | 11.7 | 68.3 | 28.9 | ND | 110.3 |
| 45 | 0.8 | 5.1 | 57.1 | 39.7 | ND | 102.8 |
| 62 | 0.7 | 4.3 | 60.2 | 45.0 | ND | 110.2 |
| Montesquieu soil | | | | | | |
| 0 | 22.3 | 75.4 | 11.9 | NA | NA | 109.6 |
| 3 | 12.7 | 65.6 | 17.2 | NA | NA | 96.2 |
| 7 | 12.7 | 65.2 | 24.8 | 2.8 | < 0.01 | 105.6 |
| 14 | 10.3 | 54.4 | 36.2 | 7.3 | < 0.01 | 108.2 |
| 28 | 5.5 | 33.6 | 51.7 | 15.7 | < 0.01 | 106.5 |
| 45 | 2.5 | 18.7 | 57.0 | 25.2 | 0.01 | 103.4 |
| 62 | 1.9 | 10.8 | 60.3 | 31.5 | ND | 104.5 |
| Sevelen soil | | | | | | |
| 0 | 28.3 | 71.9 | 8.7 | NA | NA | 108.9 |
| 3 | 17.9 | 64.9 | 19.5 | NA | NA | 104.2 |
| 7 | 14.6 | 53.5 | 30.5 | 6.2 | < 0.01 | 104.8 |
| 14 | 10.4 | 39.8 | 45.0 | 11.4 | < 0.01 | 106.6 |
| 28 | 3.9 | 16.1 | 64.9 | 23.7 | 0.01 | 105.6 |
| 45 | 2.1 | 8.0 | 60.8 | 33.1 | ND | 104.0 |
| 62 | 1.5 | 4.8 | 64.0 | 36.4 | ND | 106.7 |

NA: not applicable, traps were not evaluated on day 0

ND: not detectable

B. BOUND AND EXTRACTABLE RESIDUES

Extractable radioactivity decreased during the incubation period. The amount of non-extractable residues after CaCl_2 and acetonitrile/water extractions increased during the study reaching a maximum of between 60.2 and 64% AR after 62 days.

C. VOLATILIZATION

The radioactivity in the 1 M KOH traps accounted for between 31.5 and 45% AR after 62 days. Negligible radioactivity was detected in the ethylene glycol volatile traps for all soils after 62 days of incubation.

D. TRANSFORMATION OF PARENT COMPOUND

The amount of Ethofumesate rapidly decreased with time due to its degradation. Immediately after treatment (time 0), the parent compound represented between 94.6 and 99.6% AR, decreasing to between 33.8 and 60.5% AR after 14 days and to between 2.8 and 18.8% AR after 45 days. After 62 days it almost disappeared, representing less than 9% AR.

No major transformation products were detected. During incubation several minor regions of radioactivity were observed in some of the chromatograms. However, in all cases, individual peaks represented less than 5% AR and were not considered further, except in one case where an 18-minute peak representing 3% AR (single replicate) co-chromatographed with the reference standard NC 8493 (i.e. 2,3-dihydro-2-hydroxy-3,3-dimethyl benzofuran-5-yl methanesulphonate).

Table 8-18: Distribution of [14C]ethofumesate and metabolites in Fislis soil, as percent of applied radioactivity, during the aerobic soil transformation study with [14C]ethofumesate

Table 9. Distribution of [14C]ethofumesate and metabolites in Fislis soil, as percent of applied radioactivity, during the aerobic soil transformation study with [14C]ethofumesate.

| Day/ Sample ID | % of Applied Radioactivity in the Total System | | | | | | | Others |
|-------------------|--|--------|---------|---------|---------|--------|--------------------|--------|
| | [14C]Ethofumesate | Polars | ~15 min | ~19 min | ~21 min | ~6 min | NC8493 ~ 18 min | |
| Day 0-21 | 101.0 | ND | 0.4 | 0.4 | ND | ND | ND | ND |
| Day 0-22 | 98.2 | ND | 1.2 | 1.1 | ND | ND | ND | ND |
| Day 3-1 | 83.0 | ND | 0.5 | 1.5 | ND | ND | ND | ND |
| Day 3-20 | 86.4 | ND | 0.3 | 0.4 | ND | ND | ND | ND |
| Day 7-2 | 73.0 | ND | 0.9 | 0.5 | ND | ND | ND | 0.3 |
| Day 7-19 | 74.3 | ND | 0.4 | 2.2 | ND | ND | ND | ND |
| Day 14-3 | 51.7 | ND | 1.1 | 1.4 | ND | ND | 3.2 | ND |
| Day 14-18 | 58.1 | ND | 1.1 | 0.4 | ND | ND | ND | ND |
| Day 28-4 | 31.2 | ND | 0.3 | 1.3 | ND | 0.1 | ND | 0.3 |
| Day 28-17 | 29.9 | ND | 0.4 | 1.2 | ND | 0.3 | ND | 0.5 |
| Day 45-6 | 13.5 | ND | 0.8 | 0.6 | ND | ND | 0.9 | 0.5 |
| Day 45-7 | 9.6 | ND | 0.8 | 1.0 | 1.7 | 0.3 | ND | 0.7 |
| Day 62-13 | 6.6 | 0.4 | 1.1 | 0.7 | ND | 0.2 | ND | 0.4 |
| Day 62-14 | 6.4 | 0.5 | 1.2 | 0.9 | ND | 0.2 | ND | 0.5 |

Table 8-19: Distribution of [14C]ethofumesate and metabolites in Horn soil, as percent of applied radioactivity, during the aerobic soil transformation study with [14C]ethofumesate

| Day/ Sample ID | % of Applied Radioactivity in the Total System | | | | | | Others |
|-------------------|--|--------|---------|---------|--------|----------|--------|
| | [14C]Ethofumesate | Polars | ~15 min | ~19 min | ~6 min | ~ 22 min | |
| Day 0-49 | 96.7 | ND | ND | 0.5 | ND | ND | ND |
| Day 0-50 | 98.0 | ND | 0.3 | 0.2 | ND | ND | ND |
| Day 3-29 | 76.3 | ND | 0.4 | 0.4 | 0.3 | ND | ND |
| Day 3-48 | 75.2 | ND | 0.4 | 1.4 | 0.3 | ND | ND |
| Day 7-30 | 77.7 | ND | 0.4 | 0.5 | ND | ND | ND |
| Day 7-47 | 52.5 | ND | 1.4 | 1.2 | 0.4 | ND | ND |
| Day 14-31 | 36.3 | ND | 1.1 | 1.2 | 0.6 | ND | 1.0 |
| Day 14-46 | 31.2 | ND | 0.9 | 1.1 | 0.8 | ND | 1.3 |
| Day 28-38 | 9.1 | 0.3 | 0.7 | 1.1 | 0.3 | ND | 1.1 |
| Day 28-45 | 9.6 | 0.5 | 0.7 | 1.3 | 0.2 | ND | 1.1 |
| Day 40-34 | 3.1 | 0.7 | 0.8 | 1.1 | 0.3 | ND | 0.5 |
| Day 40-42 | 2.4 | 0.6 | 0.7 | 1.1 | 0.2 | 1.3 | ND |
| Day 62-40 | 2.8 | 0.7 | 0.4 | 0.7 | 0.1 | ND | 0.4 |
| Day 62-43 | 2.2 | 0.6 | 0.4 | 0.5 | ND | 0.8 | 0.4 |

Table 8-20: Distribution of [14C]ethofumesate and metabolites in Montesquieu soil, as percent of applied radioactivity, during the aerobic soil transformation study with [14C]ethofumesate

| Day/ Sample ID | % of Applied Radioactivity in the Total System | | | | | | |
|-------------------|--|--------|---------|---------|--------|----------|--------|
| | [14C]Ethofumesate | Polars | ~15 min | ~19 min | ~6 min | ~ 22 min | Others |
| Day 0-77 | 96.0 | ND | 2.0 | 0.6 | ND | ND | ND |
| Day 0-78 | 93.2 | ND | 1.7 | 2.0 | ND | ND | ND |
| Day 3-57 | 71.1 | ND | 1.3 | 0.3 | ND | ND | 0.2 |
| Day 3-76 | 82.8 | ND | 0.6 | 0.4 | ND | ND | ND |
| Day 7-58 | 77.4 | ND | 1.2 | 0.4 | ND | ND | 2.3 |
| Day 7-75 | 71.3 | ND | 1.6 | 1.6 | ND | ND | ND |
| Day 14-59 | 61.5 | ND | 0.2 | 1.2 | 0.3 | 2.0 | ND |
| Day 14-74 | 59.4 | ND | 1.7 | 1.5 | ND | 1.5 | ND |
| Day 28-60 | 36.5 | ND | 0.5 | 0.5 | 0.3 | ND | 0.3 |
| Day 28-73 | 38.0 | ND | 0.9 | 1.2 | 0.1 | ND | ND |
| Day 45-66 | 19.4 | 0.4 | 0.8 | 1.4 | ND | ND | 0.4 |
| Day 45-68 | 16.5 | 0.5 | 1.1 | 1.6 | ND | ND | 0.3 |
| Day 62-64 | 9.9 | 0.3 | 0.3 | 1.0 | 0.2 | 0.6 | 0.4 |
| Day 62-71 | 7.7 | 0.6 | 0.2 | 3.7 | 0.2 | ND | 0.2 |

Table 8-21: Distribution of [14C]ethofumesate and metabolites in Sevelen soil, as percent of applied radioactivity, during the aerobic soil transformation study with [14C]ethofumesate

| Day/ Sample ID | % of Applied Radioactivity in the Total System | | | | | | | |
|-------------------|--|--------|---------|---------|--------------------|--------|----------|--------|
| | [14C]Ethofumesate | Polars | ~15 min | ~19 min | NC8493 ~ 18 min | ~6 min | ~ 22 min | Others |
| Day 0-105 | 100.4 | ND | ND | ND | ND | ND | ND | 0.6 |
| Day 0-106 | 97.7 | ND | ND | 0.8 | ND | ND | ND | 1.0 |
| Day 3-85 | 78.5 | ND | 0.5 | 0.6 | ND | 0.3 | ND | 1.0 |
| Day 3-104 | 84.1 | ND | ND | 0.5 | ND | ND | ND | ND |
| Day 7-86 | 65.5 | ND | 0.4 | 0.5 | ND | 0.1 | ND | ND |
| Day 7-103 | 67.8 | ND | 0.4 | 1.2 | ND | 0.1 | ND | ND |
| Day 14-87 | 42.6 | ND | 0.7 | 1.1 | ND | 0.4 | 1.0 | ND |
| Day 14-102 | 49.7 | ND | 1.5 | 1.1 | ND | 0.9 | 1.6 | ND |
| Day 28-88 | 16.4 | ND | 0.7 | 1.3 | ND | 0.5 | ND | 0.3 |
| Day 28-101 | 18.0 | ND | 0.7 | 0.9 | ND | 0.4 | ND | 0.8 |
| Day 40-91 | 5.9 | 0.4 | 1.4 | 1.9 | ND | 0.8 | ND | 0.5 |
| Day 40-93 | 5.9 | 0.4 | 0.9 | 1.1 | 1.3 | 0.6 | ND | 0.9 |
| Day 62-92 | 2.7 | 0.6 | 0.8 | 0.6 | 0.2 | 0.3 | ND | 1.0 |
| Day 62-98 | 2.6 | 0.5 | 0.8 | 0.6 | 0.4 | 0.6 | ND | 0.7 |

Figure 8-16: Kinetic evaluation Fislis soil (SFO)

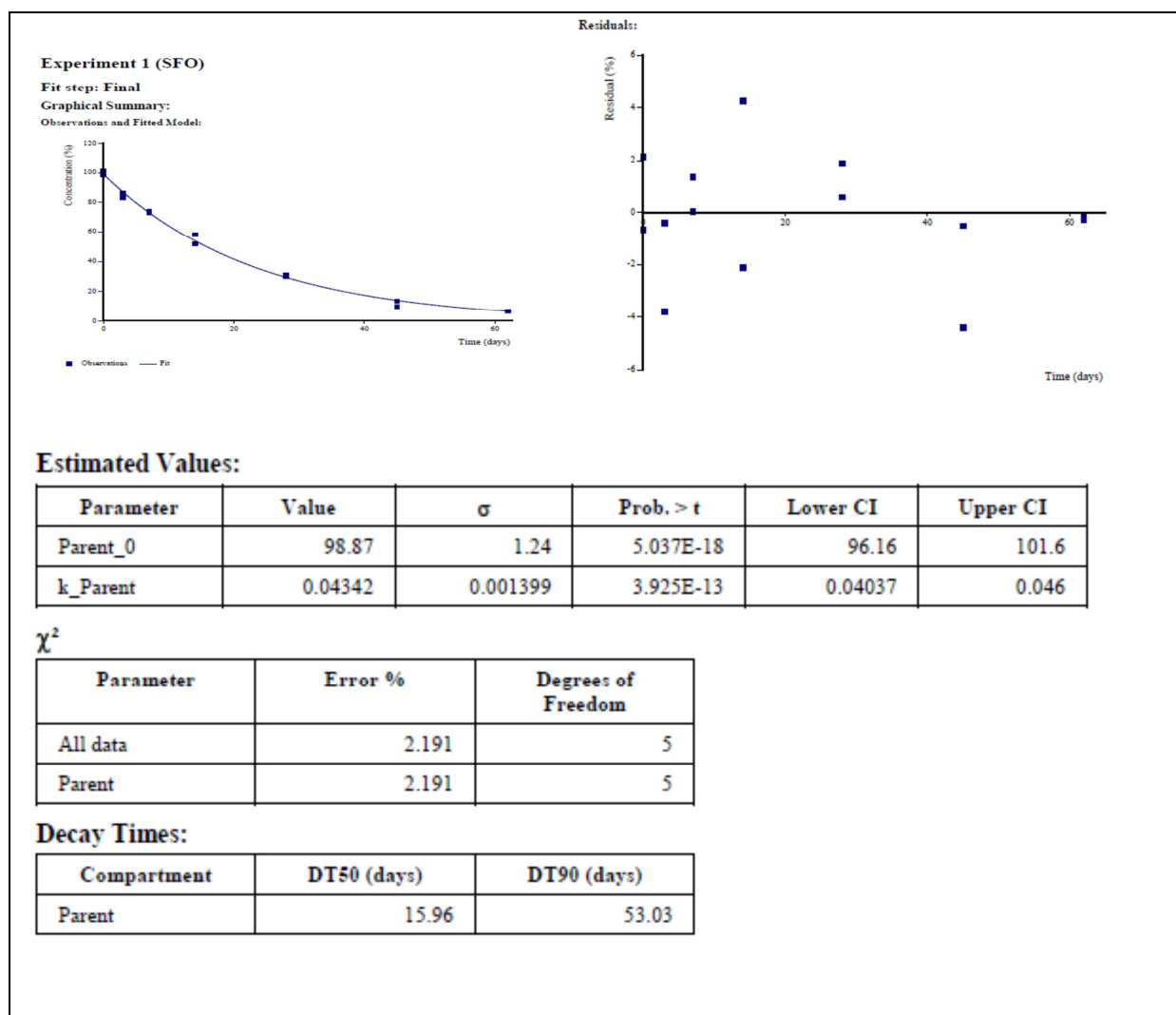
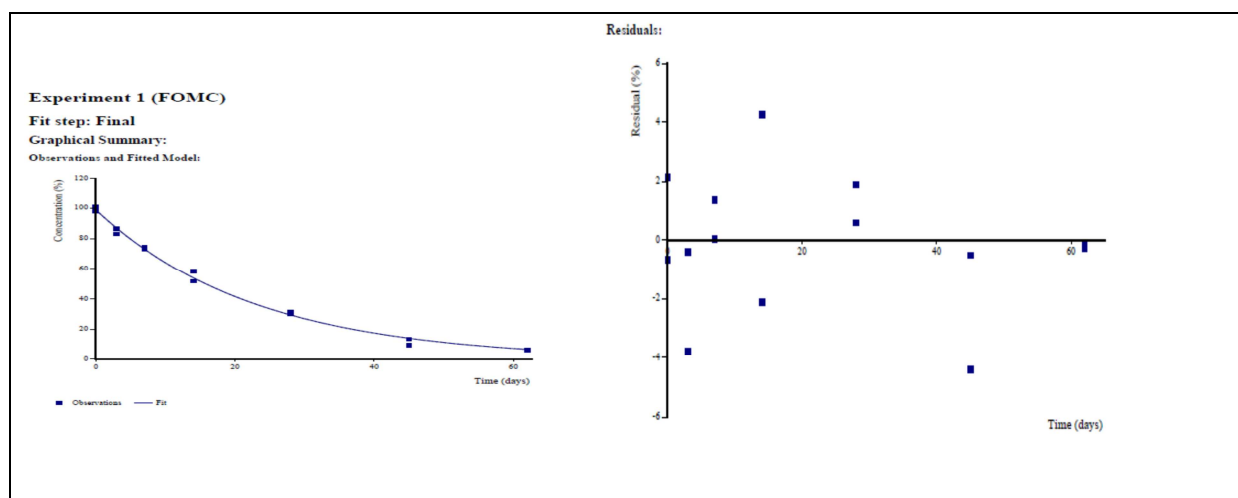


Figure 8-17: Kinetic evaluation Fislis soil (FOMC)



Estimated Values:

| Parameter | Value | σ | Prob. > t |
|-----------|-----------|----------|-----------|
| Parent_0 | 98.87 | | |
| alpha | 3.287E+06 | | |
| beta | 7.571E+07 | | |

Note: Errors and T-test values could not be calculated because the covariance matrix could not be created.

 χ^2

| Parameter | Error % | Degrees of Freedom |
|-----------|---------|--------------------|
| All data | 2.366 | 4 |
| Parent | 2.366 | 4 |

Decay Times:

| Compartment | DT50 (days) | DT90 (days) |
|-------------|-------------|-------------|
| Parent | 15.96 | 53.03 |

Additional Sections:

Figure 8-18: Kinetic evaluation Horn soil (SFO)

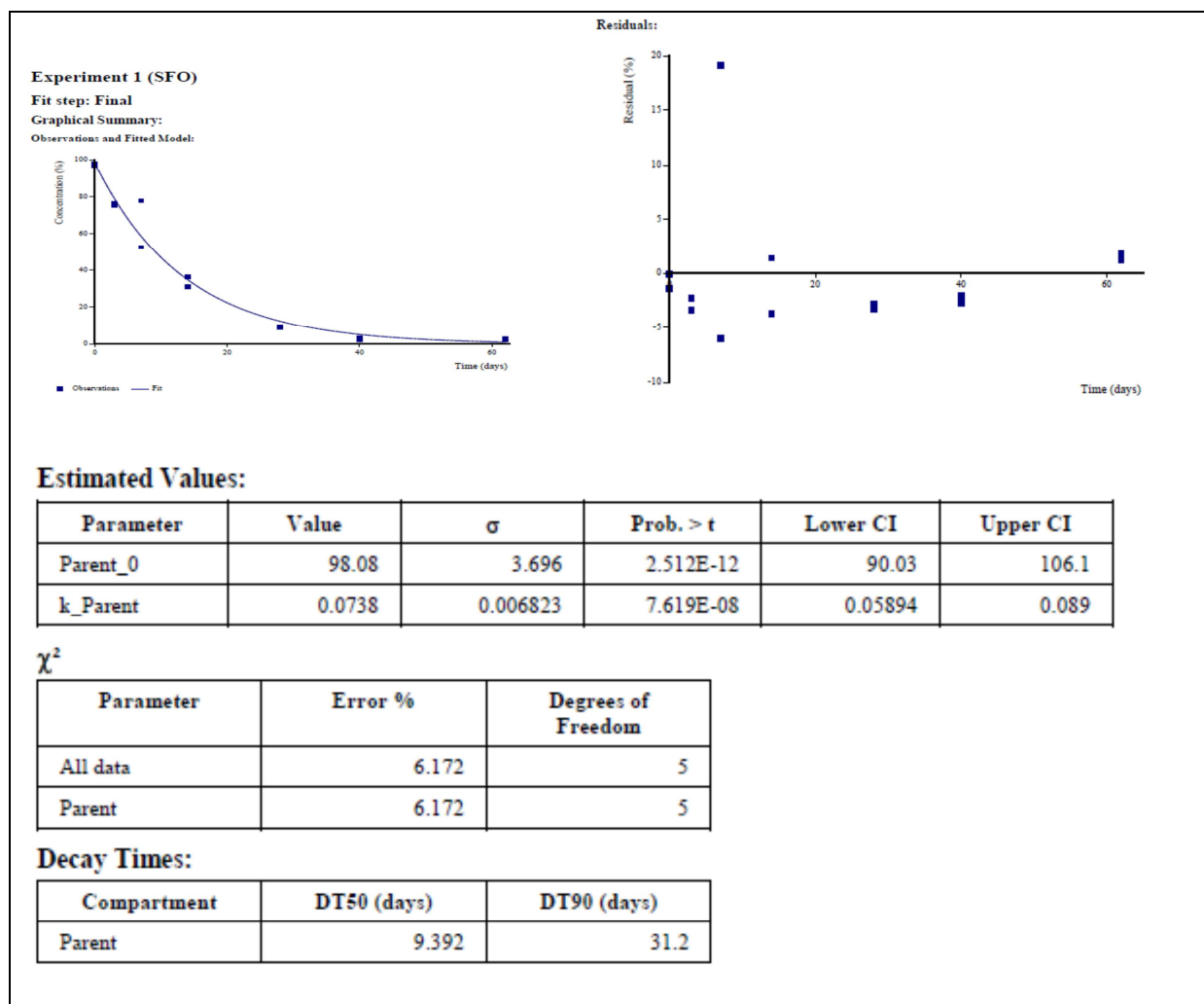


Figure 8-19: Kinetic evaluation Horn soil (FOMC)

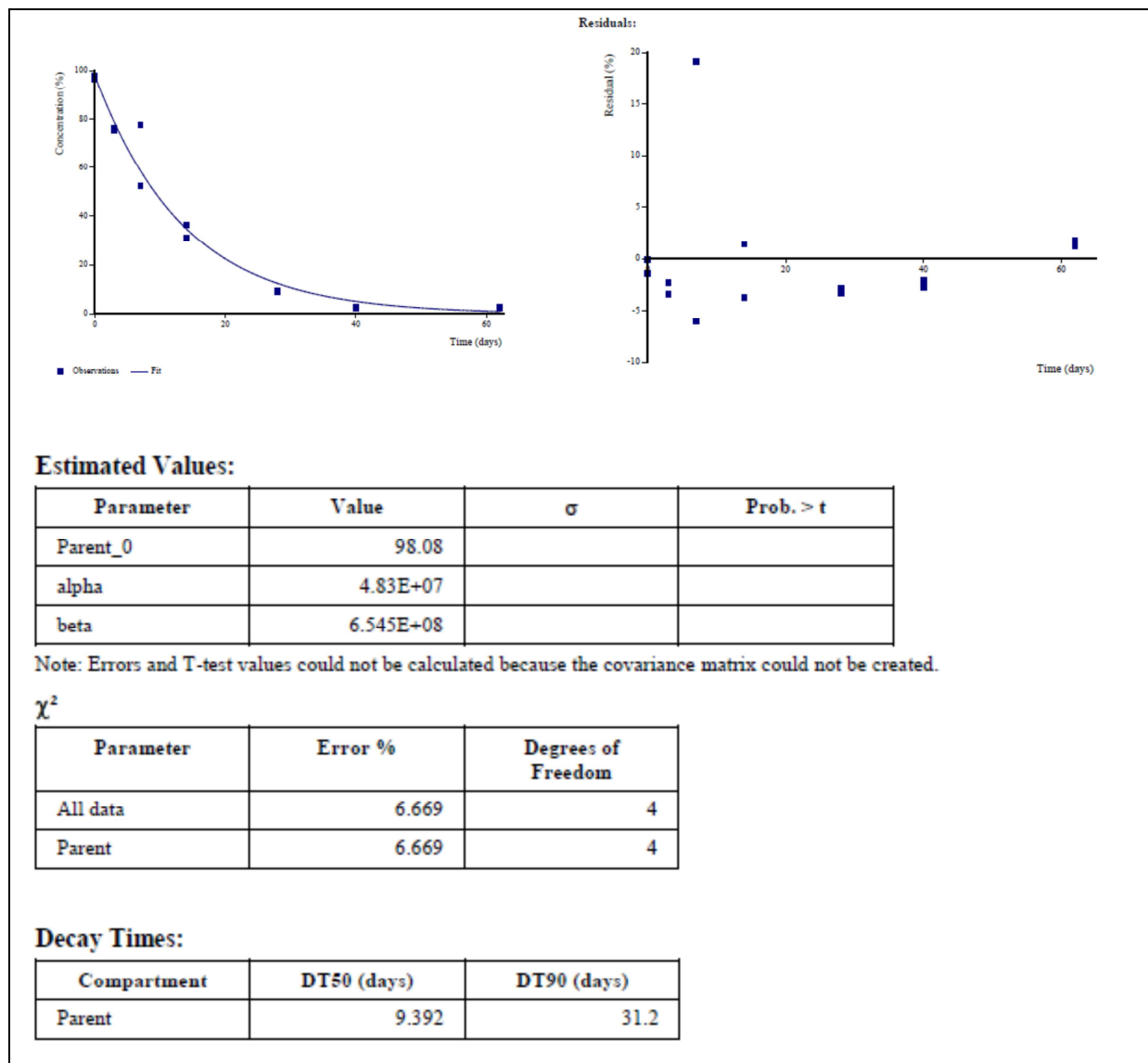


Figure 8-20: Kinetic evaluation Montesquieu soil (SFO)

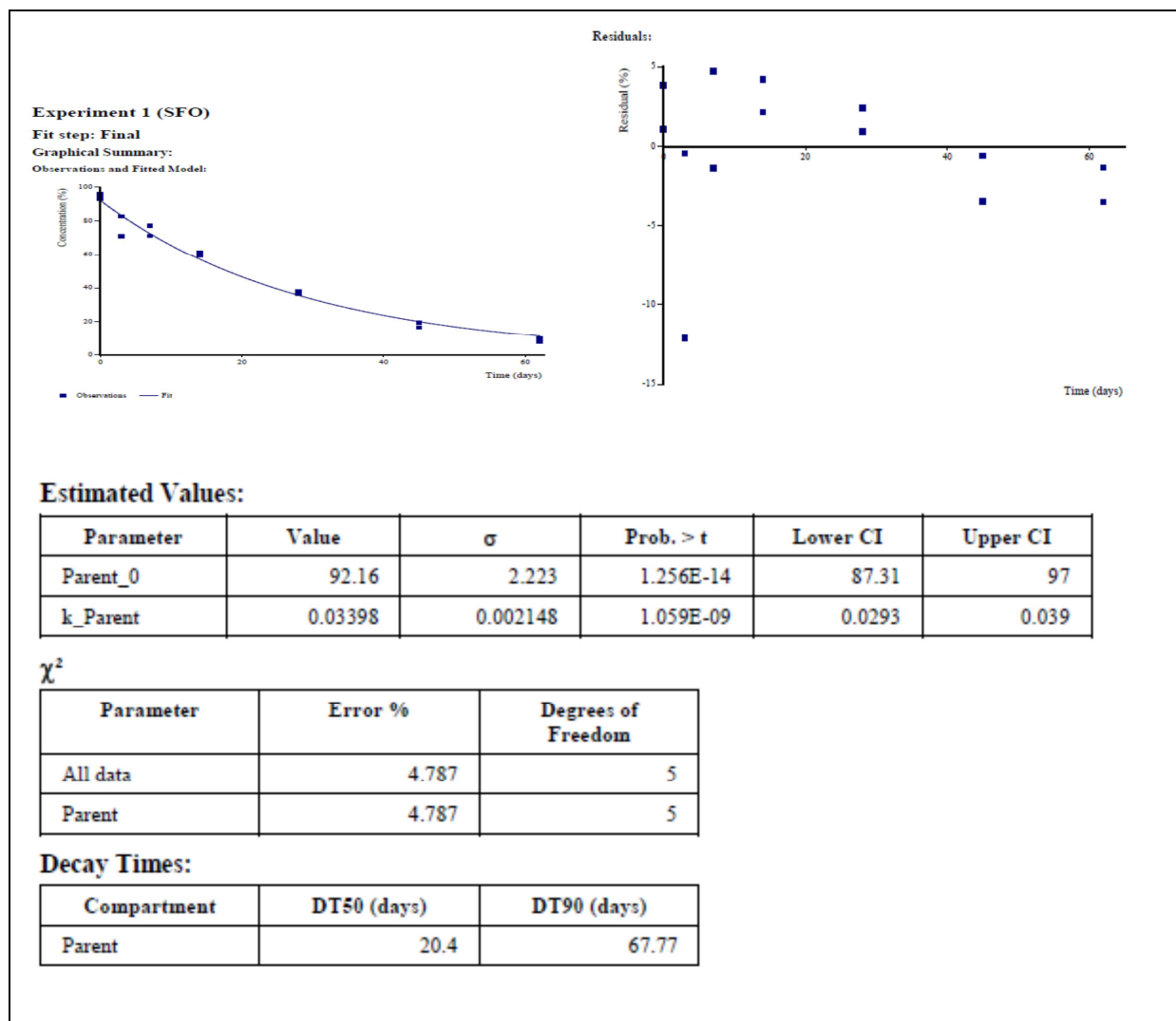
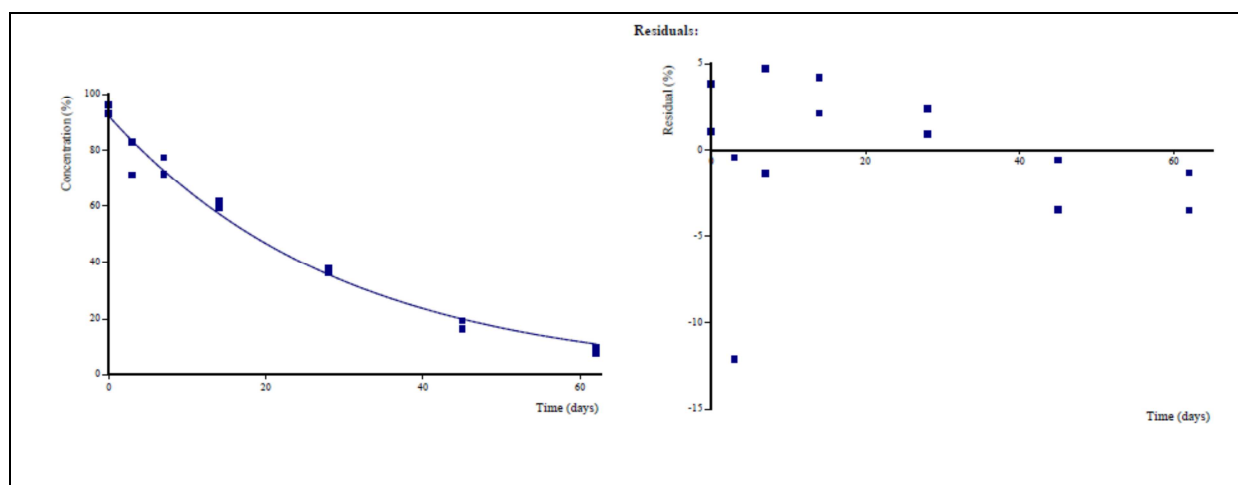


Figure 8-21: Kinetic evaluation Montesquieu soil (FOMC)



Estimated Values:

| Parameter | Value | σ | Prob. > t |
|-----------|----------|----------|-----------|
| Parent_0 | 92.16 | | |
| alpha | 5.2E+06 | | |
| beta | 1.53E+08 | | |

Note: Errors and T-test values could not be calculated because the covariance matrix could not be created.

 χ^2

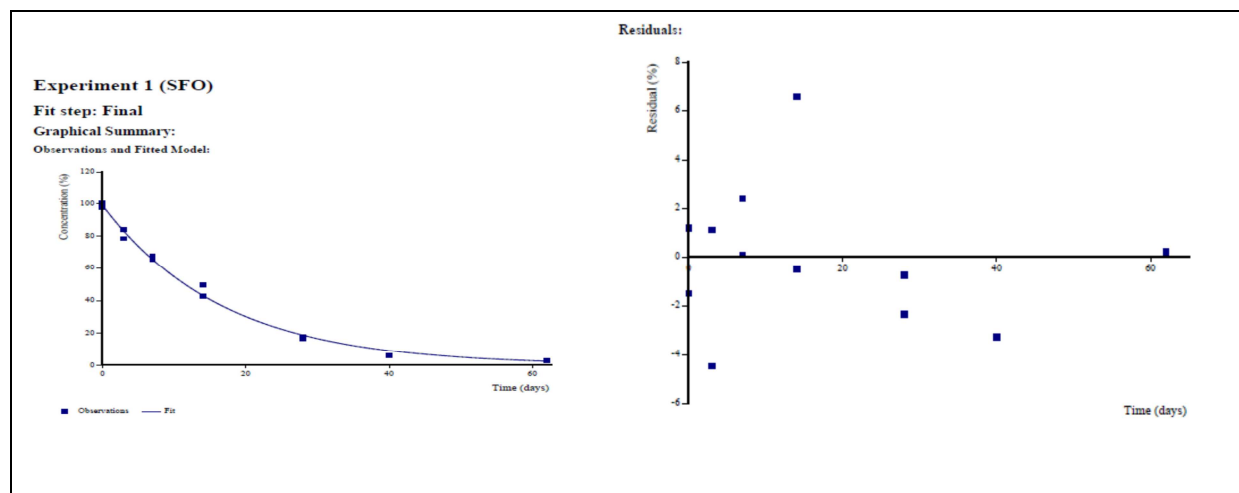
| Parameter | Error % | Degrees of Freedom |
|-----------|---------|--------------------|
| All data | 5.17 | 4 |
| Parent | 5.17 | 4 |

Decay Times:

| Compartment | DT50 (days) | DT90 (days) |
|-------------|-------------|-------------|
| Parent | 20.4 | 67.77 |

Additional Statistics:

Figure 8-22: Kinetic evaluation Sevelen soil (SFO)



Estimated Values:

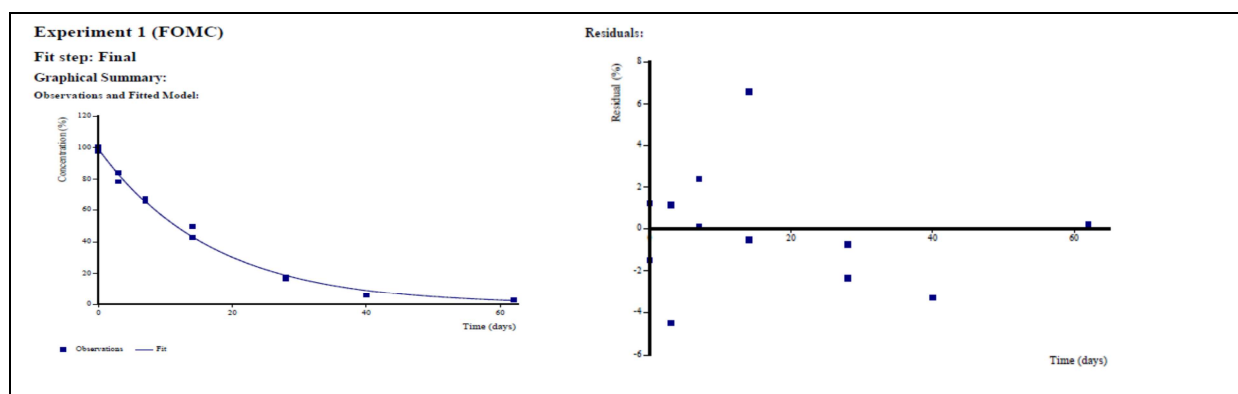
| Parameter | Value | σ | Prob. > t | Lower CI | Upper CI |
|-----------|---------|----------|-----------|----------|----------|
| Parent_0 | 99.2 | 1.632 | 1.298E-16 | 95.64 | 102.8 |
| k_Parent | 0.05951 | 0.002428 | 6.413E-12 | 0.05422 | 0.065 |

 χ^2

| Parameter | Error % | Degrees of Freedom |
|-----------|---------|--------------------|
| All data | 3.413 | 5 |
| Parent | 3.413 | 5 |

Decay Times:

| Compartment | DT50 (days) | DT90 (days) |
|-------------|-------------|-------------|
| Parent | 11.65 | 38.69 |

Figure 8-23: Kinetic evaluation Sevelen soil (FOMC)**Estimated Values:**

| Parameter | Value | σ | Prob. > t |
|-----------|-----------|----------|-----------|
| Parent_0 | 99.2 | | |
| alpha | 9.347E+08 | | |
| beta | 1.571E+10 | | |

Note: Errors and T-test values could not be calculated because the covariance matrix could not be created.

 χ^2

| Parameter | Error % | Degrees of Freedom |
|-----------|---------|--------------------|
| All data | 3.684 | 4 |
| Parent | 3.684 | 4 |

Decay Times:

| Compartment | DT50 (days) | DT90 (days) |
|-------------|-------------|-------------|
|-------------|-------------|-------------|

Table 8-22: Calculated DT₅₀ and DT₉₀ for Ethofumesate

| Soil | Model | DT ₅₀ [days] | DT ₉₀ [days] | Chi Squared (χ^2) |
|----------------------|-------|----------------------------|----------------------------|--------------------------|
| Fislis (silt loam) | SFO | 16.0 | 53.0 | 2.19 |
| Horn (loam) | SFO | 9.4 | 31.2 | 6.17 |
| Montesquieu (clay) | SFO | 20.4 | 67.8 | 4.79 |
| Sevelen (sandy loam) | SFO | 11.7 | 38.7 | 3.41 |

III. CONCLUSION

The aerobic transformation of [¹⁴C]ethofumesate in soil was assessed in four representative European soils (Fislis, Horn, Montesquieu and Sevelen soils) at a temperature $20 \pm 2^\circ\text{C}$ continuously incubated in the dark for 62 days. Average material balance ranged from 96.2 to 110.4% AR over the course of the 62-day study.

The half-life of Ethofumesate in soil test systems ranged from 9.4 to 20.4 days (SFO).

Ultimate degradation was observed by the formation of ¹⁴CO₂ over the course of the 62-day study. Evidence of primary biodegradation was observed for [¹⁴C]ethofumesate in the aerobic soil test samples. Only minor fractions representing less than 5% AR were detected in all soils. The highest fraction was identified as NC 8493.

The study demonstrated that [¹⁴C]ethofumesate degraded rapidly in soil under aerobic conditions, mainly to bound residues and carbon dioxide.

Comment RMS

The aerobic degradation of [¹⁴C]Ethofumesate was studied in four soils (silt loam, loam, clay and sandy loam) for 62 days in the dark at $20 \pm 2^\circ\text{C}$, and moisture level of pF 2.5. Ethofumesate was applied to 100 g soil aliquots at the rate of 1.0 mg/kg, corresponding to a maximum field rate of 1 kg/ha soil. Samples were first extracted with 100 mL of 0.01 M CaCl₂ using a shaker table at approximately 150 rpm for approximately 24 hours. Samples were then extracted by centrifugation and analysed by LSC. The extraction procedure was repeated up to three times with acetonitrile/water 80/20, (v/v, 3×100 mL) using shaker table at 200 rpm for 30 min. The extract was analysed by HPLC/RAM. Identification of the transformation products was done by co-chromatography with reference standards and confirmed using TLC.

The study is considered fully reliable.

The endpoints are:

| Soil | Model | DT ₅₀ [days] | DT ₉₀ [days] | Chi Squared (χ^2) |
|------|-------|----------------------------|----------------------------|-----------------------------|
|------|-------|----------------------------|----------------------------|-----------------------------|

| | | | | |
|----------------------|-----|------|------|------|
| Fislis (silt loam) | SFO | 16.0 | 53.0 | 2.19 |
| Horn (loam) | SFO | 9.4 | 31.2 | 6.17 |
| Montesquieu (clay) | SFO | 20.4 | 67.8 | 4.79 |
| Sevelen (sandy loam) | SFO | 11.7 | 38.7 | 3.41 |

| | |
|---------------------|--|
| Reference: | [¹⁴C]Ethofumesate: Aerobic degradation in nine European soils at 20°C in the dark. |
| Notifier: | UPL/Agrichem |
| Author(s), year: | Hein, W. (2012) |
| Report/Doc. number: | Study No. AS231 |
| Guideline(s): | OECD Guideline 307 |
| GLP: | Yes |
| | Not applicable to kinetic evaluation |
| Deviations: | |
| Validity: | Valid. |
| Status: | New study. |

I. MATERIALS AND METHODS

A. MATERIALS

1. **Test Material:** [C 14-U-ring]Ethofumesate
 - Radiochemical purity:** > 97% (HPLC)
 - Specific radioactivity:** 55 mCi/mmol (7.11 MBq/mg)
 - Study No.:** 11BLY014-repeat
2. **Test Material:** Ethofumesate
 - Purity:** 99.6% (HPLC)
 - CAS No.:** 26225-79-6
 - Batch No.:** SZBB091XV
 - Further relevant properties:** None
3. **Soils:** The test soils were freshly sampled from field sites in Germany, UK, North France, Austria, Spain and Italy. No Ethofumesate was used in these fields at least 3 years before sampling. All soils were collected from the top 20 cm and passed through a 2-mm sieve to assure uniformity. Soil characterisations are presented in the tables below.

Table 8-23: Characterization of soils

| Soil No. | 1 | 2 | 3 | 4 | 5 |
|--------------------------------------|------------------|------------------|------------------|---------------------|---------------------|
| Soil name / Origin | Mußbach, Germany | Lufa 5M, Germany | Lufa2.2, Germany | UK1, United Kingdom | UK2, United Kingdom |
| Soil type (USDA) | Loam | Sandy loam | Loamy sand | Clay loam | Sandy loam |
| Clay [%] | 16.4 | 10.4 | 6.5 | 37.5 | 12.3 |
| Silt [%] | 37.9 | 35.4 | 14.3 | 28.6 | 17.9 |
| Sand [%] | 45.7 | 54.2 | 79.2 | 33.9 | 69.8 |
| Org. Carbon [%] | 1.00 | 1.05 ± 0.20 | 1.87 ± 0.20 | 2.46 | 2.10 |
| pH [CaCl ₂] | 7.21 | 7.3 ± 0.1 | 5.5 ± 0.2 | 6.8 | 6.83 |
| Cation Exchange Capacity [meq/100 g] | ND | 14.9 ± 2.9 | 9.9 ± 0.7 | ND | ND |
| Soil moisture during study | 20.0 | 17.6 | 23.0 | 29.1 | 19.9 |
| pF 2.0 [Vol-%] | 37.75 | 29.39 | 23.11 | 43.01 | 21.24 |
| WHC _{max} [g/100 g] | 39.99 | 35.12 | 46.08 | 58.19 | 39.87 |

Table 8-24: Characterization of soils

| Soil No. | 6 | 7 | 8 | 9 |
|--------------------------------------|--------------|-----------|-----------|-------|
| Soil name / Origin | North France | Austria | Spain | Italy |
| Soil type (USDA) | Loam | Silt loam | Silt loam | Loam |
| Clay [%] | 15.6 | 21.5 | 25.8 | 20.3 |
| Silt [%] | 39.7 | 57.7 | 56.6 | 35.8 |
| Sand [%] | 44.7 | 20.8 | 17.6 | 43.9 |
| Org. Carbon [%] | 1.02 | 1.53 | 1.12 | 3.69 |
| pH [CaCl ₂] | 7.41 | 7.14 | 7.38 | 7.04 |
| Cation Exchange Capacity [meq/100 g] | | | | 28.64 |
| Soil moisture during study | 20.1 | 25.1 | 22.2 | 26.3 |
| pF 2.0 [Vol-%] | 30.82 | 42.07 | 37.50 | 32.21 |
| WHC _{max} [g/100 g] | 40.24 | 50.27 | 44.43 | 52.69 |

ND...not determined

Table 8-25: Soil microbial biomass (mean values)

| Soil No. | Days after treatment | Untreated [mg C/100 g soil] | Ref. item in solvent [mg C/100 g soil] | Solvent only [mg C/100 g soil] | Microbial biomass [% of OC] |
|----------|----------------------|-----------------------------|--|--------------------------------|-----------------------------|
| 1 | 0 | 35 | - | - | 3.5 |
| | 84 | 26.6 | 31.2 | 40.5 | 2.7 |
| 2 | 0 | 20.1 | - | - | 1.9 |
| | 84 | 18.2 | 22.5 | 22.4 | 1.7 |
| 3 | 0 | 35.7 | - | - | 1.9 |
| | 84 | 29.7 | 28.2 | 27.4 | 1.6 |
| 4 | 0 | 32.2 | - | - | 1.3 |
| | 84 | 38.1 | 55.2 | 59.4 | 1.5 |
| 5 | 0 | 49.8 | - | - | 2.4 |
| | 84 | 35.3 | 44.5 | 56.9 | 1.7 |
| 6 | 0 | 35.1 | - | - | 3.4 |
| | 84 | 45.1 | 50.9 | 51.8 | 4.4 |
| 7 | 0 | 73.1 | - | - | 4.8 |
| | 77 | 59.2 | 67.4 | 75.7 | 3.9 |
| 8 | 0 | 50.9 | - | - | 4.5 |
| | 77 | 49.8 | 58.9 | 56.3 | 4.4 |
| 9 | 0 | 67.1 | - | - | 1.8 |
| | 77 | 58.6 | 83.2 | 80.2 | 1.6 |

B. STUDY DESIGN

1. Experimental conditions

The target rate of Ethofumesate was set to 50.0 µg per test system (100 g dry weight aliquots of fresh soil), equivalent to 500 g a.i./ha.

Samples of collected and sieved soil, equivalent to 100 g dry weight of soil, were filled into Erlenmeyer flasks and adjusted to 45-50% of WHC_{max} by addition of water. The test vessels were treated individually with aliquots of 952 µL (soils 1-6) and 961 µL (soils 7-9) corresponding to 50.02 and 50.04 µg test item, respectively. The soils were hand shaken and solvent was given time to evaporate and the water content was then adjusted to 50% WHC_{max} . Except for time-zero vessels, vessels were closed with a trap and introduced in the temperature controlled chamber at $20 \pm 2^\circ C$.

2. Sampling

Samples were taken on 0, 3, 7, 14 (or 15), 28, 50 and 77 (or 84) days and additionally after 120 days for soil 4.

3. Description of analytical procedures

Samples were extracted with 100 mL of 0.01 M CaCl_2 , three times with 100 mL acetonitrile/water (4:1, v/v) and one time under reflux conditions with the same solvent. The CaCl_2 extracts and the pooled organic extracts were then submitted for LSC and radio-HPLC analyses.

The volatiles were trapped in the soda lime trap attachment. The trapped volatiles were measured by LSC and an identification via precipitation with $\text{Ba}(\text{OH})_2$ was performed.

The non-extractable radioactivity was measured by combustion followed by radio assay.

II. RESULTS AND DISCUSSION

A. MASS BALANCE

The material balance from all the individual test vessels ranged between 92.0% and 101.2% AR. The mean recovery of radioactivity ranged from 96.3 to 98.4% AR for all soils.

Table 8-26: Distribution of applied radioactivity (% AR)

| Day | CaCl ₂ | Room temperature extraction | Reflux-extraction | ¹⁴ CO ₂ | NER | Mass balance | [¹⁴ C]Ethofumesate | n.i. |
|-------------------------|-------------------|-----------------------------|-------------------|-------------------------------|-------|--------------|--------------------------------|------|
| Soil 1 (Germany) | | | | | | | | |
| 0 | 29.86 | 62.21 | n.m. | n.m. | 4.98 | 97.04 | 91.12 | 0.95 |
| 3 | 23.30 | 66.60 | 1.65 | 0.32 | 5.77 | 97.64 | 90.39 | 1.16 |
| 7 | 19.45 | 60.63 | 2.60 | 1.56 | 13.33 | 97.58 | 80.52 | 2.16 |
| 14 | 13.72 | 44.44 | 2.28 | 6.14 | 29.23 | 95.81 | 57.57 | 2.87 |
| 28a | 7.17 | 25.02 | 2.02 | 15.47 | 45.76 | 95.45 | 31.93 | 2.28 |
| 28b | 6.94 | 24.24 | 1.80 | 14.91 | 47.33 | 95.22 | 30.08 | 2.90 |
| 50 | 2.78 | 10.20 | 1.50 | 27.99 | 55.77 | 98.25 | 10.79 | 3.69 |
| 84 | 1.77 | 4.98 | 1.11 | 34.58 | 53.54 | 95.99 | 4.92 | 2.94 |
| Soil 2 (Germany) | | | | | | | | |
| 0 | 34.52 | 60.04 | n.m. | n.m. | 2.84 | 97.40 | 92.38 | 2.18 |
| 3 | 27.37 | 61.22 | 1.61 | 0.80 | 6.40 | 97.40 | 88.53 | 1.67 |
| 7 | 22.05 | 56.54 | 1.86 | 3.37 | 13.71 | 97.54 | 79.25 | 1.20 |
| 14 | 14.48 | 41.18 | 2.01 | 10.18 | 27.60 | 95.45 | 55.43 | 2.24 |
| 28a | 5.92 | 19.32 | 1.72 | 20.49 | 45.85 | 93.30 | 24.68 | 2.28 |
| 28b | 6.20 | 19.78 | 1.56 | 23.13 | 45.99 | 96.66 | 25.53 | 2.01 |
| 50 | 2.00 | 6.96 | 1.07 | 37.66 | 50.70 | 98.39 | 6.41 | 3.62 |
| 84 | 1.33 | 4.04 | 1.11 | 42.81 | 48.47 | 97.76 | 3.70 | 2.78 |
| Soil 3 (Germany) | | | | | | | | |
| 0 | 17.00 | 77.69 | n.m. | n.m. | 3.78 | 98.47 | 94.45 | 0.24 |
| 3 | 10.93 | 76.37 | 1.70 | 1.60 | 7.41 | 98.01 | 88.22 | 0.78 |
| 7 | 8.09 | 67.84 | 2.34 | 4.82 | 14.53 | 97.62 | 78.00 | 0.27 |
| 14 | 4.63 | 41.37 | 2.50 | 17.13 | 30.61 | 96.25 | 44.48 | 4.02 |
| 28a | 1.18 | 18.21 | 2.19 | 35.75 | 39.89 | 97.22 | 20.01 | 1.57 |
| 28b | 1.01 | 16.60 | 2.09 | 36.35 | 40.25 | 96.31 | 17.85 | 1.85 |
| 50 | 0.35 | 7.80 | 1.15 | 50.87 | 40.88 | 101.05 | 6.93 | 2.37 |
| 84 | 0.28 | 5.16 | 1.06 | 54.24 | 39.26 | 100.51 | 4.69 | 1.81 |
| Soil 4 (UK) | | | | | | | | |
| 0 | 15.21 | 59.74 | 16.48 | n.m. | 6.91 | 98.33 | 90.75 | 0.68 |
| 3 | 10.25 | 64.92 | 13.66 | 0.54 | 8.84 | 98.22 | 97.88 | 0.95 |
| 7 | 8.48 | 58.53 | 10.20 | 2.18 | 8.08 | 97.47 | 76.15 | 1.06 |
| 14 | 5.78 | 44.25 | 10.98 | 8.08 | 27.27 | 96.35 | 59.69 | 1.32 |
| 28a | 3.45 | 32.16 | 6.73 | 15.84 | 37.68 | 95.85 | 41.34 | 1.00 |
| 28b | 3.13 | 27.77 | 8.73 | 17.10 | 38.47 | 95.19 | 38.77 | 0.86 |
| 50 | 1.33 | 14.99 | 6.28 | 29.68 | 44.78 | 97.06 | 21.97 | 0.63 |
| 84 | 0.75 | 9.67 | 8.66 | 36.02 | 45.72 | 100.82 | 17.95 | 1.13 |
| 120 | 0.56 | 6.26 | 3.02 | 41.61 | 43.99 | 95.43 | 8.83 | 1.01 |
| Soil 5 (UK) | | | | | | | | |
| 0 | 17.27 | 78.58 | n.m. | n.m. | 2.65 | 98.50 | 93.98 | 1.87 |

| Day | CaCl ₂ | Room temperature extraction | Reflux-extraction | ¹⁴ CO ₂ | NER | Mass balance | [¹⁴ C]Ethofumesate | n.i. |
|--------------------------|-------------------|-----------------------------|-------------------|-------------------------------|-------|--------------|--------------------------------|------|
| 3 | 12.92 | 78.60 | 1.53 | 0.46 | 5.46 | 98.97 | 92.04 | 1.01 |
| 7 | 10.80 | 72.52 | 1.52 | 1.63 | 11.96 | 98.43 | 83.23 | 1.61 |
| 14 | 8.82 | 56.22 | 2.09 | 5.45 | 24.97 | 97.54 | 62.92 | 4.21 |
| 28a | 8.71 | 41.70 | 1.82 | 10.24 | 35.91 | 98.38 | 47.79 | 4.44 |
| 28b | 5.47 | 34.13 | 1.39 | 13.47 | 43.78 | 98.24 | 37.18 | 3.81 |
| 50 | 2.62 | 17.99 | 1.61 | 23.50 | 52.45 | 98.16 | 20.12 | 2.10 |
| 84 | 1.60 | 9.24 | 1.14 | 29.32 | 57.73 | 99.03 | 9.55 | 2.43 |
| Soil 6 (N-France) | | | | | | | | |
| 0 | 29.73 | 58.76 | 1.54 | n.m. | 2.01 | 92.04 | 89.12 | 0.91 |
| 3 | 21.74 | 66.64 | 1.91 | 0.80 | 6.70 | 97.78 | 88.79 | 1.50 |
| 7 | 16.41 | 61.63 | 2.06 | 3.82 | 14.29 | 98.22 | 78.93 | 1.17 |
| 14 | 10.29 | 39.90 | 2.19 | 11.09 | 31.64 | 95.11 | 48.19 | 4.19 |
| 28a | 4.01 | 17.71 | 1.56 | 24.42 | 47.19 | 94.88 | 19.97 | 3.31 |
| 28b | 3.50 | 16.63 | 1.55 | 25.33 | 48.71 | 95.72 | 18.82 | 2.86 |
| 50 | 1.26 | 5.92 | 1.15 | 41.03 | 49.04 | 98.39 | 5.62 | 2.71 |
| 84 | 0.94 | 3.93 | 1.10 | 45.25 | 47.29 | 98.51 | 3.74 | 2.23 |
| Soil 7 (Austria) | | | | | | | | |
| 0 | 21.19 | 72.54 | 2.52 | n.m. | 2.45 | 98.70 | 94.71 | 1.54 |
| 3 | 15.99 | 68.01 | 5.18 | 0.65 | 8.35 | 98.19 | 87.39 | 1.79 |
| 7 | 12.69 | 59.07 | 2.37 | 3.08 | 19.57 | 96.78 | 70.07 | 4.06 |
| 15 | 7.51 | 34.19 | 3.63 | 11.31 | 38.61 | 95.25 | 42.20 | 3.13 |
| 28a | 3.03 | 15.00 | 2.98 | 22.93 | 51.07 | 95.02 | 17.94 | 3.07 |
| 28b | 3.69 | 16.77 | 3.37 | 21.10 | 50.71 | 95.64 | 20.44 | 3.39 |
| 50 | 1.18 | 5.92 | 1.39 | 35.72 | 53.62 | 97.84 | 6.49 | 2.00 |
| 77 | 1.00 | 3.82 | 1.02 | 39.29 | 50.99 | 96.13 | 3.69 | 2.15 |
| Soil 8 (Spain) | | | | | | | | |
| 0 | 25.95 | 68.69 | 2.45 | n.m. | 1.84 | 98.93 | 96.05 | 1.05 |
| 3 | 20.07 | 62.08 | 8.18 | 0.51 | 7.70 | 98.54 | 85.97 | 4.36 |
| 7 | 16.59 | 63.02 | 2.88 | 2.48 | 13.15 | 98.12 | 79.90 | 2.59 |
| 15 | 10.38 | 40.88 | 5.06 | 8.94 | 30.02 | 95.29 | 52.72 | 3.60 |
| 28a | 5.43 | 21.17 | 5.69 | 18.46 | 43.44 | 94.19 | 30.16 | 2.13 |
| 28b | 5.36 | 22.38 | 5.07 | 18.71 | 43.60 | 95.12 | 30.93 | 1.88 |
| 50 | 1.92 | 10.14 | 2.85 | 31.13 | 50.01 | 96.05 | 12.50 | 2.41 |
| 77 | 1.10 | 6.24 | 1.54 | 39.04 | 48.81 | 96.74 | 7.17 | 1.71 |
| Soil 9 (Italy) | | | | | | | | |
| 0 | 16.84 | 77.75 | 1.89 | n.m. | 2.88 | 99.36 | 95.42 | 1.06 |
| 3 | 12.82 | 74.48 | 2.25 | 0.87 | 8.48 | 98.90 | 88.73 | 0.82 |
| 7 | 10.66 | 61.69 | 2.22 | 3.63 | 19.81 | 98.00 | 71.30 | 3.27 |
| 15 | 6.11 | 34.69 | 1.93 | 13.14 | 39.14 | 95.02 | 40.26 | 2.47 |
| 28a | 2.15 | 12.65 | 1.28 | 27.82 | 52.46 | 96.36 | 13.97 | 2.11 |
| 28b | 2.08 | 11.83 | 1.20 | 28.05 | 53.46 | 96.63 | 12.79 | 2.32 |

| Day | CaCl ₂ | Room temperature extraction | Reflux-extraction | ¹⁴ CO ₂ | NER | Mass balance | [¹⁴ C]Ethofumesate | n.i. |
|-----|-------------------|-----------------------------|-------------------|-------------------------------|-------|--------------|--------------------------------|------|
| 50 | 0.96 | 4.60 | 0.98 | 38.85 | 53.73 | 99.12 | 4.83 | 1.71 |
| 77 | 0.84 | 3.04 | 0.74 | 45.63 | 50.90 | 101.15 | 3.16 | 1.46 |

n.m.: not measured

NER: not extracted radioactivity / other volatiles were below 0.1%

n.i.: not identified metabolites

B. BOUND AND EXTRACTABLE RESIDUES

Extractable radioactivity decreased continuously in the course of the study. The non-extractable radioactivity increased over the incubation period reaching between 39.26 and 57.73% AR at the end of the incubation period (77 or 84 days). For soil 4, 43.99% AR was determined to be NER on 120 days after treatment (DAT).

C. VOLATILIZATION

For all soils significant mineralisation was determined. Quantities of ¹⁴CO₂ on the last sampling date (DAT 77 / 84) varied between 29.32% and 54.24% AR and for soil 4 on DAT 120 41.61% AR was determined to be ¹⁴CO₂. Other volatile radioactivity apart from ¹⁴CO₂ never exceeded 0.1% AR.

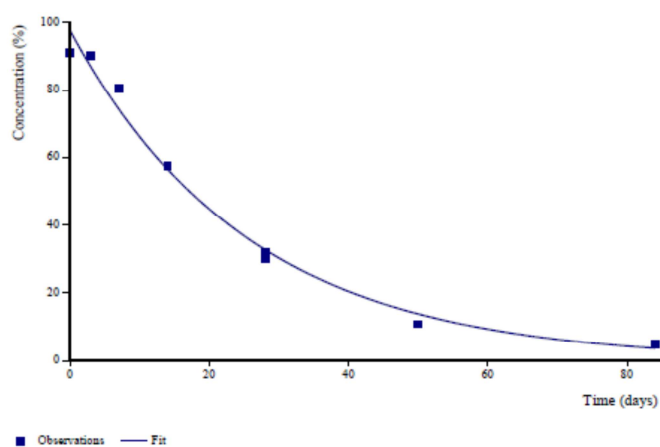
D. TRANSFORMATION OF PARENT COMPOUND

The amount of Ethofumesate continuously decreased over the incubation period. Immediately after treatment (DAT 0) the parent compound represented more than 90% AR (except for soil 6 with 89.1% AR), decreasing to between 44.48% and 62.92% AR after 14 days (soils 1-6) or between 40.26% and 52.72% AR after 15 days (soils 7-9). At the end of the incubation period less than 10% AR was assigned as unchanged Ethofumesate.

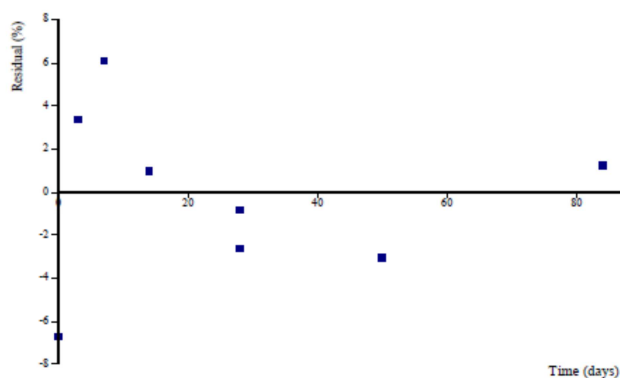
Up to 6 unknown metabolites/zones were detected during the course of the study. The sum of all non-identified metabolites/zones represented always less than 5% AR for any soil.

Table 8-27: Kinetic evaluation soil 1 (SFO)

Observations and Fitted Model:



Residuals:



Appendix 10 continued:

Estimated Values:

| Parameter | Value | σ | Prob. > t | Lower CI | Upper CI |
|-----------|---------|----------|-----------|----------|----------|
| Parent 0 | 97.83 | 3.128 | 3.55E-08 | 90.18 | 105.5 |
| k Parent | 0.03912 | 0.002994 | 6.198E-06 | 0.03179 | 0.046 |

 χ^2

| Parameter | Error % | Degrees of Freedom |
|-----------|---------|--------------------|
| All data | 5.991 | 5 |
| Parent | 5.991 | 5 |

Decay Times:

| Compartment | DT50 (days) | DT90 (days) |
|-------------|-------------|-------------|
| Parent | 17.72 | 58.86 |

Additional Statistics:

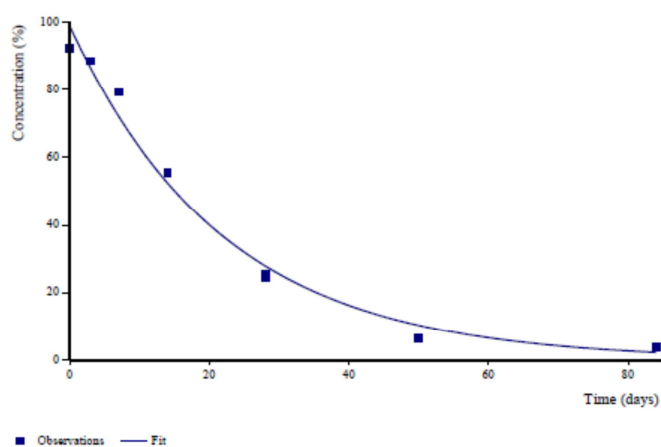
| Parameter | r^2 (Obs v Pred) | Efficiency |
|-----------|--------------------|------------|
| All data | 0.9869 | 0.9868 |
| Parent | 0.9869 | 0.9868 |

Parameter Correlation:

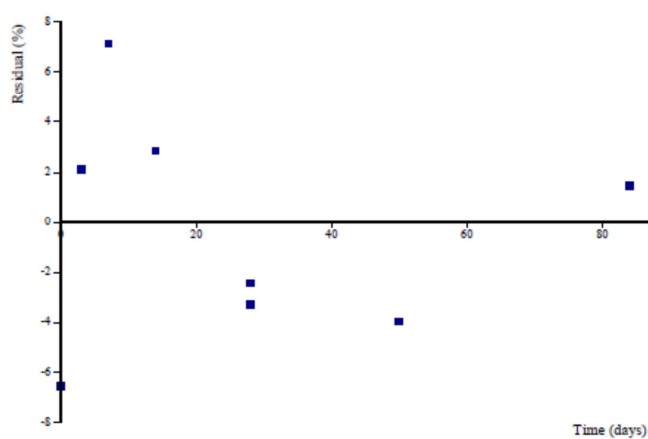
| | Parent 0 | k Parent |
|----------|----------|----------|
| Parent 0 | 1 | 0.587 |
| k Parent | 0.587 | 1 |

Table 8-28: Kinetic evaluation Soil 2 (SFO)

Observations and Fitted Model:



Residuals:



Estimated Values:

| Parameter | Value | σ | Prob. > t | Lower CI | Upper CI |
|-----------|---------|----------|-----------|----------|----------|
| Parent 0 | 98.94 | 3.583 | 7.461E-08 | 90.17 | 107.7 |
| k Parent | 0.04514 | 0.00384 | 1.144E-05 | 0.03574 | 0.055 |

 χ^2

| Parameter | Error % | Degrees of Freedom |
|-----------|---------|--------------------|
| All data | 6.89 | 5 |
| Parent | 6.89 | 5 |

Decay Times:

| Compartment | DT50 (days) | DT90 (days) |
|-------------|-------------|-------------|
| Parent | 15.36 | 51.01 |

Additional Statistics:

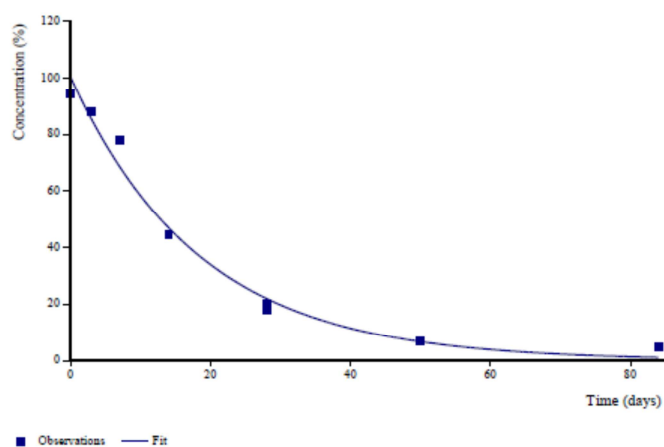
| Parameter | r^2 (Obs v Pred) | Efficiency |
|-----------|--------------------|------------|
| All data | 0.9853 | 0.985 |
| Parent | 0.9853 | 0.985 |

Parameter Correlation:

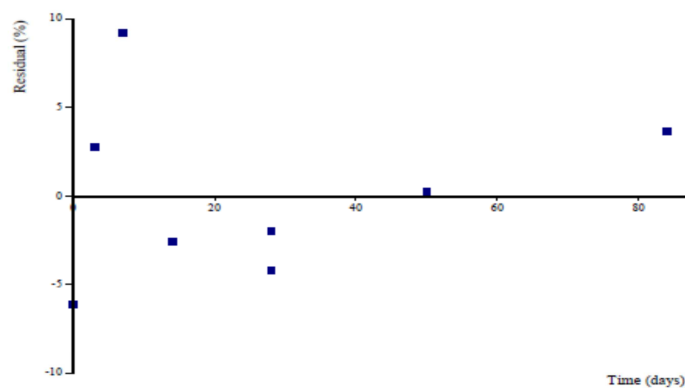
| | Parent 0 | k Parent |
|----------|----------|----------|
| Parent 0 | 1 | 0.5798 |
| k Parent | 0.5798 | 1 |

Table 8-29: Kinetic evaluation Soil 3 (SFO)

Observations and Fitted Model:



Residuals:



Estimated Values:

| Parameter | Value | σ | Prob. > t | Lower CI | Upper CI |
|-----------|---------|----------|-----------|----------|----------|
| Parent 0 | 100.6 | 4.107 | 1.526E-07 | 90.51 | 110.6 |
| k Parent | 0.05422 | 0.005123 | 2.095E-05 | 0.04168 | 0.067 |

 χ^2

| Parameter | Error % | Degrees of Freedom |
|-----------|---------|--------------------|
| All data | 7.908 | 5 |
| Parent | 7.908 | 5 |

Decay Times:

| Compartment | DT50 (days) | DT90 (days) |
|-------------|-------------|-------------|
| Parent | 12.78 | 42.47 |

Additional Statistics:

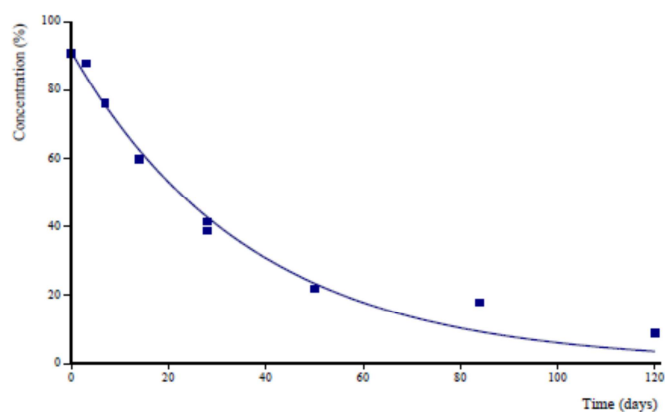
| Parameter | r^2 (Obs v Pred) | Efficiency |
|-----------|--------------------|------------|
| All data | 0.9826 | 0.9826 |
| Parent | 0.9826 | 0.9826 |

Parameter Correlation:

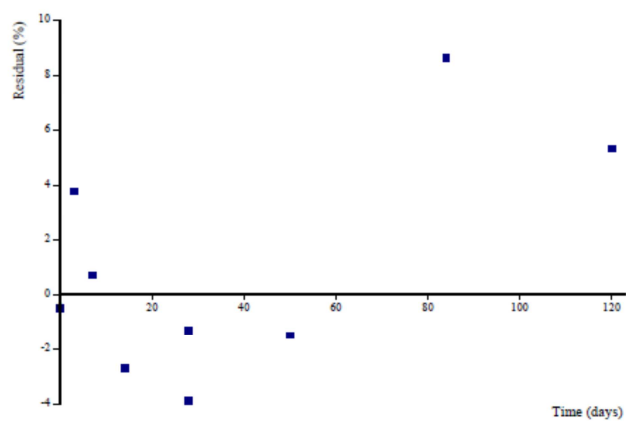
| | Parent 0 | k Parent |
|----------|----------|----------|
| Parent 0 | 1 | 0.5713 |
| k Parent | 0.5713 | 1 |

Table 8-30: Kinetic evaluation Soil 4 (SFO)

Observations and Fitted Model:



Residuals:



Estimated Values:

| Parameter | Value | σ | Prob. > t | Lower CI | Upper CI |
|-----------|---------|----------|-----------|----------|----------|
| Parent_0 | 91.24 | 3.023 | 5.646E-09 | 84.09 | 98.39 |
| k_Parent | 0.02716 | 0.00229 | 3.442E-06 | 0.02174 | 0.033 |

 χ^2

| Parameter | Error % | Degrees of Freedom |
|-----------|---------|--------------------|
| All data | 6.472 | 6 |
| Parent | 6.472 | 6 |

Decay Times:

| Compartment | DT50 (days) | DT90 (days) |
|-------------|-------------|-------------|
| Parent | 25.52 | 84.79 |

Additional Statistics:

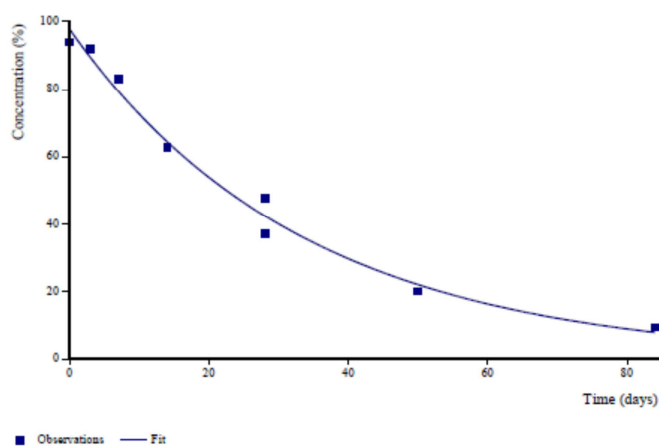
| Parameter | r^2 (Obs v Pred) | Efficiency |
|-----------|--------------------|------------|
| All data | 0.9848 | 0.981 |
| Parent | 0.9848 | 0.981 |

Parameter Correlation:

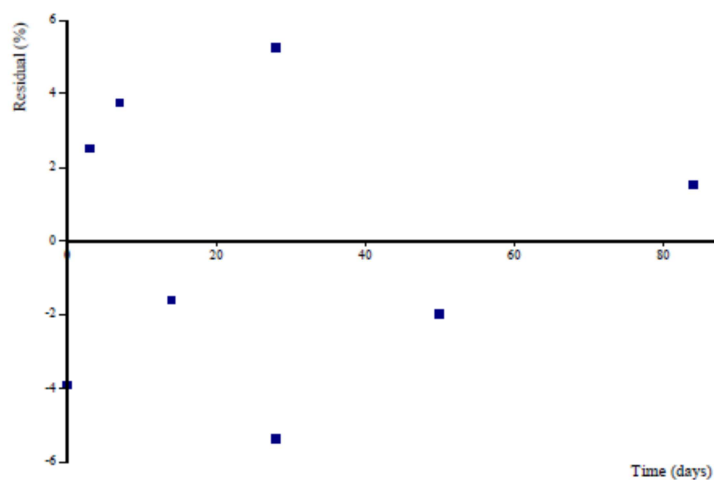
| | Parent_0 | k_Parent |
|----------|----------|----------|
| Parent_0 | 1 | 0.5993 |
| k_Parent | 0.5993 | 1 |

Table 8-31: Kinetic evaluation soil 5 (SFO)

Observations and Fitted Model:



Residuals:



Estimated Values:

| Parameter | Value | σ | Prob. > t | Lower CI | Upper CI |
|-----------|---------|----------|-----------|----------|----------|
| Parent_0 | 97.89 | 2.794 | 1.801E-08 | 91.05 | 104.7 |
| k_Parent | 0.02976 | 0.002144 | 4.357E-06 | 0.02451 | 0.035 |

 χ^2

| Parameter | Error % | Degrees of Freedom |
|-----------|---------|--------------------|
| All data | 3.47 | 5 |
| Parent | 3.47 | 5 |

Decay Times:

| Compartment | DT50 (days) | DT90 (days) |
|-------------|-------------|-------------|
| Parent | 23.29 | 77.37 |

Additional Statistics:

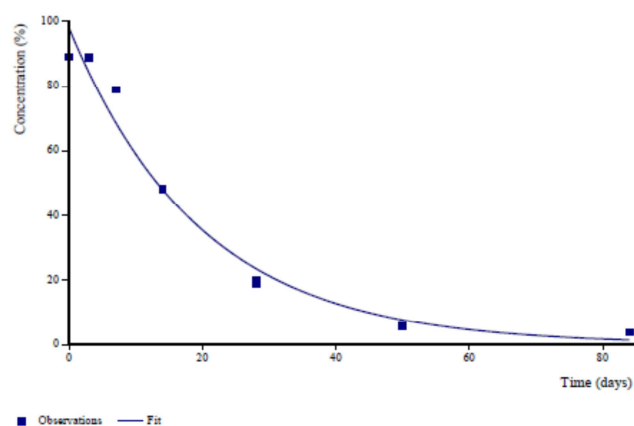
| Parameter | r^2 (Obs v Pred) | Efficiency |
|-----------|--------------------|------------|
| All data | 0.9864 | 0.9864 |
| Parent | 0.9864 | 0.9864 |

Parameter Correlation:

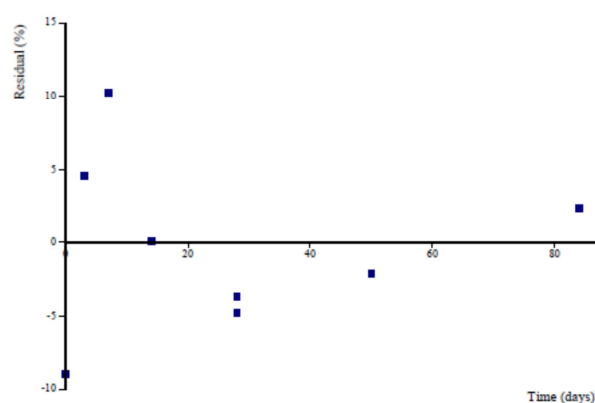
| | Parent_0 | k_Parent |
|----------|----------|----------|
| Parent_0 | 1 | 0.6005 |
| k_Parent | 0.6005 | 1 |

Table 8-32: Kinetic evaluation Soil 6 (SFO)

Observations and Fitted Model:



Residuals:



Estimated Values:

| Parameter | Value | σ | Prob. > t | Lower CI | Upper CI |
|-----------|---------|----------|-----------|----------|----------|
| Parent_0 | 98.08 | 4.919 | 5.164E-07 | 86.05 | 110.1 |
| k Parent | 0.05085 | 0.005925 | 6.874E-05 | 0.03636 | 0.065 |

 χ^2

| Parameter | Error % | Degrees of Freedom |
|-----------|---------|--------------------|
| All data | 9.635 | 5 |
| Parent | 9.635 | 5 |

Decay Times:

| Compartment | DT50 (days) | DT90 (days) |
|-------------|-------------|-------------|
| Parent | 13.63 | 45.28 |

Additional Statistics:

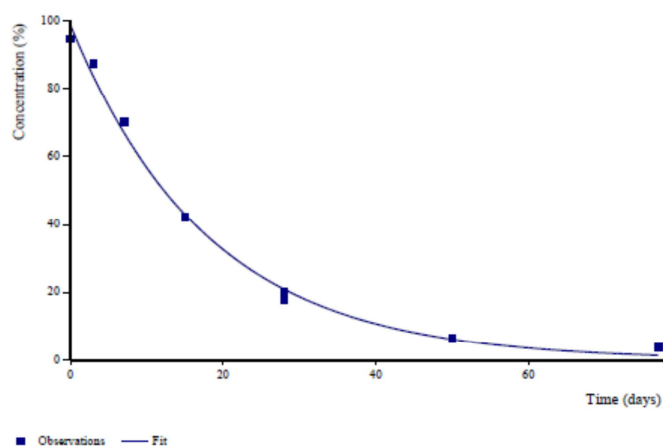
| Parameter | r^2 (Obs v Pred) | Efficiency |
|-----------|--------------------|------------|
| All data | 0.9739 | 0.9737 |
| Parent | 0.9739 | 0.9737 |

Parameter Correlation:

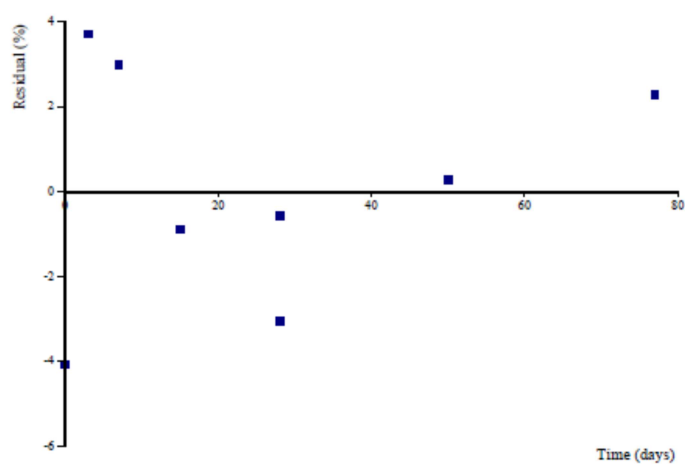
| | Parent_0 | k Parent |
|----------|----------|----------|
| Parent_0 | 1 | 0.5741 |
| k Parent | 0.5741 | 1 |

Table 8-33: Kinetic evaluation Soil 7 (SFO)

Observations and Fitted Model:



Residuals:



Estimated Values:

| Parameter | Value | σ | Prob. > t | Lower CI | Upper CI |
|-----------|---------|----------|-----------|----------|----------|
| Parent_0 | 98.79 | 2.339 | 5.884E-09 | 93.07 | 104.5 |
| k_Parent | 0.05533 | 0.002997 | 8.141E-07 | 0.048 | 0.063 |

 χ^2

| Parameter | Error % | Degrees of Freedom |
|-----------|---------|--------------------|
| All data | 4.537 | 5 |
| Parent | 4.537 | 5 |

Decay Times:

| Compartment | DT50 (days) | DT90 (days) |
|-------------|-------------|-------------|
| Parent | 12.53 | 41.61 |

Additional Statistics:

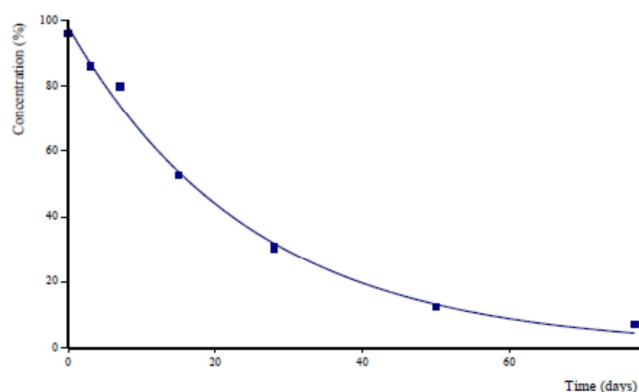
| Parameter | r^2 (Obs v Pred) | Efficiency |
|-----------|--------------------|------------|
| All data | 0.9942 | 0.9941 |
| Parent | 0.9942 | 0.9941 |

Parameter Correlation:

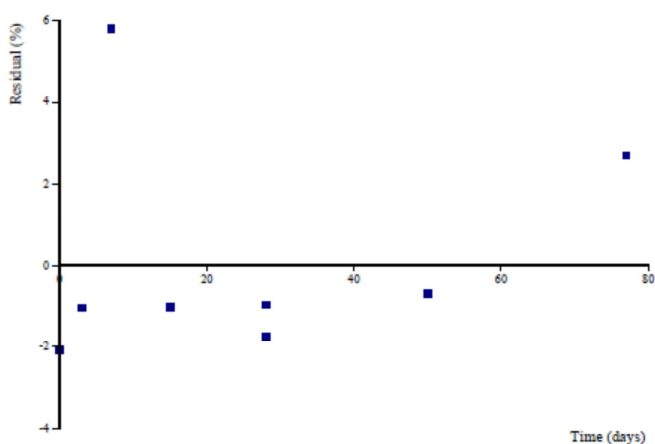
| | Parent_0 | k_Parent |
|----------|----------|----------|
| Parent_0 | 1 | 0.564 |
| k_Parent | 0.564 | 1 |

Table 8-34: Kinetic evaluation soil 8 (SFO)

Observations and Fitted Model:



Residuals:



Estimated Values:

| Parameter | Value | σ | Prob. > t | Lower CI | Upper CI |
|-----------|---------|----------|-----------|----------|----------|
| Parent_0 | 98.13 | 2.127 | 3.476E-09 | 92.92 | 103.3 |
| k_Parent | 0.04014 | 0.002042 | 5.611E-07 | 0.03515 | 0.045 |

 χ^2

| Parameter | Error % | Degrees of Freedom |
|-----------|---------|--------------------|
| All data | 4.069 | 5 |
| Parent | 4.069 | 5 |

Decay Times:

| Compartment | DT50 (days) | DT90 (days) |
|-------------|-------------|-------------|
| Parent | 17.27 | 57.36 |

Additional Statistics:

| Parameter | r^2 (Obs v Pred) | Efficiency |
|-----------|--------------------|------------|
| All data | 0.9938 | 0.9938 |
| Parent | 0.9938 | 0.9938 |

Parameter Correlation:

| | Parent_0 | k_Parent |
|----------|----------|----------|
| Parent_0 | 1 | 0.5814 |
| k_Parent | 0.5814 | 1 |

Table 8-35: Calculated DT₅₀ and DT₉₀ for Ethofumesate

| Soil No. (Country) | Model | DT ₅₀ [days] | DT ₉₀ [days] | Chi Squared (χ^2) [%] |
|--------------------|-------|----------------------------|----------------------------|---------------------------------|
| Soil 1 (Germany) | SFO | 17.72 | 58.86 | 5.99 |
| Soil 2 (Germany) | SFO | 15.36 | 51.01 | 6.89 |
| Soil 3 (Germany) | SFO | 12.78 | 42.47 | 7.91 |
| Soil 4 (UK) | SFO | 25.52 | 84.79 | 6.47 |
| Soil 5 (UK) | SFO | 23.29 | 77.37 | 3.47 |
| Soil 6 (N-France) | SFO | 13.63 | 45.28 | 9.64 |
| Soil 7 (Austria) | SFO | 12.53 | 41.61 | 4.54 |
| Soil 8 (Spain) | SFO | 17.27 | 57.36 | 4.07 |
| Soil 9 (Italy) | SFO | 11.10 | 36.88 | 7.11 |

III. CONCLUSION

The degradation of [¹⁴C]Ethofumesate was evaluated in nine soils under aerobic conditions at 20°C in the dark. The material balance ranged from 92.0 to 101.2% AR for all soils and individual sampling dates.

The half-lives of Ethofumesate in soil test systems ranged between 11.1 to 25.5 days (SFO).

Ethofumesate was degraded mainly by mineralisation (29.3% - 54.2% AR) and formation of bound residues (39.3% - 57.7% AR). No major metabolite was detected.

Comment RMS

The aerobic degradation of [^{14}C]Ethofumesate was studied in nine European agricultural soils for 84 days (for 120 days only in soil 4) under aerobic conditions in the dark at $20 \pm 2^\circ\text{C}$, and moisture content of about 45-50% of the maximum water holding capacity. Key soil parameters such as CEC and bulk density were not determined. One soil (Soil 9, Italy) was excluded by the RMS from further considerations since the physico-chemical parameters were from previous batches and were not determined for the batch actually used in the experiment. Ethofumesate was applied to 100 g soil aliquots at the rate of 0.5 mg/kg, corresponding to a maximum field rate of 500 g/ha. The study was set up with individual flasks and not in duplicates (the exception was sampling day 28, which was set up in duplicates). Samples were extracted with 100 mL of 0.01 M CaCl_2 , three times with 100 mL acetonitrile/water (4:1, v/v) and one time under reflux conditions with the same solvent. The CaCl_2 extracts and the pooled organic extracts were then submitted for LSC and radio-HPLC analyses. The report states that values in general are presented as mean values of duplicates. However, the single measured values are not reported.

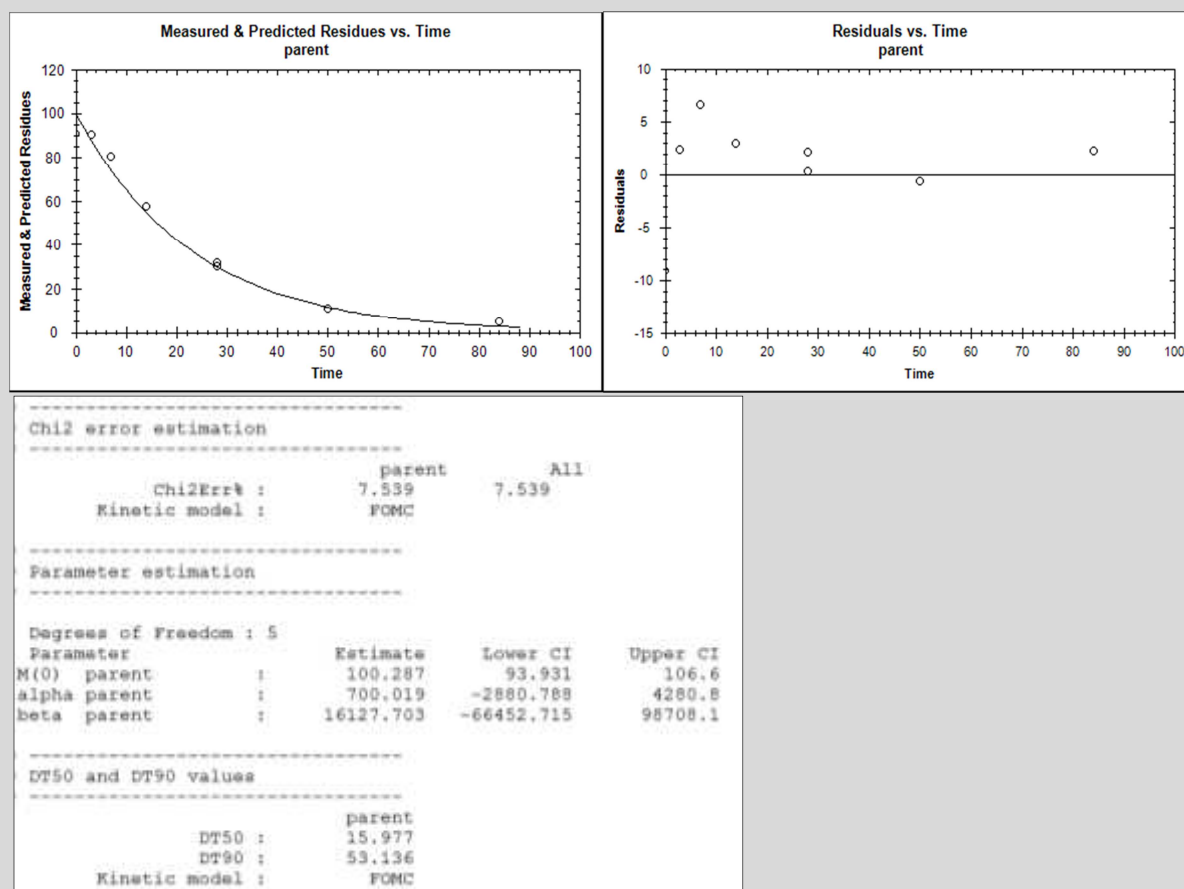
No major metabolite was detected.

Except for one soil, only SFO models are reported. Therefore, the RMS conducted additional calculations using the FOMC model (KinGUI 2; Schmitt et al. (2011)). Graphs and residuals are shown below. In all cases did the SFO provide lower χ^2 errors than FOMC.

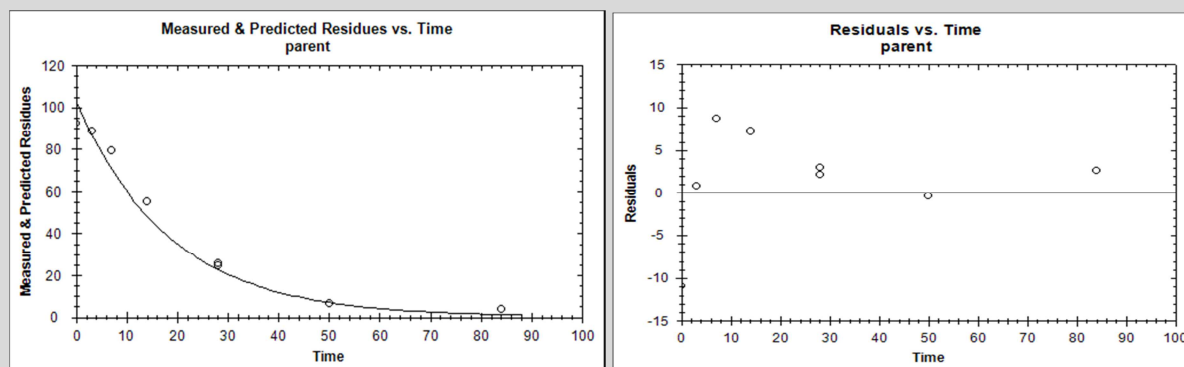
The endpoints are:

| Soil | Model | DT ₅₀ [days] | DT ₉₀ [days] | Chi Squared (χ^2) |
|-------------------|-------|----------------------------|----------------------------|-----------------------------|
| Soil 1 (Germany) | SFO | 17.72 | 58.86 | 5.99 |
| Soil 2 (Germany) | SFO | 15.36 | 51.01 | 6.89 |
| Soil 3 (Germany) | SFO | 12.78 | 42.47 | 7.91 |
| Soil 4 (UK) | SFO | 25.52 | 84.79 | 6.47 |
| Soil 5 (UK) | SFO | 23.29 | 77.37 | 3.47 |
| Soil 6 (N-France) | SFO | 13.63 | 45.28 | 9.64 |
| Soil 7 (Austria) | SFO | 12.53 | 41.61 | 4.54 |
| Soil 8 (Spain) | SFO | 17.27 | 57.36 | 4.07 |

Soil 1 FOMC



Soil 2 FOMC



```

-----
Chi2 error estimation
-----
          parent      All
Chi2Err% :      10.45      10.45
Kinetic model :      FOMC

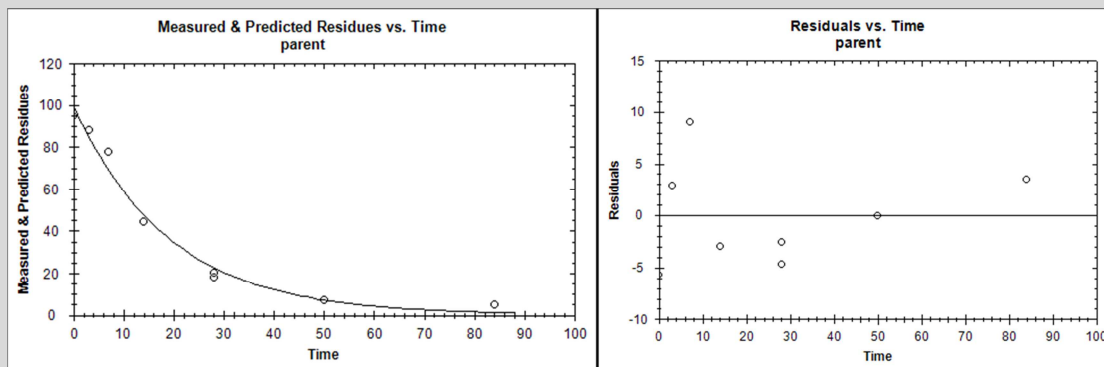
-----
Parameter estimation
-----

Degrees of Freedom : 5
Parameter      Estimate      Lower CI      Upper CI      St.Dev      Prob > t
M(0) parent    :      103.281      94.299      112.3      4.582      1.60e-06
alpha parent   :      5418.546     -2638.328     13475.4     4110.726     0.122
beta parent    :      99622.976    -48529.431     247775.4     75589.352     0.122

-----
DT50 and DT90 values
-----
          parent
DT50 :      13.745
DT90 :      42.343
Kinetic model :      FOMC

```

Soil 3 FOMC



```

-----
Chi2 error estimation
-----
          parent      All
Chi2Err% :      8.486      8.486
Kinetic model :      FOMC

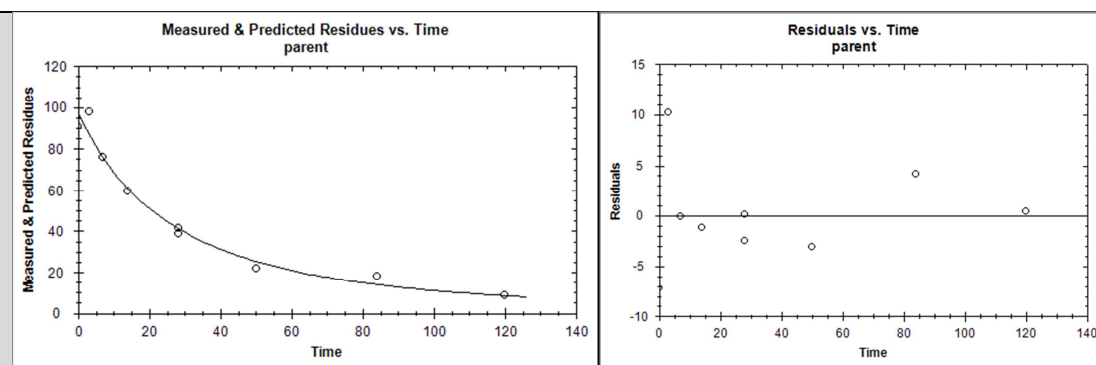
-----
Parameter estimation
-----

Degrees of Freedom : 5
Parameter      Estimate      Lower CI      Upper CI      St.Dev      Prob > t
M(0) parent    :      100.118      92.815      107.3      3.475      6.24e-4
alpha parent   :      705.870     -3810.138     5221.9     2304.124     0.38
beta parent    :      13240.479    -71660.098     98141.1     43317.417     0.38

-----
DT50 and DT90 values
-----
          parent
DT50 :      13.008
DT90 :      43.262
Kinetic model :      FOMC

```

Soil 4 FOMC



Chi2 error estimation

| | parent | All |
|---------------|--------|-------|
| Chi2Err% | 7.941 | 7.941 |
| Kinetic model | FOMC | |

Parameter estimation

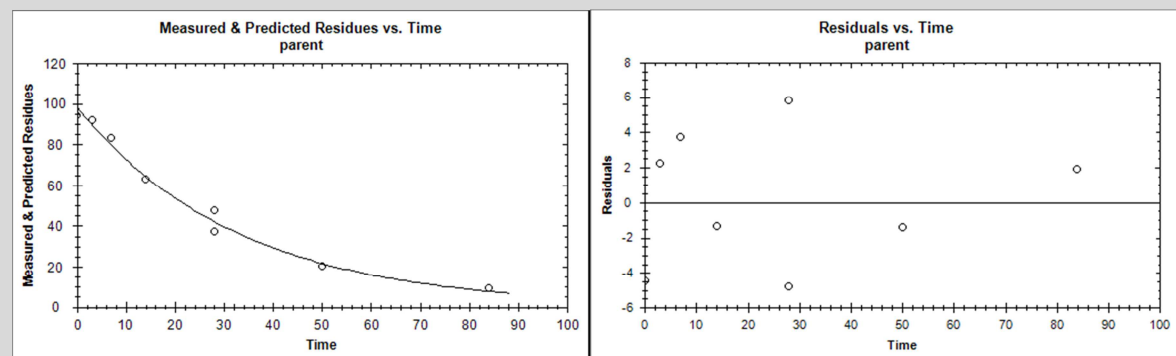
Degree of Freedom : 6

| Parameter | Estimate | Lower CI | Upper CI | St.Dev | Prob > t |
|--------------|----------|----------|----------|---------|----------|
| M(0) parent | 97.9788 | 89.7649 | 106.193 | 4.1909 | 2.01e-07 |
| alpha parent | 2.1681 | -0.3723 | 4.708 | 1.2961 | 0.0727 |
| beta parent | 87.0129 | -30.1384 | 144.164 | 44.4658 | 0.1235 |

DT50 and DT90 values

| | parent |
|---------------|--------|
| DT50 | 21.478 |
| DT90 | 107.08 |
| Kinetic model | FOMC |

Soil 5 FOMC



Chi2 error estimation

| | parent | All |
|---------------|--------|------|
| Chi2Err% | 3.81 | 3.81 |
| Kinetic model | FOMC | |

Parameter estimation

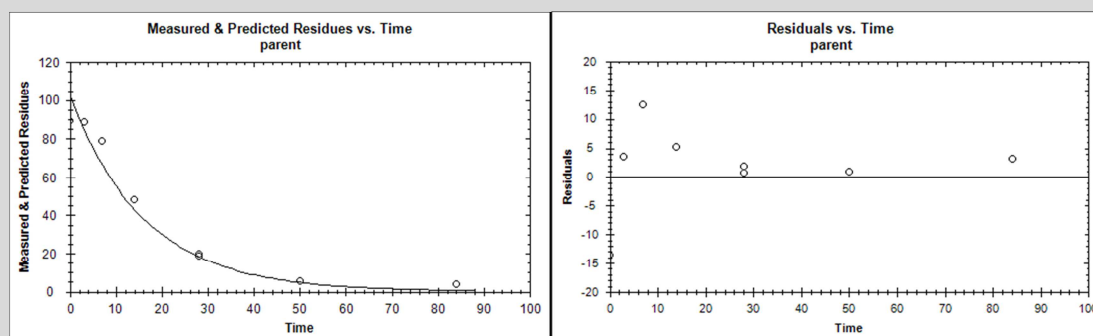
Degree of Freedom : 5

| Parameter | Estimate | Lower CI | Upper CI | St.Dev | Prob > t |
|--------------|-----------|------------|----------|-----------|----------|
| M(0) parent | 98.424 | 93.050 | 103.8 | 2.752 | 1.61e-07 |
| alpha parent | 402.191 | -2694.211 | 3498.6 | 1579.326 | 0.405 |
| beta parent | 13194.644 | -88554.543 | 114943.8 | 51913.804 | 0.405 |

DT50 and DT90 values

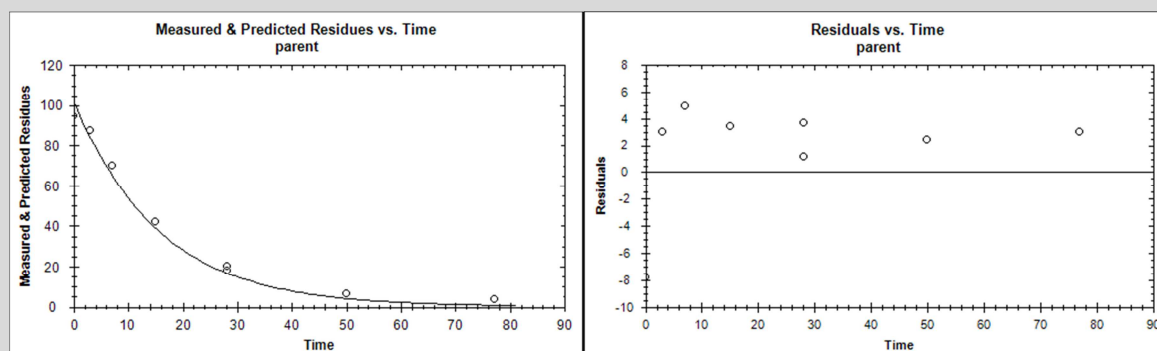
| | parent |
|---------------|--------|
| DT50 | 22.760 |
| DT90 | 75.757 |
| Kinetic model | FOMC |

Soil 6 FOMC



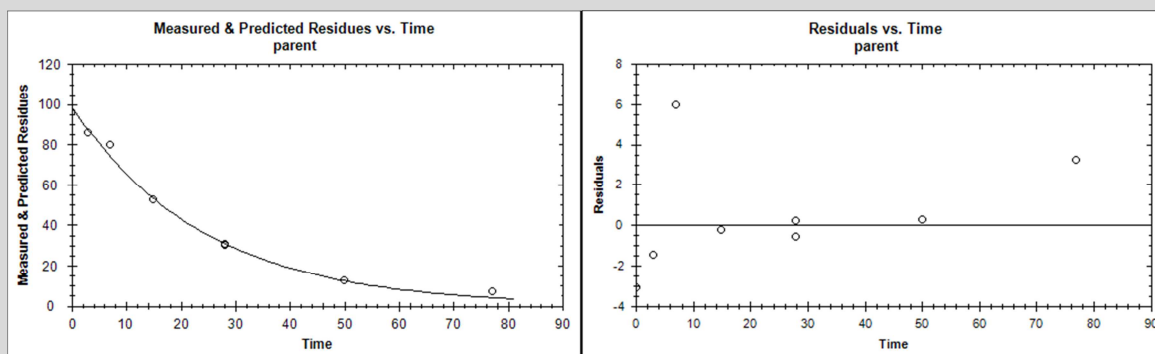
| | | | | | | |
|------------------------|-----------------|-----------|------------|----------|-----------|----------|
| Chi2 error estimation | | | | | | |
| ----- | | | | | | |
| | Chi2Errr : | parent | All | | | |
| | Kinetic model : | FOMC | 13.47 | | | |
| ----- | | | | | | |
| Parameter estimation | | | | | | |
| ----- | | | | | | |
| Degrees of Freedom : 5 | | | | | | |
| Parameter | | Estimate | Lower CI | Upper CI | St.Dev | Prob > t |
| N(0) parent | : | 1.027e+02 | 9.095e+01 | 114.5 | 5.997e+00 | 6.2e-06 |
| alpha parent | : | 6.976e+02 | -7.210e+03 | 8606.0 | 4.035e+03 | 0.495 |
| beta parent | : | 1.123e+04 | -1.161e+05 | 138565.0 | 6.457e+04 | 0.435 |
| ----- | | | | | | |
| DT50 and DT90 values | | | | | | |
| ----- | | | | | | |
| | | parent | | | | |
| | DT50 : | 11.156 | | | | |
| | DT90 : | 37.110 | | | | |
| | Kinetic model : | FOMC | | | | |

Soil 7 FOMC



| | | | | | |
|------------------------|---|-----------|------------|----------|-----------|
| Chi2 error estimation | | | | | |
| ----- | | | | | |
| | | parent | | All | |
| Chi2Err% | : | 7.903 | | 7.903 | |
| Kinetic model | : | FOMC | | | |
| ----- | | | | | |
| Parameter estimation | | | | | |
| ----- | | | | | |
| Degrees of Freedom : 5 | | | | | |
| Parameter | | Estimate | Lower CI | Upper CI | St.Dev |
| (0) parent | : | 102.514 | 95.608 | 109.4 | 3.524 |
| alpha parent | : | 835.935 | -3169.909 | 4841.8 | 2043.835 |
| eta parent | : | 12897.739 | -48973.586 | 74769.1 | 31567.583 |
| | | | | | Prob> t |
| | | | | | 4.50e-07 |
| | | | | | 0.35 |
| | | | | | 0.35 |
| ----- | | | | | |
| DT50 and DT90 values | | | | | |
| ----- | | | | | |
| | | parent | | | |
| DT50 | : | 10.699 | | | |
| DT90 | : | 35.576 | | | |
| Kinetic model | : | FOMC | | | |
| ----- | | | | | |

Soil 8 FOMC



| | | | | | |
|------------------------|-----------------|-----------|----------|----------|-----------|
| Chi2 error estimation | | | | | |
| ----- | | | | | |
| | | parent | All | | |
| | Chi2Err% | 4.713 | 4.713 | | |
| | Kinetic model : | FOMC | | | |
| ----- | | | | | |
| Parameter estimation | | | | | |
| ----- | | | | | |
| Degrees of Freedom : 5 | | | | | |
| Parameter | | Estimate | Lower CI | Upper CI | St.Dev |
| N(0) parent | : | 99.127 | 95.078 | 103.2 | 2.066 |
| alpha parent | : | 1247.998 | 234.717 | 2261.3 | 516.989 |
| beta parent | : | 29825.747 | 5593.174 | 54058.3 | 12363.785 |
| | | | | | Prob > t |
| | | | | | 3.71e-08 |
| | | | | | 0.0303 |
| | | | | | 0.0303 |
| ----- | | | | | |
| DT50 and DT90 values | | | | | |
| ----- | | | | | |
| | | parent | | | |
| | DT50 : | 16.570 | | | |
| | DT90 : | 55.080 | | | |
| | Kinetic Model : | FOMC | | | |
| ----- | | | | | |

| | |
|---------------------|---|
| Reference: | Stereoselective degradation of ethofumesate in turfgrass and soil. |
| Notifier: | UPL/Agrichem, Taskforce |
| Author(s), year: | Wang P., Jiang S.R., Qiu J., Wang Q.X., Wang P. and Zhou Z.Q. (2005) |
| Report/Doc. number: | Pesticide Biochemistry and Physiology 82 (2005), p 197-204 |
| Guideline(s): | None |
| GLP: | No |
| Deviations: | Not applicable |
| Validity: | Not valid |
| Status: | Peer-reviewed publication. |

Study Summary

The two enantiomers of Ethofumesate ((+)- and (-)-Ethofumesate) were studied for their degradation behaviour in four agricultural soils from China. The enantiomers were separated using high performance liquid chromatography-chiral stationary phase (HPLC-CSP) method. Before treatment, soils were air-dried and passed through 2 mm sieve and adjusted to moisture content of 30%. Soil subsamples (100 g dry weight) were treated with 10 µg/g of each enantiomer. The flasks were then sealed and stored at 25°C in the dark. For each sampling time a 5 g dry weight treated soil sample was taken for analysis.

The enantiomeric ratio (ER) [(+) / (-)] was used as a measure of the enantioselectivity of the two isomers in soil. One soil showed signs of enantioselective degradation, i.e. the preferential degradation of (-)-enantiomer led to nearly 1 week difference on half-lives between the two enantiomers. For the other soils no significant difference in degradation between the two enantiomers was observed.

Comment RMS

Results indicate no significant difference among stereoisomers in 3 out of the four soils investigated. In one soil, the difference was statistically significant according to the statistic test performed (24.6 d for the (+) and 17.9 d for the (-) ethofumesate). In the remaining soils the difference was < 2 days. Based on this information it can be concluded that the fate and behaviour of both enantiomers of Ethofumesate is comparable. Although the study could potentially provide useful information on enantioselectivity, from a regulatory point of view there are some limitations: history of previous pesticide use, sampling depth, bulk density, water holding capacity, and microbial biomass (which are indispensable for a degradation study) were not determined or recorded. Moreover, it is questionable if the soils are relevant for European agricultural areas. In view of these limitations, the study is not further considered.

B.8.1.1.1.2. Anaerobic degradation of the active substance

| | |
|---------------------|--|
| Reference: | Anaerobic soil metabolism (14C) ethofumesate |
| Notifier: | Taskforce |
| Author(s), year: | Waring, A.R. (1992) |
| Report/Doc. number: | A83390 / W 135 / M-155658-01 |
| Guideline(s): | |
| GLP: | yes |
| Deviations: | Not specified |
| Validity: | Valid |
| Status: | Previous evaluation in DAR for original approval / baseline dossier. |

Study summary based on previous draft assessment report

Materials and Methods

The anaerobic transformation of U-phenyl-14C-labelled ethofumesate (NC8438, radiochemical purity >98%) was investigated in a sandy loam soil in accordance with US EPA Guideline 162-2, 1982.

Table 8-36: Soil characterization

| Soil | OM (%) | pH | sand (%) | silt (%) | clay (%) | FC (% at 33 kPa) | CEC meq/100 g |
|------------|-----------|-----|-------------|-------------|-------------|---------------------|------------------|
| Sandy loam | 3.5 | 7.6 | 62 | 23 | 15 | 17.3 | 15 |

The soil samples were treated with 4.8 mg NC8438/kg (corresponding to 4.8 kg/ha) or ten times this dose (48 mg/kg) in four soil samples to facilitate identification of metabolites. The test substance, dissolved in acetonitrile, was applied dropwise onto the soil surfaces, and incubated in the dark at ca. 25°C and 75% of their 33 kPa moisture content. After 30 days of aerobic conditions, the samples were flooded with deionised water. Anaerobic conditions were established after another 39 days. ¹⁴CO₂ and organic volatiles were trapped in ethanediol, sulphuric acid and ethanolamine. Single (on day 30) or duplicate samples were taken for analysis at 30, 60, 99, 129 and 221 days after application of the test substance. The soil samples were extracted with dichloromethane followed by acetonitrile:water (4:1v/v). The radioactivity was quantified by LSC and characterised by TLC.

Results

The material balances of applied radioactivity on different sampling occasions are given in the table below.

Table 8-37: Material balance of 14C-ethofumesate (NC8438) and residues during aerobic and anaerobic incubation in a sandy loam soil. The figures represent % of applied radioactivity.

| Occasion | Days after application | NC8438 (%) | ¹⁴ CO ₂ (%) | Unextracted (%) | Total recovery (%) |
|------------------------|------------------------|---------------|--------------------------------------|--------------------|-----------------------|
| Pre-flooding | 30 | 65 | 2.1 | 18 | 92 |
| 30 days after flooding | 60 | 62 | 2.8 | 19 | 94 |

| | | | | | |
|-----------------------------|-----|----|-----|----|----|
| 30 days after anaerobiosis | 99 | 55 | 3.2 | 23 | 91 |
| 60 days after anaerobiosis | 129 | 50 | 4.4 | 24 | 90 |
| 90 days after anaerobiosis | 159 | 50 | 4.7 | 25 | 90 |
| 152 days after anaerobiosis | 221 | 58 | 2.5 | 19 | 92 |

Other transformation products than $^{14}\text{CO}_2$ identified were NC20645 (max. 2.6%), NC8493 (max. 0.7%), NC9607 (max. 1.2%) and NC10458 (max 0.8%). The anaerobic half-life of ethofumesate was calculated to 759 days, assuming first order kinetics.

Comments RMS

The anaerobic transformation of U-phenyl- ^{14}C -labelled ethofumesate (radiochemical purity >98%) was investigated in a sandy loam soil. Generally, the selected soil is appropriate. However, the history of previous pesticide use is not reported.

Samples were spiked with ethofumesate at a rate of 4.8 mg/kg (corresponding to 4.8 kg/ha) or ten times this dose (48 mg/kg) in four soil samples to facilitate identification of metabolites. After 30 days of aerobic conditions (75% of moisture at 33 kPa, 25°C), samples were flooded with deionised water and anaerobic conditions were established after another 39 days. Samples were extracted with dichloromethane followed by a mixture of acetonitrile and water (4:1v/v). The radioactivity was quantified by LSC and characterised by TLC; the LOQ is not reported.

Duplicate samples were not taken until 60 days after application. Nevertheless, the study shows that transformation of ethofumesate was very slow after establishment of anaerobic conditions and is considered acceptable.

Main findings:

- Virtually no degradation of Ethofumesate under anaerobic conditions
- Detected metabolites were: NC20645 (max. 2.6% AR), NC8493 (max. 0.7% AR), NC9607 (max. 1.2% AR) and NC10458 (max 0.8%). None of them exceeds 5% AR.
- No reliable degradation half-life could be calculated.

| | |
|---------------------|---|
| Reference: | THE SOIL DEGRADATION OF RADIOLABELLED NC 8438 |
| Notifier: | |
| Author(s), year: | Adcock, J. W.; Challis, I. R.; Warner, P. A.; 1974; Amended: 1975-05-01 |
| Report/Doc. number: | A83266 / W 10/2 / M-155706-02-1 |
| Guideline(s): | None |
| GLP: | no |
| Deviations: | |
| Validity: | Not valid |
| Status: | Previous evaluation in DAR for original approval / baseline dossier. |

Comment RMS

The study was also submitted as an aerobic route study and was evaluated in the respective section.

B.8.1.1.1.3. Soil photolysis

| | |
|---------------------|--|
| Reference: | THE PHOTODEGRADATION OF ETHOFUMESATE (SCHERING CODE NO. ZK 49913) ON SOIL SURFACES |
| Notifier: | Taskforce |
| Author(s), year: | Brehm, M.; 1989 |
| Report/Doc. number: | A83341 / M-155610-01 |
| Guideline(s): | USEPA Pesticide Assessment Guidelines, Subdivision N - Chemistry: Environmental Fate, § 161-3 NTIS PB 83 -153973 - 18th October 1982 |
| GLP: | yes |
| Deviations: | Not specified |
| Validity: | Not valid |
| Status: | Previous evaluation in DAR for original approval / baseline dossier. |

Study summary based on previous draft assessment report

Materials and Methods

The photolytical transformation of ^{14}C -ethofumesate (radiochemical purity >98%) was investigated on a sandy loam soil in accordance with US EPA Guidelines 161-3. The test substance was sprayed at a rate of 1.5 kg as/ha on glass plates (20 x 20 cm) covered with 0.5 mm layers of soil (for soil properties, see table below).

Table 8-38: Soil characteristics

| Soil | OM (%) | pH | sand (%) | silt (%) | clay (%) | MHC (%), (at 1/3 bar) | CEC meq/100 g |
|---------------------|-----------|-----|-------------|-------------|-------------|--------------------------|------------------|
| Abington sandy loam | 2.8 | 7.2 | 58 | 20 | 14 | n.r. | 13.6 |

The plates were irradiated with a xenon arc lamp, equipped with an UV-transmissive water jacket and a metallic reflector. The light intensity in the wave-lengths 290 - 320 nm was 0.2 mWatt/cm², comparable to that of natural sunlight (midday, summer, 40° northern latitude, cloudless sky). The plates were continuously illuminated and kept in ventilated irradiation boxes at a temperature below 30°C. Volatiles were trapped in ethyleneglycol and ethanolamine. Dark controls were run in parallel. Triplicate irradiated and dark plates were sampled for analysis at various intervals for 212 hours. The soil samples were extracted with methanol prior to analysis with HPLC and LSC.

Results

In irradiated samples, 35% of applied radioactivity was identified as parent compound after 212 hours, 18% was bound residues and 0.9% was volatilised. The main product of photolysis was NC 8493, accounting for ca. 30% of applied at the end of the study. In the dark control, 89% was unaltered, 5.3% bound residues and no volatiles

were recovered by the same time. Total recovery was 93 - 100% of applied for irradiated samples and 99 - 104% for non-irradiated samples throughout the study. The photolytical half-life of the parent compound was calculated to 6.8 days ($r^2=1.0$) based on first order kinetics, corresponding to an estimated environmental half-life of 14 days, assuming 12 hours daylight.

Comments RMS

The photolytical transformation of ^{14}C -ethofumesate (radiochemical purity >98%) was investigated on a sandy loam soil in accordance with US EPA Guidelines 161-3.

A layer (0.5 mm thickness) of sandy loam (sieved at < 0.2 mm) was applied on glass plates (20 x 20 cm). The glass plates were then dried at 80°C, which is in contrast to the air-drying recommended in the draft OECD guideline on phototransformation of chemicals on soil surfaces (OECD, 2002), and stored at ambient temperature for up to 14 days. The final water content was 2.1%. This is significantly below the water content of 75% of field capacity required by the draft OECD guideline. However, in the photolysis study by Stupp and Weuthen (2013) it was shown that soil moisture had no significant influence on the degradation of ethofumesate in microbially active soils. They incubated two sets of soils - one air-dried, the other at 50% water holding capacity - under irradiated and dark conditions for 13 days. Samples were only taken at the last sampling interval. In the irradiated and dark dry test systems, respectively, similar degradation as for the moist soil samples was observed. For details, please refer to the photolysis study by Stupp and Weuthen (2013) below.

The plates were then irradiated with a xenon arc lamp, equipped with an UV-transmissive water jacket and a metallic reflector. The light intensity in the wave-lengths 290 - 320 nm was 0.2 mW/cm². The plates were continuously illuminated and kept in ventilated irradiation boxes at a temperature below 30°C. Triplicate irradiated and dark plates were sampled for analysis at various intervals for 212 hours. The soil samples were extracted with methanol prior to analysis with HPLC and LSC. Neither the limit of detection (LOD), nor the limit of quantification (LOQ) is reported. Except for the time zero sample, recoveries in irradiated samples are consistently below 90%. Therefore, this study is considered not acceptable and is superseded by the two newly submitted soil photolysis studies.

| | |
|---------------------|--|
| Reference: | PHOTODEGRADATION STUDY OF 14C-ETHOFUMESATE IN SOIL |
| Notifier: | Taskforce |
| Author(s), year: | Burri, R.; 1995 |
| Report/Doc. number: | A87626 / M-161570-01 |
| Guideline(s): | USEPA 540/9-82-021 |
| GLP: | yes |
| Deviations: | Not specified |
| Validity: | Not valid |
| Status: | Previous evaluation in DAR for original approval / baseline dossier. |

Study summary based on previous draft assessment report

Materials and Methods

The photolytical transformation of ^{14}C -ethofumesate (radiochemical purity >98%) was investigated on a Speyer 2.2 soil (for soil properties, see table below) in accordance with US EPA Guidelines 161-3.

Table 8-39: Soil characteristics

| Soil | OC (%) | pH | sand (%) | silt (%) | clay (%) | MWC (%) | CEC meq/100 g |
|-----------------------|-----------|-----|-------------|-------------|-------------|---------|------------------|
| Speyer 2.2 loamy sand | 2.3 | 5.8 | 89 | 5.6 | 5.1 | 44 | 9.7 |

The test substance was applied to the soil at a rate of 15.3 mg/kg. The test soil was prepared as 1.0 mm layers on glass plates (5 x 10 cm). The plates were covered with a double Quartz-glass set up and exposed to artificial light using a 12 hours dark/light cycle for 30 days. The light intensity in the wave-lengths 300 - 800 nm was about 90 - 100 kLux (equal to 132 - 147 W/m²), and comparable to that of natural sunlight (midday, summer, cloudless sky). The illuminated and dark plates were kept in metal chambers at 22±1°C and 75% of field capacity. Volatiles were trapped in ethyleneglycol and NaOH. Dark controls were run in parallel. Single illuminated and dark plates and volatile traps were sampled for analysis at various intervals for 30 days. The soil samples were extracted stepwise with acetonitrile, methanol and methanol:water (8:2) prior to analysis with LSC and TLC. Selected samples were analysed by HPLC.

Results

Table 8-40: Degradation product patterns of ^{14}C -ethofumesate in extracts of soil after exposure to artificial light (values in percent of the radioactivity applied)

| Code | Identity | Rf-Value | | Sampling Interval (days) | | | | | |
|------|----------|----------|------|--------------------------|------|------|------|------|------|
| | | SS1 | SS2 | 0 | 3 | 7 | 14 | 21 | 30 |
| D1 | Parent | 0.42 | 0.49 | 98.7 | 95.4 | 90.8 | 82.3 | 72.7 | 74.7 |
| D2 | Unknown | 0.11 | 0.01 | n.d. | n.d. | n.d. | n.d. | 1.5 | n.d. |
| D3 | Unknown | 0.08 | 0.01 | n.d. | n.d. | n.d. | 1.1 | 1 | 2.2 |

| | | | | | | | | | |
|-------|---------|------|------|------|------|------|------|------|-----|
| D4 | Unknown | 0.01 | 0.01 | n.d. | n.d. | 2.4 | 2.1 | 4.9 | 7.1 |
| Total | | | | 98.7 | 85.4 | 93.2 | 85.5 | 80.1 | 84 |

In illuminated samples, 75% of applied radioactivity was identified as parent compound after 30 days, 6.0% was bound residues and 6.7% volatilised. Three unknown radioactive fractions (D2 - D4) besides the parent compound was observed, each accounting for 2 - 7% of applied after 30 days. In the dark control, 89% was parent compound, 7.2% bound residues and 0.9% volatiles by the same time. One unknown radioactive fraction (D4) accounted for 3.3% after 30 days. Total recovery was 98±4% of applied for illuminated samples and 100±2% for non-illuminated samples throughout the study. The photolytical half-life of the parent compound under simulated natural sunlight was calculated to 65 days, based on first order kinetics. In the dark samples, the parent compound half-life was calculated to 198 days.

Comments RMS

The photolytical transformation of ^{14}C -ethofumesate (radiochemical purity >98%) was investigated on a Speyer 2.2 soil. The test substance applied to a 1 mm thick soil layer at a rate of 15.3 mg/kg. Both the irradiated and the dark sample were incubated at a moisture content of 75% field capacity. The light intensity in the wave-lengths 300 - 800 nm was about 132 - 147 W/m². The soil samples were extracted stepwise with acetonitrile, methanol and methanol:water (8:2) prior to analysis with LSC and TLC.

The extractable radioactivity from illuminated soil plates represented almost exclusively the parent compound. Three unknown radioactive fractions (D2 to D4) were detected. Radioactive fractions D2 and D3 were found in minor amounts (maximally 2.2 % of the radioactivity applied). Increasing amounts of fraction D4 occurred during 30 days of illumination, resulting in a maximal amount of 7.1 % at day 30. D4 was not further identified. Since the samples were not available anymore, new photolysis studies were submitted by both notifiers.

| | |
|---------------------|--|
| Reference: | [Phenyl-UL-14C]Ethofumesate:Phototransformation on soil |
| Notifier: | Taskforce |
| Author(s), year: | Stupp, H. P.; Weuthen, M.; 2013 |
| Report/Doc. number: | EnSa-12-0221/ M-455051-01-1 |
| Guideline(s): | US EPA OCSP Test Guideline No. 835.2410 Environmental Chemistry and Fate, Guidelines for Registration of Pesticides in Canada, 1987 OECD Draft Test Guideline: Phototransformation of Chemicals on Soil Surfaces |
| GLP: | yes |
| Deviations: | Not specified |
| Validity: | Valid |
| Status: | New study |

MATERIALS AND METHODS

Materials :

Test Material :

[phenyl-UL-¹⁴C]Ethofumesate

Specific radioactivity: 3.78 MBq/mg (102.2 µCi/mg)

Soils :

The soil Hoefchen am Hohenseh 4a is a representative soil for agricultural use.

Table 8-41: Soil characteristics

| Parameter | Soil Hoefchen Am Hohenseh 4a |
|---|--|
| Geographic location - city - state - country | Burscheid NRW Germany |
| Site description | grassland |
| Soil taxonomic classification (USDA) | loamy, mixed, mesic Typic Argudalfs |
| Texture class (USDA) - sand (50 µm – 2 mm) [%] - silt (2 µm – 50 µm) [%] - clay (< 2 µm) [%] | silt loam 25 61 14 |
| pH - in CaCl ₂ (soil/CaCl ₂ 1/2) - in water (soil/water 1/1) - in KCl | 6.5 6.6 6.1 |
| Organic matter ^{a)} [%] | 4.5 |
| Organic carbon [%] | 2.6 |
| Microbial biomass [mg microbial carbon/kg dry soil] - day 0 | 1031 |
| CEC [meq/100 g] | 12.4 |
| Field moisture capacity at 0.33 bar | 23.4 water / 100 g soil dry wt |

Methods :Study design

The test systems consisted of quartz glass vessels (36 mm inner diameter, 35 mm height, inner surface area 10.2 cm²) each containing 3 g of soil (dry weight), which provided about 3 mm soil depth. A glass neck with ground joint was attached to the side of the wall. There, the flask was either closed with a solid trap attachment, a small glass tube of 90 mm length and 12 mm inner diameter, in which volatile compounds were bound to soda lime and polyurethane foam (irradiated vessels) or with a glass stopper (dark vessels). Radiolabeled [phenyl-UL-¹⁴C]Ethofumesate was applied directly to the surface of the soil samples at a nominal concentration of about 102 µg / test system with a surface of 10.2 cm² (3 g soil, dry weight). The treated samples were continuously exposed to artificial irradiation (xenon lamp with < 290 nm cut-off filter, 924 W m⁻²). In addition, dark controls were set up.

Experimental Conditions

Soil moisture was adjusted to about 50% of the maximum water holding capacity. A supplementary test was performed on air-dried soil samples.

Sampling

Samples were taken in duplicate after 0, 1, 3, 6, 9, 10, 13 and 14 days (air-dried samples 13 days).

Analytical Procedures :

The soil samples were extracted three times with 10 mL acetonitrile/water (80/20, v/v) at ambient temperature and once with 10 mL acetonitrile/water (80/20, v/v) at aggravated conditions (microwave extraction, about 70 °C). The ethofumesate residues and transformation products in concentrates of the combined extracts were determined by LSC and reversed phase HPLC with radioactivity detection. Identification of the parent compound in the stock solution was done by NMR, HPLC-MS and HPLC-MS/MS. Two transformation products in the extracts were identified by HPLC co-chromatography with reference substances.

RESULT AND DISCUSSION

Mass balance and distribution of radioactivity:

Table 8-42: Distribution over 14 days in % of AR in irradiated samples in soil Hoefchen

| | Environmen-tal Conditions Phoenix, Arizona, USA | DAT | | | | | | | |
|--|--|-------|-------|-------|------|-------|------|------|-------|
| | | 0 | 3 | 8 | 15 | 23 | 26 | 33 | 36 |
| Compound | Experimental | 0 | 1 | 3 | 6 | 9 | 10 | 13 | 14 |
| Ethofumesate | Mean | 101.7 | 103.1 | 79.1 | 80.0 | 67.8 | 68.1 | 84.8 | 86.2 |
| NC 20645 (AE C63975 (K ⁺ salt)) | Mean | 0.2 | 0.5 | 0.7 | 0.5 | 2.2 | 2.8 | 4.8 | 1.7 |
| NC 8493 (AE C508493) | Mean | 0.04 | n.d. | 18.8 | 8.4 | 24.2 | 18.4 | 0.1 | 7.3 |
| Diffuse RA | Mean | 2.1 | 0.5 | 1.3 | 0.8 | 1.1 | 2.5 | 1.3 | 1.3 |
| Total extract | Mean | 104.1 | 104.2 | 101.7 | 91.2 | 98.5 | 95.0 | 93.2 | 99.0 |
| ¹⁴ CO ₂ | Mean | n.a. | <0.1 | 0.0 | 0.3 | 0.7 | 1.0 | 0.6 | 1.0 |
| Volatile organics | Mean | n.a. | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | 0.0 | <0.1 |
| Non-extractable Residues | Mean | 0.1 | 0.9 | 1.7 | 2.4 | 3.0 | 3.5 | 5.8 | 3.8 |
| Total recovery % | Mean | 104.2 | 105.1 | 103.5 | 93.9 | 102.3 | 99.5 | 99.6 | 103.9 |

Table 8-43: Distribution over 14 days in % of AR in non-irradiated samples in soil Hoefchen

| Compound | | DAT | | | | | | | |
|--|------|-------|-------|------|-------|------|------|------|------|
| | | 0 | 1 | 3 | 6 | 9 | 10 | 13 | 14 |
| Ethofumesate | Mean | 101.7 | 101.4 | 96.0 | 98.4 | 95.3 | 94.1 | 94.8 | 93.7 |
| NC 20645 (AE C63975 (K ⁺ salt)) | Mean | 0.2 | 0.1 | 0.2 | 0.3 | 0.2 | 0.2 | 0.3 | 0.2 |
| NC 8493 (AE C508493) | Mean | 0.04 | n.d. | n.d. | 1.1 | 0.01 | n.d. | n.d. | n.d. |
| Diffuse RA | Mean | 2.1 | 0.6 | 0.5 | 1.1 | 0.4 | 0.9 | 0.7 | 0.6 |
| Total extract. Residues | Mean | 104.1 | 102.1 | 96.9 | 101.3 | 96.3 | 95.6 | 96.7 | 95.3 |
| ¹⁴ CO ₂ | Mean | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| Volatile | Mean | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |

| | | | | | | | | | |
|-----------------------------|------|-------|-------|------|-------|-------|------|-------|-------|
| Non-extractable Res. | Mean | 0.1 | 0.8 | 1.7 | 2.8 | 4.3 | 4.3 | 7.2 | 7.0 |
| Total Residues % | Mean | 104.2 | 102.9 | 98.6 | 104.1 | 100.7 | 99.9 | 103.9 | 102.4 |

Non-extractable and Extractable Residues

For irradiated test systems, the extractable radioactivity remained on a high level and varied between 91.2% (DAT-6) and 104.2% of AR (DAT-1) throughout the incubation period of 14 days. Non-extractable residues (NER) accounted for 0.1% of AR at DAT-0 and increased up to a maximum of 5.8% of AR at DAT-13.

Volatilization and Mineralization :

$^{14}\text{CO}_2$ formation in the irradiated samples increased up to 1.0% of AR (DAT-10 and DAT-14). Organic volatile formation was negligible throughout the study ($\leq 0.1\%$). The formation of $^{14}\text{CO}_2$ and organic volatiles was not investigated for the dark samples.

Transformation of Test material and Transformation Products :

In the irradiated test systems, Ethofumesate decreased from an average of 101.7% of AR at DAT-0 to a minimum of 67.8% at DAT-9. At the end of the study (DAT-14), ethofumesate accounted for 86.2% of AR. The degradation behavior in the individual test vessels was scattering as expected for soil photolysis. One transformation product $> 10\%$ of AR was detected and identified as NC 8493 (ethofumesate-2-hydroxy). It reached a maximum concentration of 24.2% of AR (DAT-9). The amounts of NC 20645 AE C639175 (AE C639175 = K⁺ salt of NC 20645, ethofumesate-carboxylic acid,), a minor transformation product which was identified by HPLC co-chromatography, increased up to 4.8% of AR (DAT-13). In addition, up to 10 minor metabolites were characterized according to their retention times. Each individual one accounted for $\leq 1.0\%$ of AR. The diffuse radioactivity which was not assigned to individual peaks was 2.5% of AR at maximum. $^{14}\text{CO}_2$ formation in the irradiated samples increased up to 1.0% of AR (DAT-10 and DAT-14). Organic volatile formation was negligible throughout the study ($\leq 0.1\%$).

In the extracts of the dark test systems, ethofumesate decreased from an average of 101.7% of AR at DAT-0 to 93.7% of AR by the end of the study (DAT-14). Various minor transformation products were detected in the extracts. NC 20645 (AE C639175) and NC8493 accounted for maximum amounts of 0.3 and 1.1% of AR, respectively. In addition, seven unidentified transformation products were detected. None of them exceeded 0.6% of AR. The diffuse radioactivity which was not assigned to individual peaks accounted for up to 2.1% of AR. The formation of $^{14}\text{CO}_2$ and organic volatiles was not investigated for the dark samples.

In order to test the effects of the dryness on degradation, a supplementary test was performed. Air-dried soil samples treated with the test item (analogously to the main test) were incubated under irradiated and dark conditions for 13 days. Samples were only taken at the last sampling interval. In the irradiated and dark dry test systems, respectively, a similar pattern as for the moist soil samples was observed. This demonstrates that the soil moisture had no significant influence on the degradation of Ethofumesate in microbial active soils.

The experimental DT_{50} values of ethofumesate in the irradiated and dark samples were 36.6 and 109.7 days, respectively, according to single first order kinetics. The main degradation product is NC 8493 (ethofumesate-2-hydroxy).

Conclusion:

The photolysis on soil surface contributes to the degradation of ethofumesate. The main degradation products are NC 8493 and NC 20645 (tested for chromatographic comparison as salt, AE C639175).

Comments RMS

The phototransformation of [phenyl-UL-14C]Ethofumesate was studied on a silt loam from Burscheid, Germany, at a nominal application rate of 1 kg ethofumesate / ha for 14 days at 20 ± 1 °C and at a soil moisture of about 50% of the maximum water holding capacity. The test substance was applied directly to the surface of the soil samples at a nominal concentration of about 102 µg / test system with a surface of 10.2 cm² (3 g soil, dry weight). The treated samples were continuously exposed to artificial irradiation (xenon lamp with < 290 nm cut-off filter, 924 W m⁻²). Samples were extracted three times with 10 mL acetonitrile/water (80/20, v/v) at ambient temperature and once with 10 mL acetonitrile/water (80/20, v/v) at aggravated conditions (microwave extraction, about 70 °C). The ethofumesate residues and transformation products in concentrates of the combined extracts were determined by LSC and reversed phase HPLC with radioactivity detection.

The study is fully reliable and the main findings are:

| | Irradiated | Dark |
|--|------------|-------|
| Experimental DT50 (days) | 36.6 | 109.7 |
| Experimentl DT90 (days) | 121.7 | 364.3 |
| Net Experimental Half-life ¹⁾ | 55 days | |
| Environmental DT50 (days), Phonex, AZ, USA | 94.2 days | |

¹⁾ Calculated from net rate constant (rate constant of irradiated samples - rate constant of dark samples)

| | |
|---------------------|---|
| Reference: | Soil photolysis of Ethofumesate |
| Notifier: | UPL/Agrichem |
| Author(s), year: | Hennecke, D. (2003) |
| Report/Doc. number: | GAB-002/7-06 |
| Guideline(s): | Draft OECD Test Guideline: Phototransformation of Chemicals on soil surfaces. SETAC-Europe, 1995 |
| GLP: | Yes Not applicable to kinetic evaluation |
| Deviations: | None |
| Validity: | Not valid. |
| Status: | New study. |

I. MATERIALS AND METHODS

A. MATERIALS

| | |
|--|---|
| 1. Test Material: | Ethofumesate |
| Description: | White powder |
| Purity: | 98.59% |
| CAS No.: | 26225-79-6 |
| Lot No.: | 1997/1 |
| 2. Test Material (Reference R): | ¹⁴ C-Ethofumesate |
| Radiochemical purity: | ≥ 98.6% |
| Specific radioactivity: | 2.44 GBq/mmol = 66 mCi/mmol |
| Lot No.: | CFQ12926 |
| 3. Test Material: | 2,3-dihydro-3,3-dimethyl-2-oxo-5-benzofuranylmethanesulfonate |
| Code: | NC 9607 |
| Purity: | 99.5% |
| CAS No.: | 26244-33-7 |
| Lot No.: | 01009 |
| Further relevant properties: | None |
| 4. Test Material: | 2,3-dihydro-2-hidroxy-3,3-dimethyl-5-benzofuranylmethanesulfonate |
| Code: | NC 8493 |
| CAS No.: | 26322-82-7 |

Further relevant properties: None

5. Test Material: α -(2-hydroxy-5-methanesulphonyl-oxyphenyl)isobutyric acid

Code: NC 20645

CAS No.: Unknown

Further relevant properties: None

6. Soils: The test soils were Lufa 2.2 standard soil from Speyer, Germany. Sampling and sieving was done by the Lufa Speyer.

Table 8-44: Physical and chemical properties of the soil used in the soil photolysis study

| Soil Property | Lufa 2.2 soil |
|--|---------------|
| Soil type (USDA) | Loamy sand |
| Sand [%] | 73.8 |
| Silt [%] | 18.3 |
| Clay [%] | 8.1 |
| pH [CaCl ₂] | 5.6 |
| Organic carbon [%] | 2.3 |
| Cation Exchange Capacity [mval/100 g dry mass] | 11 |
| MWHC [g/kg dry mass] | 500 |

B. STUDY DESIGN

1. Experimental conditions

The water content of the air-dried soil was determined before start. Thin layers of air dried soil, 20.28 g, were placed in each tray. Afterwards, Ethofumesate was applied at rate of 47.5 mg/kg (dry mass). Because of the high specific radioactivity of the labelled test substance and because of the high application rates, the application solution was prepared by mixing unlabelled Ethofumesate with ¹⁴C-labelled Ethofumesate at known ratio. The application solution was then prepared adding dichloromethane to a total volume of 50 mL. The application solution was applied homogeneously onto the soil surface and the dichloromethane was allowed to evaporate from the soil surface. The tray was closed with the plate and transferred into the Suntest apparatus. The dark control was maintained with the same conditions but on a tray of stainless steel, which was then wrapped with aluminium foil and transferred into incubator at 20°C. The soil samples were incubated in Suntest apparatus with a xenon lamp and performed by continuous irradiation of the samples at the incubation temperature 20 ± 5°C for up to 28 days. The irradiation corresponds to sunlight occurring on a clear sunny day around noon in Central Europe.

2. Sampling

Sampling was performed after 0, 1, 3, 6, 10, 15 and 28 days of irradiation. The soil samples were worked-up immediately after sampling. In addition, the absorption traps were removed and the trapping solutions were analysed for radioactivity.

3. Description of analytical procedures

The samples were extracted with 25 mL acetone three times using horizontal shaker for 10 minutes. The soil and liquid phase was separate by centrifugation for 10 minutes. Afterwards the three extracts were combined and purified using a filter paper which was then washed with 5 mL acetone. The extracts were evaporated and the dry residue was dissolved in 1 mL of HPLC mobile phase.

After extraction with acetone the solid residue was extracted with 0.05 M H_3PO_4 by shaking for 5 minutes and then centrifuged for 5 minutes.

The extracts were air dried and five replicates of each soil sample were combusted in order to quantify the non-extractable radioactivity which was quantified using LSC.

All extracts were analysed by reversed-phase radio-HPLC for the test substance and potential degradation products. The limit of detection and limit of determination for Ethofumesate was found to be 0.012 mg/L and 0.034 mg/L, respectively.

II. RESULTS AND DISCUSSION

A. DATA

Table 8-45: Distribution of radioactivity (% ITR) of Ethofumesate

| Sample | Extract | | NER [% ITR] | Volatiles absorbed in | | | Total recovery [% ITR] |
|-----------------------|--------------------|---|----------------|-----------------------|-----------------|------------------------------------|------------------------------|
| | Organic [% ITR] | H ₃ PO ₄ [% ITR] | | glycol [% ITR] | acid [% ITR] | base (CO ₂) [% ITR] | |
| Irradiation time 0 d | | | | | | | |
| sample A | 91.7 | 2.2 | 1.9 | | | | 95.7 |
| sample B | 88.6 | 2.1 | 1.8 | | | | |
| sample C | 90.7 | 2.3 | 1.9 | | | | 94.2 |
| Irradiation time 1 d | | | | | | | |
| Irradiated * | 82.1 | 5.3 | 5.1 | 0.0 | 0.0 | 0.2 | 92.7 |
| dark | 84.7 | 4.4 | 4.1 | 0.0 | 0.0 | 0.0 | 93.2 |
| Irradiation time 3 d | | | | | | | |
| Irradiated * | 69.3 | 8.5 | 8.2 | 0.0 | 0.0 | 0.6 | 86.6 |
| dark | 77.3 | 8.0 | 7.0 | 0.0 | 0.0 | 0.0 | 92.3 |
| Irradiation time 6 d | | | | | | | |
| Irradiated * | 65.9 | 5.3 | 5.8 | 0.1 | 0.0 | 2.5 | 79.6 |
| dark | 70.7 | 6.6 | 5.9 | 0.0 | 0.0 | 0.0 | 83.2 |
| Irradiation time 10 d | | | | | | | |
| Irradiated * | 63.8 | 5.8 | 6.0 | 0.1 | 0.0 | 3.6 | 79.3 |
| dark | 74.9 | 5.9 | 6.0 | 0.0 | 0.0 | 0.0 | 86.8 |
| Irradiation time 15 d | | | | | | | |
| Irradiated * | 60.5 | 11.2 | 10.7 | 0.1 | 0.0 | 3.8 | 86.3 |
| dark | 76.5 | 9.1 | 8.5 | 0.0 | 0.0 | 0.0 | 94.1 |
| Irradiation time 28 d | | | | | | | |
| Irradiated * | 63.3 | 7.2 | 7.8 | 0.2 | 0.1 | 12.1 | 90.7 |
| dark | 67.7 | 11.9 | 13.5 | 0.0 | 0.0 | 0.0 | 93.1 |

* Mean of both parallel samples

Table 8-46: Distribution of radioactivity in the extracts determined by radio-HPLC

| Sample | organic extract | | | | H ₃ PO ₄ -extract | | |
|---------|---|-------------------------|-------------------|---------------------------|---|-------------------------|---------------------------|
| | extractable radioactivity (% ITR) | ethofumesate (% ITR) | NC8493 (% ITR) | not identified (% ITR) | extractable radioactivity (% ITR) | ethofumesate (% ITR) | not identified (% ITR) |
| 0d, A | 91.7 | 91.7 | 0 | 0 | 1.9 | 1.9 | 0 |
| 0d, B | 88.6 | 86.9 | 0 | 1.8 | 1.8 | 1.8 | 0 |
| 0d, C | 90.7 | 89.2 | 0 | 1.5 | 1.9 | 1.9 | 0 |
| 1d, A | 83.3 | 77.1 | 6.2 | 0 | 5.2 | 5.2 | 0 |
| 1d, B | 80.9 | 70.9 | 7.8 | 2.2 | 5.3 | 5.3 | 0 |
| 1d, DC | 84.7 | 82.7 | 2 | 0 | 4.1 | 4.1 | 0 |
| 3d, A | 74.3 | 67.2 | 7 | 0 | 5.8 | 3 | 2.8 |
| 3d, B | 64.4 | 46.7 | 17.7 | 0 | 11.1 | 5.9 | 5.2 |
| 3d, DC | 77.3 | 72.7 | 3.7 | 1 | 8 | 6.5 | 1.5 |
| 6d, A | 67.7 | 56.9 | 8.1 | 2.7 | 4.9 | 2 | 2.9 |
| 6d, B | 64.1 | 50.7 | 10.8 | 2.5 | 5.7 | 2.1 | 3.6 |
| 6d, DC | 70.7 | 64.3 | 6.4 | 0 | 6.5 | 5.3 | 1.2 |
| 10d, A | 63.5 | 50.4 | 11.3 | 1.8 | 5.4 | 2.2 | 3.2 |
| 10d, B | 64 | 51.1 | 10.7 | 2.2 | 6.1 | 2.3 | 3.8 |
| 10d, DC | 74.9 | 68.1 | 5.7 | 1.1 | 6 | 5.3 | 0.7 |

| | | | | | | | |
|---------|------|------|------|-----|------|-----|-----|
| 15d, A | 59.8 | 37.6 | 18.7 | 3.6 | 11.7 | 4.4 | 7.3 |
| 15d, B | 61.2 | 41.7 | 16.7 | 2.7 | 10.8 | 4 | 6.8 |
| 15d, DC | 76.5 | 70.1 | 6.4 | 0 | 9.1 | 7.4 | 1.7 |
| 28d, A | 64.4 | 43.5 | 19.3 | 1.8 | 7.1 | 2.1 | 5 |
| 28d, B | 62.1 | 44 | 15.5 | 2.6 | 7.2 | 2.1 | 5.1 |
| 28d, DC | 67.7 | 55.6 | 12.2 | 0 | 12 | 9.2 | 2.8 |

B. MASS BALANCE

The total recovery of radioactivity was between 79 and 96% ITR. Despite the fact that the recovery was in some cases below 90% AR, for the 28 day sampling a recovery of > 90% AR was shown. Also the overall average recoveries were 87% (irradiated) and 91% (dark), i.e. confirming the general validity of the study.

C. BOUND AND EXTRACTABLE RADIOACTIVITY

The non-extractable radioactivity (NER) amounted from 2% up to 10.7% ITR, depending on the duration of irradiation.

The extractable radioactivity decreased with increasing time of irradiation.

D. VOLATILISATION

The amount of $^{14}\text{CO}_2$ increased with increasing time of irradiation up to 12% ITR after 28 days of continuous irradiation. Neither volatile metabolites with low molecular weight nor acidic volatile metabolites were produced during soil photolysis of Ethofumesate.

E. TRANSFORMATION OF PARENT COMPOUND

For Central Europe the irradiance value of Basel at 50° northern latitude the DT_{50} equivalent days of natural summer sunlight were calculated. Considering only decline in the irradiated samples without considering decline in the dark controls, DT_{50} of about 50 days was calculated (assuming first order kinetics).

Considering only photolytic degradation the half-life of Ethofumesate applied on soil in natural summer sunlight at 50° northern latitude was estimated to be 65 days.

As a major metabolite NC 8493 was found at maximum amount formed by photolysis of 19.3% ITR after 28 days.

III CONCLUSION

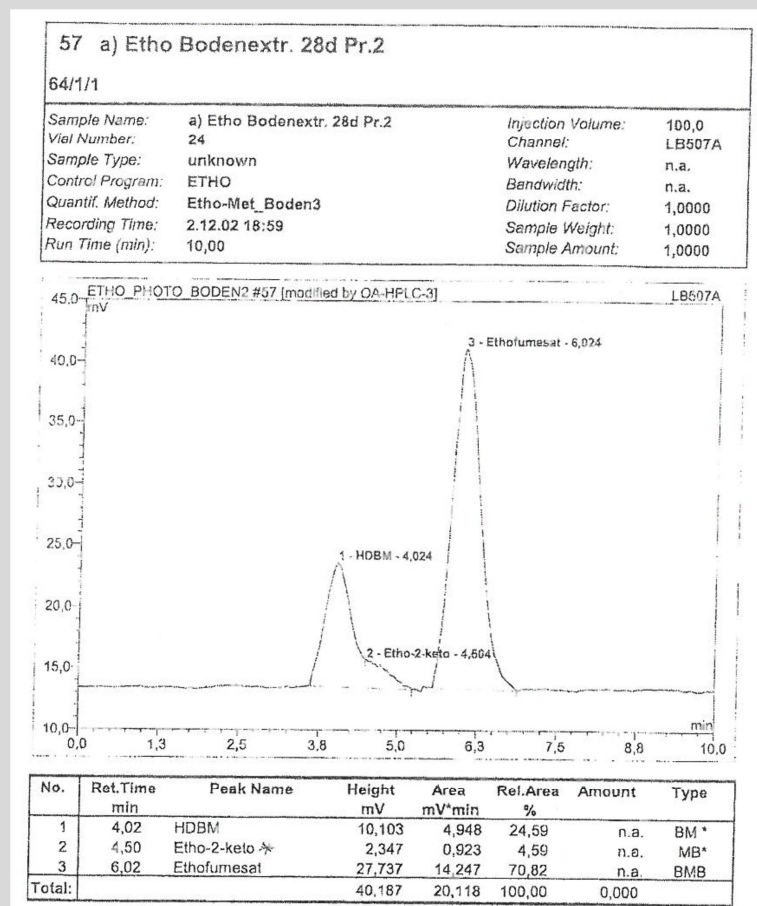
The degradation of Ethofumesate in Lufa 2.2 standard soil exposed to light using Suntest apparatus was determined during 28 days of continuous irradiation. In view of the results obtained it is assumed that photolysis is a process with minor importance for the decline of Ethofumesate applied on soil.

Comments RMS

The phototransformation of Ethofumesate was studied in an air-dried loamy sand following 28 days of continuous irradiation in a Suntest apparatus at $20 \pm 5^\circ\text{C}$. The soil samples were treated with a mixture of ^{14}C -labelled and unlabelled Ethofumesate at a rate of 47.5 mg/kg (dry mass). The study is characterized by low recoveries. In the irradiated study, at 4 out of 7 sampling dates the recoveries were below 90 % (range: 79.3 – 86.6%). In the dark study, at 2 out of 7 sampling dates the recoveries were below 90 % (range: 83.2 – 86.8 %). Such low recoveries undermine the validity of the study. The study is not valid.

At day 15 and 28, the sum of unidentified radioactivity in the extractable fraction (organic and H_3PO_4 -extract) accounts for 10.2 and 7.25% AR, respectively. In an addendum to the study, the applicant has made the case that the unknown radioactivity in the two extracts (acetone and H_3PO_4) cannot be summed up as the peak can be attributed to two different degradation products (see figures below). The RMS agrees with this interpretation and as a consequence, unidentified radioactivity does not exceed 10% AR.

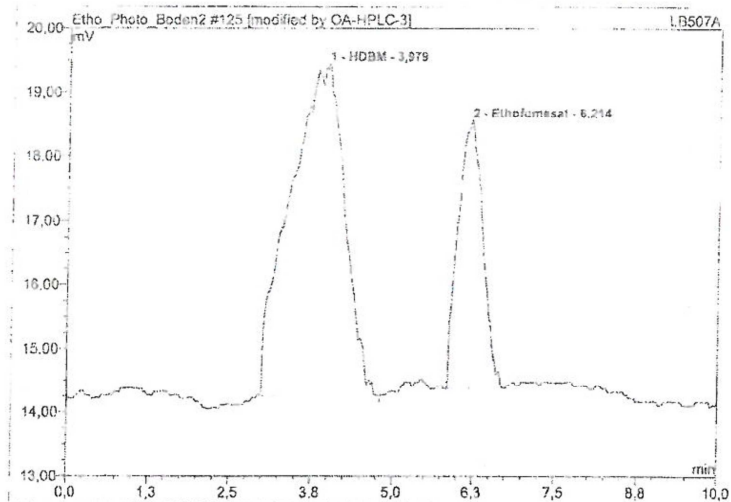
Radio-chromatogram of the organic extract at sampling day 28



Radio-chromatogram of the H₃PO₄-extract at sampling day 28

125 a) Etho H3PO4-Extr. 28d Pr.2

| | | | |
|------------------|------------------------------|-------------------|--------|
| Sample Name: | a) Etho H3PO4-Extr. 28d Pr.2 | Injection Volume: | 150,0 |
| Vial Number: | 9 | Channel: | LB507A |
| Sample Type: | unknown | Wavelength: | n.a. |
| Control Program: | ETHO | Bandwidth: | n.a. |
| Quantif. Method: | Etho-Met_Boden4 | Dilution Factor: | 1,0000 |
| Recording Time: | 10.1.03 12:01 | Sample Weight: | 1,0000 |
| Run Time (min): | 10,00 | Sample Amount: | 1,0000 |



| No. | Ret.Time min | Peak Name | Height mV | Area mV*min | Rel.Area % | Amount µg/ml | Type |
|--------|-----------------|-------------|--------------|----------------|---------------|-----------------|------|
| 1 | 3,98 | HDBM | 5,189 | 4,992 | 72,82 | n.a. | BMB* |
| 2 | 6,21 | Ethofumesat | 4,183 | 1,863 | 27,18 | n.a. | BMB* |
| Total: | | | 9,371 | 6,855 | 100,00 | 0,000 | |

B.8.1.1.2. Rate of degradation**B.8.1.1.2.1. Laboratory studies****B.8.1.1.2.1.1. Aerobic degradation of the active substance**

| | |
|---------------------|--|
| Reference: | THE DEGRADATION OF 14C-NC 8438 IN A SANDY LOAM SOIL FROM COLORADO USA |
| Notifier: | Taskforce |
| Author(s), year: | Adcock, J. W.; Challis, I. R.; Pearce, J. C.; 1975 |
| Report/Doc. number: | A83269 / W 13 / M-155538-01-1 |
| Guideline(s): | None |
| GLP: | No |
| Deviations: | |
| Validity: | Not valid |
| Status: | Previous evaluation in DAR for original approval / baseline dossier. |

Study summary based on previous draft assessment report**Materials and Methods**

The aerobic and anaerobic transformation of benzene-(random ring-) ^{14}C - and ^{35}S -labelled ethofumesate (NC8438) in a 20% EC formulation (Nortron) was investigated in a sandy loam from Colorado.

Table 8-47: Soil characteristics

| Soil | OC (%) | pH | sand (%) | silt (%) | clay (%) | MHC (%) | CEC meq/100 g |
|---------------------|-----------|-----|-------------|-------------|-------------|---------|------------------|
| Colorado sandy loam | 1.9 | 7.7 | 41 | 45 | 14 | 28 | n.r. |

n.r = not reported

The soils were treated with the formulated NC8438 at a dose of 3 mg as/kg (corresponding to 3.36 kg as/ha) and incubated in the dark at $20\pm^{\circ}\text{C}$ and 65% of its field moisture capacity. In the anaerobic, and in samples for later timepoints in the aerobic and sterile soils, $^{14}\text{CO}_2$ and other volatile compounds were trapped in methanol/ethanolamine (1:1). In the aerobic studies, triplicate samples were taken for analysis at various intervals up to 302 days. In the anaerobic studies, samples were taken 0 and 30 days after application (prior to induction of anaerobic conditions), and 60 and 90 days after application (after induction of anaerobiosis). The soil samples were extracted with methanol/water (9:1). In the aerobic studies, the soil samples taken at day 45 were further extracted with 6M HCl, 2M NaOH, 10M NaOH, N,N-dimethyl formamide, acetic acid or acetic anhydride. The radioactivity was quantified by LSC and characterised by TLC.

Results

The material balance of applied radioactivity at termination of the aerobic studies are given in the table below.

Table 8-48: Material balance of applied ^{14}C -ethofumesate and ^{35}S -ethofumesate (figures within brackets) (NC8438) and residues after aerobic incubation in two sandy loam soils. The figures represent % of applied radioactivity.

| Soil | Days after application | NC8438 (%) | $^{14}\text{CO}_2$ (%) | Unextractable (%) | Total recovery (%) |
|----------|------------------------|------------|------------------------|-------------------|--------------------|
| Colorado | 302 (200) | 6.7 (10) | 38 | 53 (90) | 98 |

No $^{35}\text{SO}_2$ or other transformation products were detected. The transformation of ^{14}C -ethofumesate followed first order kinetics.

In the anaerobic study, 94% of the ^{14}C - and ^{35}S -labelled parent compound present after 30 days of aerobic conditions remained unaltered 60 days after induction of anaerobiosis. In the aerobic study, after 302 days of incubation 6.7% AR could be attributed to ethofumesate, whereas bound residue and CO_2 accounted for 53.1 %AR and 38.3 % AR, respectively.

Comments RMS

In a non-guideline study, the aerobic and anaerobic transformation of ^{14}C - and ^{35}S - labelled ethofumesate in a 20% EC formulation (Nortron) was investigated in a sandy loam from Colorado. Details on the soils (such as sampling depth, previous use and history of pesticide applications) are not reported. The experiment was conducted with the formulated product; however, the effect of formulation on microbial activity and/or biomass was not tested. Moreover, the microbial biomass of the soils was not determined. This is especially critical, since – according to the study protocol – the soil was air-dried and sieved and then immediately spiked with the test solution without any pre-incubation of the soil. Therefore, it is highly probable that the microbial activity could not recover from the dry phase and therefore results of the study appear not reliable.

Soil samples were incubated in screw-cap jars. Lids were lightly placed on all jars, except the 230 and 300 day groups, to prevent excessive moisture loss. The lids were occasionally removed to allow aeration of the soil. Therefore, volatiles and $^{14}\text{CO}_2$ might have been lost and the mass balance is highly questionable.

The experiment was set up without replicates. Triplicate samples were taken for analysis. Only the values for extractable ethofumesate are reported in triplicates. For the non-extractable fraction, only means of three measurements and for CO_2 only two of the three measured values are available.

The report states that only ethofumesate and bound residue were detected in the aerobic study, whereas no metabolites occurred. However, neither the limit of detection, nor the limit of quantification of any of the investigated compounds is reported.

No extraction was performed immediately after application of the test substance at day zero.

In view of the above mentioned deficiencies, the study is considered as not acceptable.

The following six degradation studies were evaluated and summarized in the course of the previous evaluation: Harris, R. J.; Whiteoak, R. J.; (1977); Harris, R. J.; Whiteoak, R. J.; (1978); Harris, R. J.; Reary, J. B.; (1979); Harris, R. J.; Reary, J. B.; (1980); Harris, R. J.; (1976a); Harris, R. J.; (1976b). In the previous DAR, the studies were summarised in one combined summary and they were all deemed not valid. For the current re-evaluation, the RMS did choose not to provide detailed study summaries but rather to better explain the reasons for their previous exclusion.

Summary original DAR

Methods

The dissipation of unlabelled ethofumesate, applied separately or together with each of the herbicides trichloroacetic acid (6 ppm), pyrazone (3 ppm), atrazin (2 ppm), diuron (3 ppm), desmedipham (1 ppm), phenmedipham (1 ppm), pebulate (4 ppm) or cycloate (4 ppm) was investigated under aerobic conditions in different soils. The treated soils were incubated at 22°C and 50 - 60% of their maximum water holding capacity. Single samples were taken for analysis at regular intervals up to 140 days.

Results

The recovery efficiency of the method of analysis for ethofumesate varied between 46 and 103%. The dissipation half-lives of ethofumesate varied between 18 and 43 days in the different soils. Application together with the other compounds tested did not significantly influence the transformation rate of ethofumesate in this study.

RMS Comments original DAR

The fact that no replicate sampling were performed and the insufficient recoveries obtained from the used methods of analysis, makes the results questionable. Besides, no material balances were established, only the decline of parent compounds was reported. The results of the studies indicate that the use of tank mixtures with ethofumesate and the above mentioned compounds causes no significant effect on the dissipation rate of ethofumesate. The data from this study are not further considered in the evaluation of ethofumesate.

| | |
|---------------------|--|
| Reference: | LABORATORY STUDY TO COMPARE THE RESIDUE DECLINE OF ETHOFUMESATE AND ATRAZINE (APPLIED SEPARATELY OR TOGETHER) IN TWO SOIL TYPES |
| Notifier: | Taskforce |
| Author(s), year: | Harris, R. J.; Whiteoak, R. J.; 1977 |
| Report/Doc. number: | A83304 / W 49 / M-155573-01-1 |
| Guideline(s): | None |
| GLP: | No |
| Deviations: | |
| Validity: | Not valid |
| Status: | Previous evaluation in DAR for original approval / baseline dossier. |

Study summary based on previous draft assessment report

Materials and Methods

The aerobic degradation unlabelled ethofumesate was investigated in a sandy loam and a silt loam from UK.

Table 8-49: Soil characteristics.

| Soil | OC (%) | pH | sand (%) | silt (%) | clay (%) | Water content at FC (g/100g) | CEC meq/100 g soil |
|------------|--------|-----|----------|----------|----------|------------------------------|--------------------|
| Sandy loam | 0.8 | 7.8 | 57 | 26 | 19 | 25.3 | n.r. |
| Silt loam | 2.2 | 7.5 | 24 | 56 | 17 | 33.6 | n.r. |

n.r = not reported

The soils were treated with the ethofumesate at a dose of 2 mg as/kg and incubated in the dark at 22±2°C and 60% of their field capacity. The applied analytical method was cross referenced to R.J. Harris, Fisons Report RESID/75/31 (June 1975) "Analytical method for residues of NC 8438 in soil treated with NORTRON".

Comments RMS

The study was regarded as not valid in the previous evaluation.

Soils are insufficiently characterized since pesticide application history of the sites and sampling depth are not reported. Soils were stored outdoors in plastic trays and not under controlled conditions (4°C). The microbial biomass was not determined. No replicates were reported. The recovery in fortified samples ranges between 68% (which is below the levels required by OECD 307) and 87%. No mass balance is reported. The data from this study are not further considered in the re-evaluation of ethofumesate.

| | |
|---------------------|--|
| Reference: | LABORATORY STUDY TO COMPARE THE RESIDUE DECLINE OF ETHOFUMESATE AND DIURON (APPLIED SEPARATELY OR TOGETHER) IN TWO SOIL TYPES |
| Notifier: | Taskforce |
| Author(s), year: | Harris, R. J.; Whiteoak, R. J.; 1978 |
| Report/Doc. number: | A83305 / W 50 / M-155574-01-1 |
| Guideline(s): | None |
| GLP: | No |
| Deviations: | |
| Validity: | Not valid |
| Status: | Previous evaluation in DAR for original approval / baseline dossier. |

Study summary based on previous draft assessment report

Materials and Methods

The aerobic degradation unlabelled ethofumesate was investigated in a sandy loam and a silt loam from UK.

Table 8-50: Soil characteristics.

| Soil | OC (%) | pH | sand (%) | silt (%) | clay (%) | Water content at FC (g/100g) | CEC meq/100 g soil |
|------------|--------|-----|----------|----------|----------|------------------------------|--------------------|
| Sandy loam | 0.8 | 7.8 | 57 | 26 | 19 | 25.3 | n.r. |
| Silt loam | 2.2 | 7.5 | 24 | 56 | 17 | 33.6 | n.r. |

n.r = not reported

The soils were treated with the ethofumesate at a dose of 2 mg as/kg and incubated in the dark at 22±2°C and 60% of their field capacity. The applied analytical method was cross referenced to R.J. Harris, Fisons Report RESID/75/31 (June 1975) "Analytical method for residues of NC 8438 in soil treated with NORTRON".

Comments RMS

With respect to aerobic degradation of ethofumesate, the study is a duplication of the study by Harris and Whiteoak (1977). The study was regarded as not valid in the previous evaluation.

Soils are insufficiently characterized since pesticide application history of the sites and sampling depth are not mentioned. Soils were stored outdoors in plastic trays and not under controlled conditions (4°C). The microbial biomass was not determined. No replicates were reported. The mean recovery determined in fortification

experiments is low (80.2 % for the sandy loam, 77.5% for the silt loam), but still in the range of the OECD 307. However, no mass balance is reported. The data from this study are not further considered in the re-evaluation of ethofumesate.

| | |
|---------------------|--|
| Reference: | LABORATORY STUDY TO COMPARE THE RESIDUE DECLINE OF EC FORMULATIONS OF ETHOFUMESATE, DESMEDIPHAM AND PHENMEDIPHAM (APPLIED SEPARATELY OR TOGETHER) IN TWO SOIL TYPES |
| Notifier: | Taskforce |
| Author(s), year: | Harris, R. J.; Reary, J. B.; 1979 |
| Report/Doc. number: | A83309/ W 54 / M-155578-01-1 |
| Guideline(s): | None |
| GLP: | No |
| Deviations: | |
| Validity: | Not valid |
| Status: | Previous evaluation in DAR for original approval / baseline dossier. |

Study summary based on previous draft assessment report

Materials and Methods

The aerobic degradation unlabelled ethofumesate applied as a 20% EC formulation was investigated in a sandy loam and a silt loam from UK.

Table 8-51: Soil characteristics.

| Soil | OC (%) | pH | sand (%) | silt (%) | clay (%) | Water content at FC (g/100g) | CEC meq/ 100 g soil |
|------------|--------|-----|----------|----------|----------|------------------------------|---------------------|
| Sandy loam | 0.8 | 7.8 | 57 | 26 | 19 | 60 | n.r. |
| Silt loam | 2.2 | 7.5 | 24 | 56 | 17 | 98.4 | n.r. |

n.r = not reported

The soils were treated with formulated ethofumesate at a dose of 2 mg as/kg and incubated in the dark at 22±2°C and 60% of their field capacity. The applied analytical method was cross referenced to R.J. Harris, Fisons Report RESID/75/31 (June 1975) "Analytical method for residues of NC 8438 in soil treated with NORTRON".

Comments RMS

The study was regarded as not valid in the previous evaluation.

Soils are insufficiently characterized since pesticide application history of the sites and sampling depth are not mentioned. Soils were stored outdoors in plastic trays and not under controlled conditions (4°C). The microbial biomass was not determined. No replicates were reported. The mean recovery determined in fortification experiments (in the sandy loam 87.7% and in the silt loam 73.6%) is in the range of the OECD 307. However, no mass balance is reported. The study was conducted with the formulated product, yet no influence of the formulation itself on microbial activity was tested. The data from this study are not further considered in the re-evaluation of ethofumesate.

| | |
|---------------------|--|
| Reference: | LABORATORY STUDY TO COMPARE THE RESIDUE DECLINE OF ETHOFUMESATE, PEBULATE AND CYCLOATE (APPLIED SEPARATELY OR TOGETHER) IN TWO SOIL TYPES |
| Notifier: | Taskforce |
| Author(s), year: | Harris, R. J.; Reary, J. B.; 1980 |
| Report/Doc. number: | A83310/ W 55 /M-155579-01-1 |
| Guideline(s): | None |
| GLP: | No |
| Deviations: | |
| Validity: | Not valid |
| Status: | Previous evaluation in DAR for original approval / baseline dossier. |

Study summary based on previous draft assessment report

Materials and Methods

The aerobic degradation unlabelled ethofumesate applied as a 20% EC formulation was investigated in a sandy clay loam and a clay loam from UK.

Table 8-52: Soil characteristics.

| Soil | OC (%) | pH | sand (%) | silt (%) | clay (%) | Water content at FC (g/100g) | CEC meq/ 100 g soil |
|-----------------|--------|-----|----------|----------|----------|------------------------------|---------------------|
| Sandy clay loam | 1.1 | 7.9 | 48.3 | 23 | 23 | 44 | n.r. |
| Clay loam | 2.8 | 7.8 | 19 | 35 | 38 | 62 | n.r. |

n.r = not reported

The soils were treated with formulated ethofumesate at a dose of 0.72 mg as/kg and incubated in the dark at 22±2°C and 50% of their field capacity. The applied analytical method was cross referenced to R.J. Harris, Fisons Report RESID/75/31 (June 1975) "Analytical method for residues of NC 8438 in soil treated with NORTON".

Comments RMS

The study was regarded as not valid in the previous evaluation.

Soils are insufficiently characterized since pesticide application history of the sites and sampling depth are not mentioned. Soils were stored outdoors in plastic trays and not under controlled conditions (4°C). The microbial biomass was not determined. No replicates were reported. The recoveries determined in fortification experiments were 72.4% for the sandy clay loam and 67.4% for the clay loam (which is below the levels required by OECD 307). However, no mass balance is reported. The data from this study are not further considered in the evaluation of ethofumesate.

| | |
|---------------------|---|
| Reference: | LABORATORY STUDY TO COMPARE THE RESIDUE DECLINE OF NC 8438 AND TRICHLOROACETIC ACID (APPLIED SEPARATELY OR TOGETHER) IN TWO SOIL TYPES |
| Notifier: | Taskforce |
| Author(s), year: | Harris, R. J.; 1976a |
| Report/Doc. number: | A83301 / W 45 / M-155570-01-1 |
| Guideline(s): | None |
| GLP: | No |
| Deviations: | |
| Validity: | Not valid |
| Status: | Previous evaluation in DAR for original approval / baseline dossier. |

Study summary based on previous draft assessment report

Materials and Methods

The aerobic degradation unlabelled ethofumesate applied as a 20% EC formulation was investigated in a sandy loam and a silt loam from UK.

Table 8-53: Soil characteristics.

| Soil | OC (%) | pH | sand (%) | silt (%) | clay (%) | Water content at FC (g/100g) | CEC meq/100 g soil |
|------------|--------|-----|----------|----------|----------|------------------------------|--------------------|
| Sandy loam | 0.8 | 7.8 | 57 | 26 | 19 | 25.3 | n.r. |
| Silt loam | 2.2 | 7.5 | 24 | 56 | 16 | 33.6 | n.r. |

n.r = not reported

The soils were treated with formulated ethofumesate at a dose of 2 mg as/kg and incubated in the dark at 22±2°C and 60% of their field capacity. The applied analytical method was cross referenced to R.J. Harris, Fisons Report RESID/75/31 (June 1975) "Analytical method for residues of NC 8438 in soil treated with NORTRON".

Comments RMS

The study was regarded as not valid in the previous evaluation.

Soils are insufficiently characterized since pesticide application history of the sites and sampling depth are not mentioned. Soils were stored outdoors in plastic trays and not under controlled conditions (4°C). The microbial biomass was not determined. No replicates were reported. Recoveries are generally between 70 % and 90 %. No mass balance is reported. The data from this study are not further considered in the re-evaluation of ethofumesate.

| | |
|---------------------|---|
| Reference: | LABORATORY STUDY TO COMPARE THE RESIDUE DECLINE OF NC 8438 AND PYRAZONE (APPLIED SEPARATELY OR TOGETHER) IN TWO SOIL TYPES |
| Notifier: | Taskforce |
| Author(s), year: | Harris, R. J.; 1976b |
| Report/Doc. number: | A83302 / W 46 / M-155571-01-1 |
| Guideline(s): | None |
| GLP: | No |
| Deviations: | |
| Validity: | Not valid |
| Status: | Previous evaluation in DAR for original approval / baseline dossier. |

Study summary based on previous draft assessment report

Materials and Methods

The aerobic degradation unlabelled ethofumesate applied as a 20% EC formulation was investigated in a sandy loam and a silt loam from UK.

Table 8-54: Soil characteristics.

| Soil | OC (%) | pH | sand (%) | silt (%) | clay (%) | Water content at FC (g/100g) | CEC meq/ 100 g soil |
|------------|--------|-----|----------|----------|----------|------------------------------|---------------------|
| Sandy loam | 0.8 | 7.8 | 57 | 26 | 19 | 25.3 | n.r. |
| Silt loam | 2.2 | 7.5 | 24 | 56 | 16 | 33.6 | n.r. |

n.r = not reported

The soils were treated with formulated ethofumesate at a dose of 2 mg as/kg and incubated in the dark at 22±2°C and 60% of their field capacity. The applied analytical method was cross referenced to R.J. Harris, Fisons Report RESID/75/31 (June 1975) "Analytical method for residues of NC 8438 in soil treated with NORTRON".

Comments RMS

The study was regarded as not valid in the previous evaluation.

Soils are insufficiently characterized since pesticide application history of the sites and sampling depth are not mentioned. Soils were stored outdoors in plastic trays and not under controlled conditions (4°C). The microbial biomass was not determined. No replicates were reported. Recoveries are generally between 70 % and 90 %, except for the time zero sample (53-80%).

No mass balance is reported. The data from this study are not further considered in the re-evaluation of ethofumesate.

| | |
|---------------------|---|
| Reference: | [14C]-ETHOFUMESATE: AEROBIC METABOLISM IN TWO SOILS AT TWO MOISTURE CONTENTS |
| Notifier: | Taskforce |
| Author(s), year: | Waring, A. R.; 1992 |
| Report/Doc. number: | A83385 / W 129 / M-155653-01-1 |
| Guideline(s): | USEPA (=EPA): subdiv.N, 162-1 |
| GLP: | Yes |
| Deviations: | |
| Validity: | Valid |
| Status: | Previous evaluation in DAR for original approval / baseline dossier. |

Comments RMS

The study was also submitted as a route study and was evaluated in the respective section.

The regulatory endpoints are:

| | Kinetic Model | DT50 (d) | DT90 (d) | Chi ² (%) |
|---------------------|---------------|----------|----------|----------------------|
| Abington sandy loam | SFO | 137 | 454 | 6.89 |

| | |
|---------------------|--|
| Reference: | AEROBIC METABOLISM IN A STANDARD SOIL (SPEYER 2.2) (14C)-Ethofumesate |
| Notifier: | Taskforce |
| Author(s), year: | Waring, A. R.; 1993 |
| Report/Doc. number: | A83398 / W 156 / M-155666-01-1 |
| Guideline(s): | None |
| GLP: | Yes |
| Deviations: | |
| Validity: | Not valid |
| Status: | Previous evaluation in DAR for original approval / baseline dossier. |

Comments RMS

The study was also submitted as a route study and was evaluated in the respective section.

| | |
|---------------------|--|
| Reference: | DEGRADATION IN SOIL UNDER AEROBIC CONDITIONS 14C Ethofumesate |
| Notifier: | Taskforce |
| Author(s), year: | Cameron, B. D.; Phillips, M.; Hall, B. E.; 1991 |
| Report/Doc. number: | A87600 / W 500 / M-161526-01-1 |
| Guideline(s): | BBA: IV, Section 4.1 (1986) |
| GLP: | Yes |
| Deviations: | |
| Validity: | Not valid |
| Status: | Previous evaluation in DAR for original approval / baseline dossier. |

Comments RMS

The study was also submitted as a route study and was evaluated in the respective section.

| | |
|---------------------|--|
| Reference: | THE SOIL DEGRADATION OF RADIOLABELLED NC 8438 |
| Notifier: | Taskforce |
| Author(s), year: | Adcock, J. W.; Challis, I. R.; Warner, P. A.; 1974 |
| Report/Doc. number: | A83266 / W10/2 / M-155706-02-1; Amended: 1975-05-01 |
| Guideline(s): | None |
| GLP: | No |
| Deviations: | |
| Validity: | Not valid |
| Status: | Previous evaluation in DAR for original approval / baseline dossier. |

Comments RMS

The study was also submitted as a route study and was evaluated in the respective section.

| | |
|---------------------|--|
| Reference: | ADDITIONAL LABORATORY STUDY OF THE DEGRADATION OF NC 8438 IN TWO STANDARD SOILS FROM W. GERMANY |
| Notifier: | Taskforce |
| Author(s), year: | Harris, R. J.; Whiteoak, R. J.; 1975 |
| Report/Doc. number: | A83299 / W 43 / M-155568-01-1 |
| Guideline(s): | BBA: 36 |
| GLP: | No |
| Deviations: | |
| Validity: | Not valid |
| Status: | Previous evaluation in DAR for original approval / baseline dossier. |

Study summary based on previous draft assessment report

Materials and Methods

The aerobic degradation of unlabelled ethofumesate applied as a 20% EC formulation was investigated in a sandy loam and two sands from Germany.

Table 8-55: Soil characteristics

| Soil | OC (%) | pH | < 0.02 mm (%) | silt (%) | clay (%) | Water content at 40 % MWHC (g/100g) | CEC meq/ 100 g soil |
|------------|--------|-----|---------------|----------|----------|-------------------------------------|---------------------|
| Sand | 0.8 | 7.0 | 4.2 | n.r. | n.r. | 11.7 | n.r. |
| Sand | 2.58 | 6.8 | 10.1 | n.r. | n.r. | 11.8 | n.r. |
| Sandy loam | 1.0 | 5.2 | 19.5 | n.r. | n.r. | 9.3 | n.r. |

n.r = not reported

The soils were treated with formulated ethofumesate at a dose of 10 mg as/kg and incubated in the dark at 22±2°C and 60% of their field capacity. Samples were extracted with 300 ml of a 2:1 (v/v) dichloromethane: methanol mixture. After filtration, the extraction was repeated. Duplicate aliquots were analysed for most samples. The combined organic extract was dried by passing through anhydrous sodium sulphate and was taken to dryness in a Kuderna-Danish evaporator. Determination of extracts was carried out by GLC.

Comments RMS

The study was regarded as not valid in the previous evaluation.

Soils are insufficiently characterized since pesticide application history of the sites; sampling depth and soil texture are not reported. Soils were stored outdoors in plastic trays and not under controlled conditions (4°C). The microbial biomass was not determined and the effect of the formulation on microbial activity not investigated. Recoveries are generally above 90 %. No mass balance is reported. Neither the limit of quantification nor the limit of detection is reported. The authors themselves question the relevance of the results: “the possibility that the high application rate [...] may have contributed to the slower decline has not been investigated.” Time zero concentrations were not measured and sampling intervals are in part approximates not suited for exact kinetic evaluation (e.g. 8 ¼ weeks, 4 ½ weeks).

The data from this study are not further considered in the re-evaluation of ethofumesate.

| | |
|---------------------|--|
| Reference: | Fertilization can modify the non-target effects of pesticides on soil microbial communities. |
| Notifier: | UPL / Taskforce |
| Author(s), year: | Muñoz-Leoz, B., Garbisu, C., Antigüedad, I., Ruiz-Romera, E. 2012 |
| Report/Doc. number: | M-458656-01-1 |
| Guideline(s): | ISO 16072, 2002. Soil Quality and Laboratory Methods for Determination of Microbial Soil Respiration. ISO 17155, 2002. Soil Quality and Determination of Abundance and Activity of Soil Microflora Using Respiration Curves |
| GLP: | No |
| Deviations: | |
| Validity: | Relevant; not reliable. |
| Status: | Scientific peer-reviewed literature |

Study summary

A three-month laboratory mesocosm experiment was performed to investigate interactions between pesticides (difenoconazole: fungicide, deltamethrin: insecticide, ethofumesate: herbicide) and fertilizers (NPK synthetic fertilizer, compost) regarding the potential non-target effects of pesticides on soil microbial communities. To this aim, pesticides and fertilizers were applied to soil at a rate of 5 mg active ingredient kg⁻¹ DW soil and 185 mg N kg⁻¹ DW soil, respectively. Soil sampling was done after 0, 7, 30, 60 and 90 days of incubation in order to determine pesticide degradation rates and microbial properties: enzyme activities, basal respiration, substrate-induced respiration, potentially mineralizable N, nitrification rate and denitrification potential. By the end of the incubation, ethofumesate in non-fertilized soils was degraded by 93%, with a half-life of 29 days. NPK fertilization led to a 26% increase in ethofumesate half-life in soil. A short-term antagonistic effect between NPK fertilization and ethofumesate presence was found regarding their inhibitory effect on potentially mineralizable N. In compost-fertilized soils, ethofumesate counteracted the stimulatory effect of compost on denitrification potential.

Comment RMS

Ethofumesate showed no effect on soil microbial respiratory activity and only slight effects on potentially mineralizable nitrogen, nitrification rate and denitrification potential. Ethofumesate led to a slightly lower enzyme activity at day 90. Several interactions between fertilizer application and effects of ethofumesate on microbial communities were observed. Better fits were achieved when using a bi-phasic degradation model. The degradation rate of the unfertilized control (DT₅₀ 29.2 days) is in the range of the laboratory and the normalized field studies.

However, in order to be fully reliable for regulatory purposes, key information is missing such as analytical recoveries and a full mass balance.

| | |
|---------------------|--|
| Reference: | Non-target effects of three formulated pesticides on microbially-mediated processes in a clay-loam soil. |
| Notifier: | Taskforce |
| Author(s), year: | Muñoz-Leoz, B.; Garbisu, C.; Charcosset, J.-Y.; Sanchez-Perez, J.M.; Antigüedad, I.; Ruiz-Romera, E.; 2013 |
| Report/Doc. number: | M-462303-01-1 |
| Guideline(s): | ISO 16072, 2002. Soil Quality and Laboratory Methods for Determination of Microbial Soil Respiration. ISO 17155, 2002. Soil Quality and Determination of Abundance and Activity of Soil Microflora Using Respiration Curves |
| GLP: | No |
| Deviations: | |
| Validity: | Relevant; not reliable. |
| Status: | Scientific peer-reviewed literature |

Study summary

An experiment was performed to study non-target effects of inter alia ethofumesate (herbicide) on microbial parameters in a clay-loam soil. Pesticides were applied as commercial formulations to soil samples at different concentrations (5, 50 and 500 mg kg⁻¹ dws) and then incubated under laboratory conditions for 3 months. Throughout the incubation period, microbial parameters were determined at days 7, 30, 60 and 90. At 5 mg kg⁻¹ dws, ethofumesate did not cause significant changes in soil microbial parameters. In contrast, at 500 mg kg⁻¹ dws, pesticide application decreased overall soil microbial activity, negatively affecting the activity of soil enzymes.

Similarly, at 500 mg kg⁻¹ dws, ethofumesate caused a pesticide-induced stress on soil microbial communities, as reflected by the respiratory quotient. Besides, ethofumesate at 50 and 500 mg kg⁻¹ dws resulted in lower values of denitrification potential. It was concluded that, although pesticide concentration had a somewhat inconsistent and erratic effect on soil microbial parameters, pesticide application at 500 mg kg⁻¹ dws did have an impact on many of the microbial parameters studied here.

Comments RMS

The study seems to have followed the OECD 307 guideline. Pesticide degradation rates were dependent upon concentration: higher values of half-life time were observed at increasing pesticide concentrations. Better fits were achieved when using a bi-phasic degradation model. At 5 mg kg⁻¹ dw, no pesticide-related relevant changes in soil microbial communities occurred. At higher concentrations, adverse impacts on soil microbial communities were detected. In particular, at 500 mg kg⁻¹ dw soil, ethofumesate application decreased overall soil microbial activity, negatively affecting the activity of soil enzymes. At high concentrations, ethofumesate

caused a pesticide-induced stress on soil microbial communities, as reflected by the respiratory quotient and a lower of N_{\min} at the end of the incubation.

The experiments were conducted with a 50% EC formulation of ethofumesate. The degradation rate for the lowest relevant concentration (DT_{50} 28.5 days) is in the range of the laboratory and the normalized field studies.

In order to be acceptable for regulatory purposes, key parameters would have been determined (as required by OECD 307) such as volatiles, evolved CO_2 , and non-extractable residues. Moreover, the degradation of ethofumesate is only graphically displayed. The measured values are not reported and therefore, the degradation rate cannot be independently verified. For instance, the authors have set the time-zero concentration (which was apparently not measured) to 100% of the dosed rate, which is not in line with FOCUS (2006).

Reference: **Influence of soil humidity on herbicide degradation - laboratory tests.**

| | |
|---------------------|-------------------------------------|
| Notifier: | Taskforce |
| Author(s), year: | Kucharski, M.; Sadowski, J.; 2006 |
| Report/Doc. number: | M-459319-01-1 |
| Guideline(s): | None |
| GLP: | No |
| Deviations: | |
| Validity: | Relevant; not reliable. |
| Status: | Scientific peer-reviewed literature |

Study summary

The aim of these studies was to define the dynamics of the degradation of fluazifop, ethofumesate and clopyralid and the influence of humidity on the rate of degradation in soil. After sampling of soil from a field in the vicinity of Wrocław, Poland, humidity of the required level was established (20, 60 and 90% maximum soil water capacity). One hour after herbicide application, samples were collected and residues were determined by high-performance liquid chromatography (HPLC) with UV detection and gas chromatography (GLC) with ECD detection. The half-life of ethofumesate in soil was 80, 49 or 24 days at 20, 60 or 90% maximum soil water capacity.

Comments RMS

Only the abstract of the study is available in English, the main study is in Polish. The half-life of ethofumesate in soil was 80, 49 or 24 days at 20, 60 or 90% maximum soil water holding capacity. However, in order to be fully reliable for regulatory purposes, key information such as analytical recoveries and a full mass balance is missing.

| | |
|---------------------|---|
| Reference: | Degradation of ethofumesate in soil under laboratory conditions. |
| Notifier: | Taskforce |
| Author(s), year: | Kucharski, M.; Sadowski, J.;2009 |
| Report/Doc. number: | M-458624-01-1 |
| Guideline(s): | None |
| GLP: | No |
| Deviations: | |
| Validity: | Relevant; not reliable. |
| Status: | Scientific peer-reviewed literature |

Study summary

The aim of the research was to determine the influence of the soil type and adjuvants on the dynamics of ethofumesate degradation in soil. Two soil types were collected from the field and used for the laboratory experiments. On both soils, ethofumesate was applied at a rate of 800 g/ha, alone and in mixture with adjuvant based on methylated crop oil and surfactant adjuvant. Residues of ethofumesate were determined using HPLC with UV detection.

The type of soil influenced the degradation rates of ethofumesate. Significant differences in degradation rate between soils during the first period after treatment (36 days) influenced the DT₅₀ indicator. The addition of oil adjuvant slowed down the degradation of ethofumesate and increased the level of residue in soils. The DT₅₀ value for ethofumesate + oil adjuvant was about 8-10 days higher in comparison with the DT₅₀ for ethofumesate alone. No significant differences were observed between degradation rates and the DT₅₀ for ethofumesate applied alone and with surfactant adjuvant.

Comments RMS

In order to be acceptable for regulatory purposes, key parameters would have been determined (as required by OECD 307) such as volatiles, evolved CO₂, and non-extractable residues. Moreover, the degradation of ethofumesate is only graphically displayed. The measured values are not reported and therefore, the degradation rate cannot be independently verified.

B.8.1.1.2.1.2. Aerobic degradation of metabolites, breakdown and reaction products

| | |
|---------------------|--|
| Reference: | NC8493 (A Metabolite of Ethofumesate) – Aerobic Rate of Degradation in Three Soils. |
| Notifier: | UPL/Agrichem |
| Author(s), year: | Malekani, K. (2013) |
| Report/Doc. number: | Smithers Viscient Study No. 13845.6134 |
| Guideline(s): | OECD Guideline 307 OPPTS Guideline 835.4100 |
| GLP: | Yes |
| Deviations: | |
| Validity: | Valid |
| Status: | New study. |

I. MATERIALS AND METHODS

A. MATERIALS

1. **Test material:** NC8493 (2,3-dihydro-2-hydroxy-3,3-dimethyl benzofuran-5-yl methanesulphonate)
- Batch No.:** EPP/VMV 358A
- Purity:** 99.8%
- CAS No.:** 26322-82-7

2. Soils:

Three freshly sampled field soils were used: Fislis (France), Horn (Switzerland) and Sevelen (Switzerland). None of the soils had knowingly received pesticide applications in the last 3 years. All soils were sieved with 2-mm sieve and moisture was adjusted to a pF 2.5. At start and at study termination, the microbial biomass of the soil was determined.

Table 8-56: Characterization of soil

| Soil Property | Fislis | Horn | Sevelen |
|--|-----------|-------|------------|
| Soil type (USDA) | Silt Loam | Loam | Sandy Loam |
| Sand [%] | 11.89 | 41.87 | 54.61 |
| Silt [%] | 62.84 | 34.92 | 37.36 |
| Clay [%] | 25.27 | 23.21 | 8.03 |
| Bulk density disturbed [kg/dm ³] | 1.39 | 1.41 | 1.37 |
| pH [CaCl ₂] | 6.82 | 7.23 | 7.51 |
| Cation Exchange Capacity [mmol/z//100 g B] | 25.15 | 23.24 | 7.26 |
| Field moisture | | | |
| pF 1.0 [%] | 62.24 | 60.99 | 47.43 |
| pF 2.0 [%] | 42.56 | 38.72 | 32.76 |
| pF 2.5 [%] | 35.45 | 33.69 | 23.58 |

Table 8-57: Soil microbial biomass

| Interval | Soil biomass [mg C/100 g soil] | Organic C [%] | Biomass as organic C ^a [%] |
|---------------------|--------------------------------|---------------|---------------------------------------|
| Fislis Soil | | | |
| Post-handling | 18.1 | 2.1 | 0.86 |
| Start of incubation | 19.4 | 2.2 | 0.88 |
| End of incubation | 9.8 | 2.0 | 0.49 |
| Horn Soil | | | |
| Post-handling | 50.8 | 2.4 | 2.12 |
| Start of incubation | 37.7 | 2.5 | 1.51 |
| End of incubation | 22.2 | 2.8 | 0.79 |
| Sevelen Soil | | | |
| Post-handling | 22.1 | 1.6 | 1.38 |
| Start of incubation | 23.3 | 3.2 | 0.73 |
| End of incubation | 21.0 | 3.1 | 0.68 |

a Biomass as % OC = [Soil Biomass / (%OC × 1000 mg/g)] × 100%

B. STUDY DESIGN

1. Experimental conditions

Each soil (100 g dry weight) was added to the test vessel and the soil moisture was adjusted to pF2.5. After equilibration to test conditions for four days the samples were treated at the rate of 0.5 mg/kg, corresponding to an expected field rate of 500 g/ha. The solvent was given time to evaporate and the soil was gently shaken to ensure homogeneity. The samples were incubated in the dark at $20 \pm 2^\circ\text{C}$ and aerated continuously with moisturised air.

2. Sampling

The samples were taken immediately after application (day 0), 1, 2, 4, and 24 hours and 3 and 7 days after application. At each sampling interval, two replicates were analysed by LC-MS/MS to determine concentration of the NC8493.

3. Description of analytical procedures

Soil extractions were carried out using 150 mL acetonitrile:water (4:1, v:v) and the soil and solvent mixture was shaken for 1 minute and then centrifuged for approximately 10 minutes. The procedure was repeated and combined extracts were brought to a final volume of 300 mL with the extraction solvent, mixed well and the aliquots filtered.

Aliquots of the 4-hour sampling post-extracted soil (PES) samples were submitted to reflux extraction. The PES was refluxed with acetonitrile:water (4:1, v:v) for 4 hours. The cooled mixture was transferred to centrifuge bottles using acetonitrile:water (4:1, v:v) as a rinse and centrifuged for 10 minutes. The supernatant was decanted and adjusted to 175 mL with 4:1 acetonitrile:water, filtered and analysed by LC-MS/MS.

II. RESULTS AND DISCUSSION

A. MASS BALANCE

The samples analysed at time 0 ranged from 82.4 to 89.4% of the initial dose (calculated based on the concentration of NC8493 in the spiked control extract at time 0) and the average results for samples analysed at 24 hours of incubation ranged from < LOQ to 4.2% of the initial dose and < LOQ for the remainder of the 7-day study.

LOD: 0.006 mg/kg

LOQ: 0.03 mg/kg

B. VOLATILIZATION

Volatile components were not recovered in this study.

C. TRANSFORMATION

NC 8493 degraded very rapidly in soil, the calculated half-life (SFO) ranged from 0.05 to 0.07 days. For all soils SFO was the optimum kinetic model and showed acceptable visual fit.

Table 8-58: Concentrations of NC8493 measured in Fislis soil samples during the 7-day aerobic soil degradation study.

| Interval | Dose Concentration (mg/kg) | Concentration in Extract (ng/mL) | Calculated Concentration in Soil (mg/kg) | % of Initial Applied ^a |
|------------------------|----------------------------|----------------------------------|--|-----------------------------------|
| Spiked Control Extract | 0.5 | 208 | 0.624 | 100 |
| Time 0 | 0.5 | 181 | 0.543 | 87.0 |
| | 0.5 | 176 | 0.528 | 84.6 |
| | | | Mean | 85.8 |
| 1 Hour | 0.5 | 147 | 0.441 | 70.7 |
| | 0.5 | 163 | 0.489 | 78.4 |
| | | | Mean | 74.5 |
| 2 Hours | 0.5 | 81.5 | 0.245 | 39.2 |
| | 0.5 | 55.0 | 0.165 | 26.4 |
| | | | Mean | 32.8 |
| 4 Hours | 0.5 | 18.8 | 0.0564 | 9.0 |
| | 0.5 | 14.3 | 0.0429 | 6.9 |
| | | | Mean | 8.0 |
| 4 Hours (Reflux PES) | 0.5 | < LOD | < LOD | < LOD |
| | 0.5 | < LOD | < LOD | < LOD |
| | | | Mean | < LOD |
| 24 Hours | 0.5 | 8.67 | 0.0260 | 4.2 |
| | 0.5 | < LOD | < LOD | < LOD |
| | | | Mean | 4.2 |
| 3 Days | 0.5 | <0.03 | < LOQ | < LOD |
| | 0.5 | <0.03 | < LOQ | < LOD |
| | | | Mean | < LOD |
| 7 Days | 0.5 | < LOD | < LOQ | < LOD |
| | 0.5 | < LOD | < LOQ | < LOD |
| | | | Mean | NA |

ND = Not Detected, LOQ = Limit of Quantitation, LOD = Limit of Detection

Table 8-59: Concentrations of NC8493 measured in Horn soil samples during the 7-day aerobic soil degradation study.

| Interval | Dose Concentration (mg/kg) | Concentration in Extract (ng/mL) | Calculated Concentration in Soil (mg/kg) | % of Initial Applied ^a |
|------------------------|----------------------------|----------------------------------|--|-----------------------------------|
| Spiked Control Extract | 0.5 | 199 | 0.597 | 100 |
| Time 0 | 0.5 | 172 | 0.516 | 86.4 |
| | 0.5 | 178 | 0.534 | 89.4 |
| | | | Mean | 87.9 |
| 1 Hour | 0.5 | 118 | 0.354 | 59.3 |
| | 0.5 | 110 | 0.330 | 55.3 |
| | | | Mean | 57.3 |
| 2 Hours | 0.5 | 88.2 | 0.265 | 44.3 |
| | 0.5 | 102 | 0.306 | 51.3 |
| | | | Mean | 47.8 |
| 4 Hours | 0.5 | 17.2 | 0.0516 | 8.6 |
| | 0.5 | 20.1 | 0.0603 | 10.1 |
| | | | Mean | 9.4 |
| 4 Hours (Reflux PES) | 0.5 | < LOD | < LOD | < LOD |
| | 0.5 | < LOD | < LOD | < LOD |
| | | | Mean | < LOD |
| 24 Hours | 0.5 | < LOD | < LOD | < LOD |
| | 0.5 | < LOD | < LOD | < LOD |
| | | | Mean | < LOD |
| 3 Days | 0.5 | < 0.05 | < LOQ | < LOD |
| | 0.5 | < 0.05 | < LOQ | < LOD |
| | | | Mean | < LOD |
| 7 Days | 0.5 | < LOD | < LOD | < LOD |
| | 0.5 | < LOD | < LOD | < LOD |
| | | | Mean | < LOD |

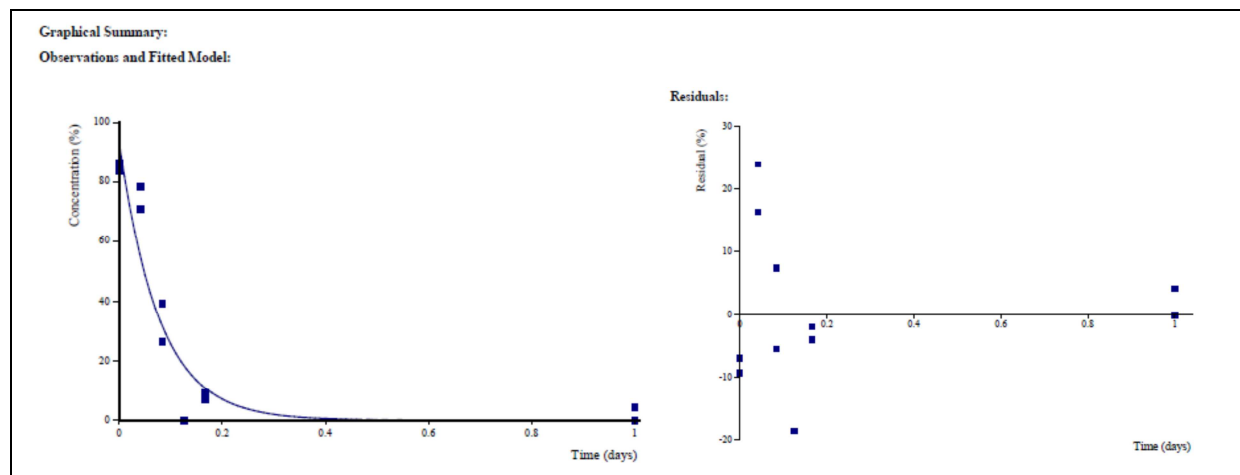
D = Not Detected, BQ = Below Quantitation

Table 8-60: Concentrations of NC8493 measured in Sevelen soil samples during the 7-day aerobic soil degradation study.

| Interval | Dose Concentration (mg/kg) | Concentration in Extract (ng/mL) | Calculated Concentration in Soil (mg/kg) | % of Initial Applied ^a |
|------------------------|----------------------------|----------------------------------|--|-----------------------------------|
| Spiked Control Extract | 0.5 | 210 | 0.630 | 100 |
| Time 0 | 0.5 | 180 | 0.540 | 85.7 |
| | 0.5 | 173 | 0.519 | 82.4 |
| | | | Mean | 84.0 |
| 1 Hour | 0.5 | 135 | 0.405 | 64.3 |
| | 0.5 | 102 | 0.306 | 48.6 |
| | | | Mean | 56.4 |
| 2 Hours | 0.5 | 83.4 | 0.250 | 39.7 |
| | 0.5 | 68.4 | 0.205 | 32.6 |
| | | | Mean | 36.1 |
| 4 Hours | 0.5 | 10.6 | 0.0318 | 5.0 |
| | 0.5 | 13.9 | 0.0417 | 6.6 |
| | | | Mean | 5.8 |
| 4 Hours (Reflux PES) | 0.5 | < LOD | < LOD | < LOD |
| | 0.5 | < LOD | < LOD | < LOD |
| | | | Mean | < LOD |
| 24 Hours | 0.5 | 7.68 | 0.0230 | 3.7 |
| | 0.5 | 10.1 | 0.0303 | 4.8 |
| | | | Mean | 4.2 |
| 3 Days | 0.5 | <0.05 | <LOQ | <LOD |
| | 0.5 | <0.05 | <LOQ | <LOD |
| | | | Mean | NA |
| 7 Days | 0.5 | < LOD | < LOD | < LOD |
| | 0.5 | < LOD | < LOD | < LOD |
| | | | Mean | < LOD |

^a D = Not Detected, BQ = Below Quantitation

Figure 8-24: Kinetic evaluation soil Fislis (SFO)



Estimated Values:

| Parameter | Value | σ | Prob. > t | Lower CI | Upper CI |
|-----------|-------|----------|-----------|----------|----------|
| Parent_0 | 93.08 | 8.984 | 5.739E-07 | 73.06 | 113.1 |
| k_Parent | 12.89 | 2.421 | 0.0001675 | 7.5 | 18.29 |

 χ^2

| Parameter | Error % | Degrees of Freedom |
|-----------|---------|--------------------|
| All data | 27.74 | 4 |
| Parent | 27.74 | 4 |

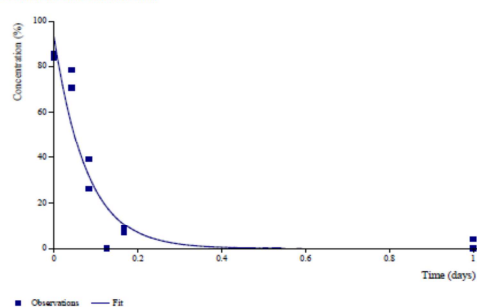
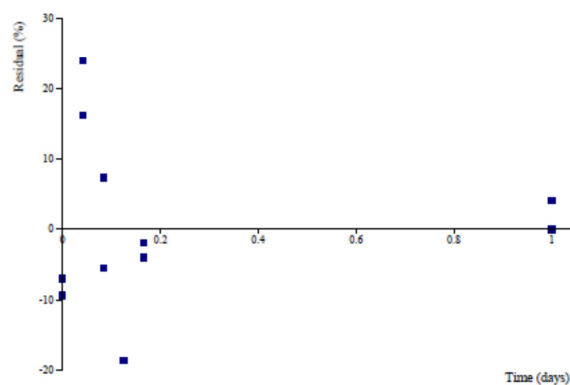
Decay Times:

| Compartment | DT50 (days) | DT90 (days) |
|-------------|-------------|-------------|
| Parent | 0.05376 | 0.1786 |

Figure 8-25: Kinetic evaluation soil Fislis (FOMC)**Experiment 1 (FOMC)**

Graphical Summary:

Observations and Fitted Model:

**Residuals:****Estimated Values:**

| Parameter | Value | σ | Prob. > t |
|-----------|-----------|----------|-----------|
| Parent_0 | 93.08 | | |
| alpha | 6.674E+06 | | |
| beta | 5.176E+05 | | |

Note: Errors and T-test values could not be calculated because the covariance matrix could not be created.

 χ^2

| Parameter | Error % | Degrees of Freedom |
|-----------|---------|--------------------|
| All data | 30.56 | 3 |
| Parent | 30.56 | 3 |

Decay Times:

| Compartment | DT50 (days) | DT90 (days) |
|-------------|-------------|-------------|
| Parent | 0.05376 | 0.1786 |

Figure 8-26: Kinetic evaluation soil Horn (SFO)

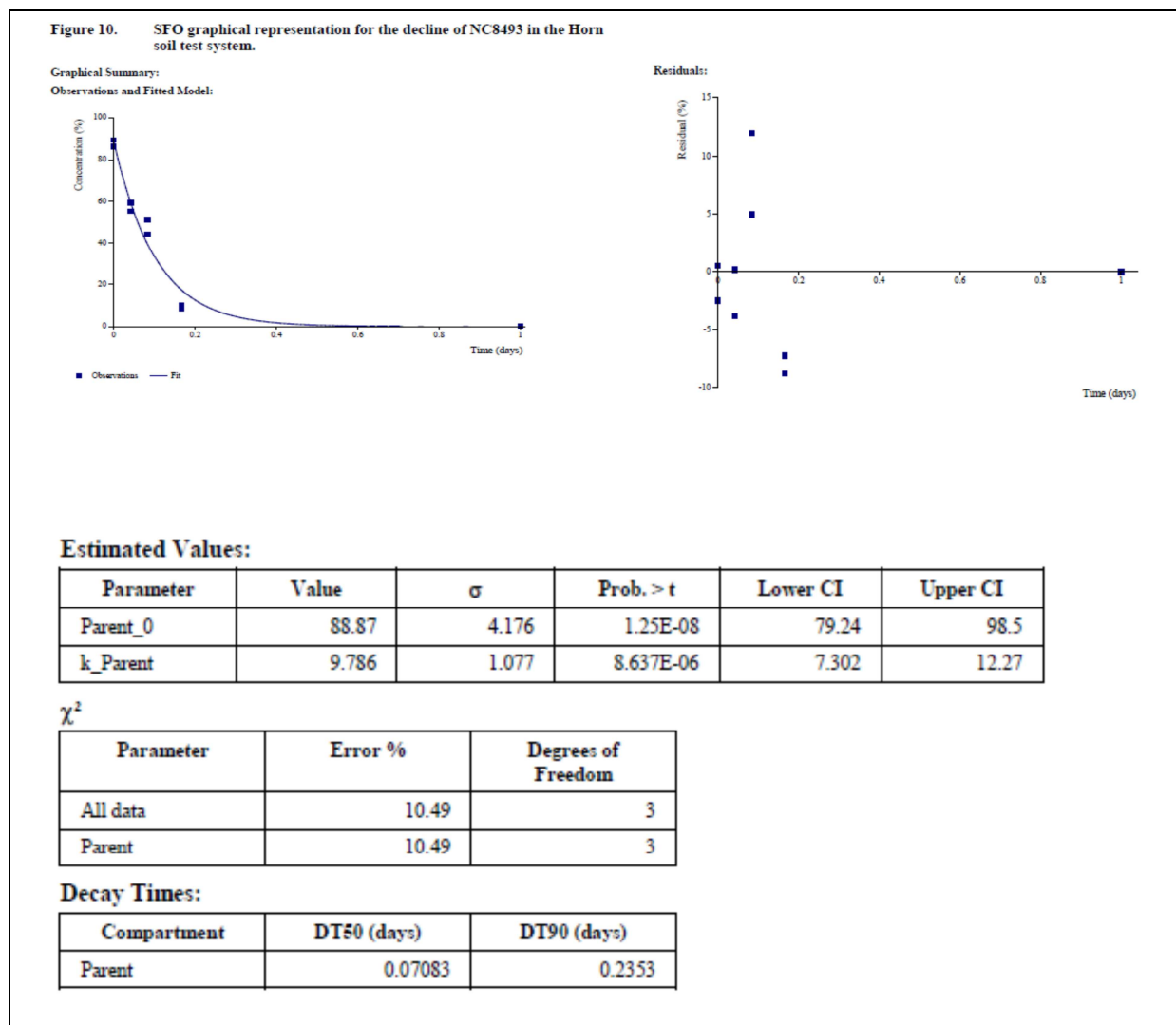
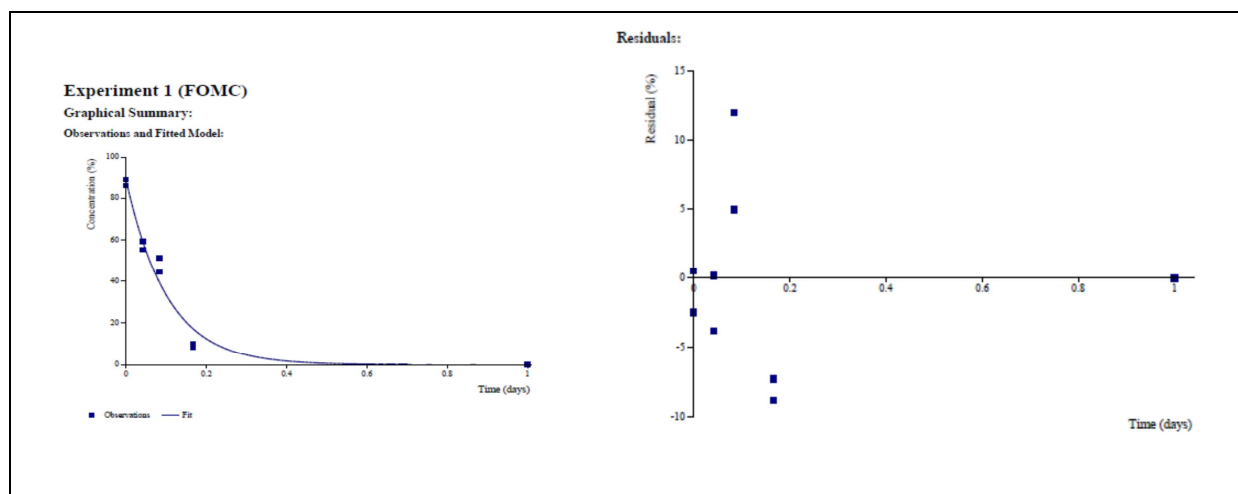


Figure 8-27: Kinetic evaluation soil Horn (FOMC)



Initial Values for This Step:

| Parameter | Initial Value | Bounds | Fixed |
|--------------|---------------|------------------|-------|
| Parent_0 | 100 | 0 to (unbounded) | No |
| alpha_Parent | 0.1 | 0 to (unbounded) | No |
| beta_Parent | 0.1 | 0 to (unbounded) | No |

Estimated Values:

| Parameter | Value | σ | Prob. > t |
|-----------|-----------|----------|-----------|
| Parent_0 | 88.87 | | |
| alpha | 1.07E+07 | | |
| beta | 1.093E+06 | | |

Note: Errors and T-test values could not be calculated because the covariance matrix could not be created.

 χ^2

| Parameter | Error % | Degrees of Freedom |
|-----------|---------|--------------------|
| All data | 11.98 | 2 |
| Parent | 11.98 | 2 |

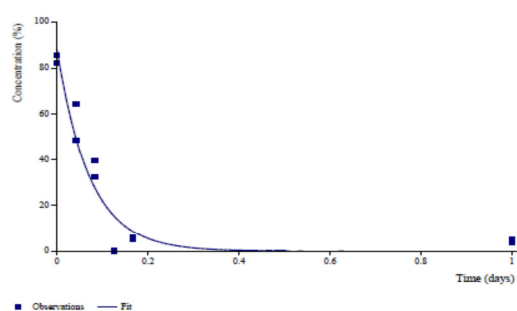
Decay Times:

| Compartment | DT50 (days) | DT90 (days) |
|-------------|-------------|-------------|
| Parent | 0.07083 | 0.2353 |

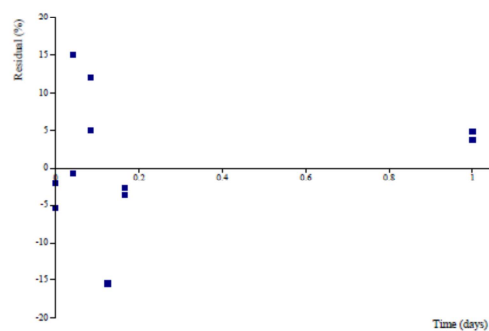
Figure 8-28: Kinetic evaluation soil Sevelen (SFO)

Figure 11. SFO graphical representation for the decline of NC8493 in the Sevelen soil test system.

Graphical Summary:
Observations and Fitted Model:



Residuals:



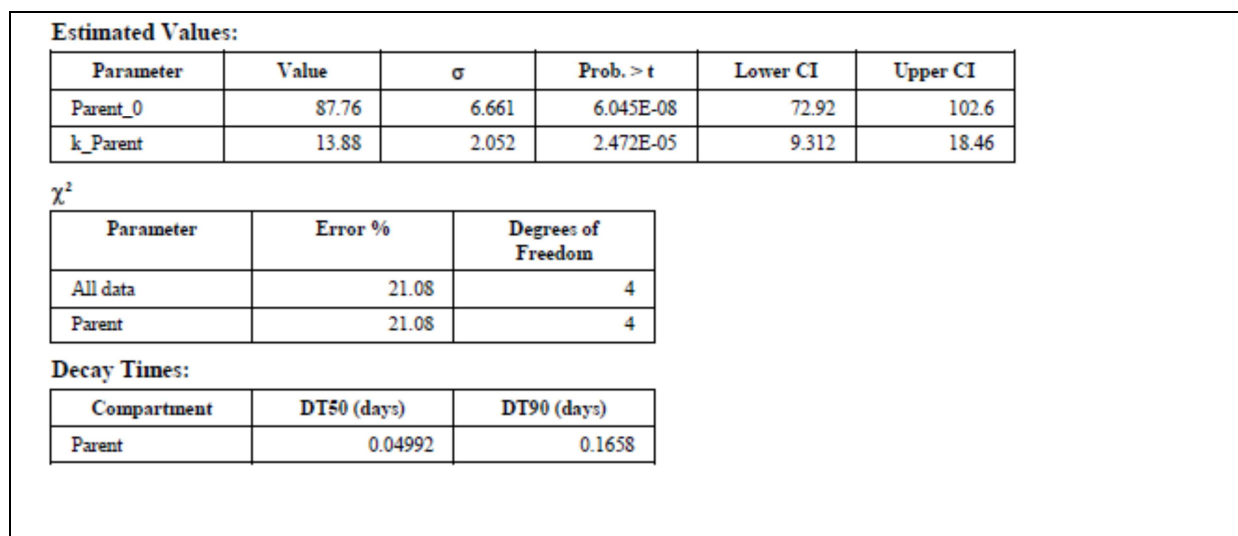


Figure 8-29: Kinetic evaluation soil Sevelen (FOMC)

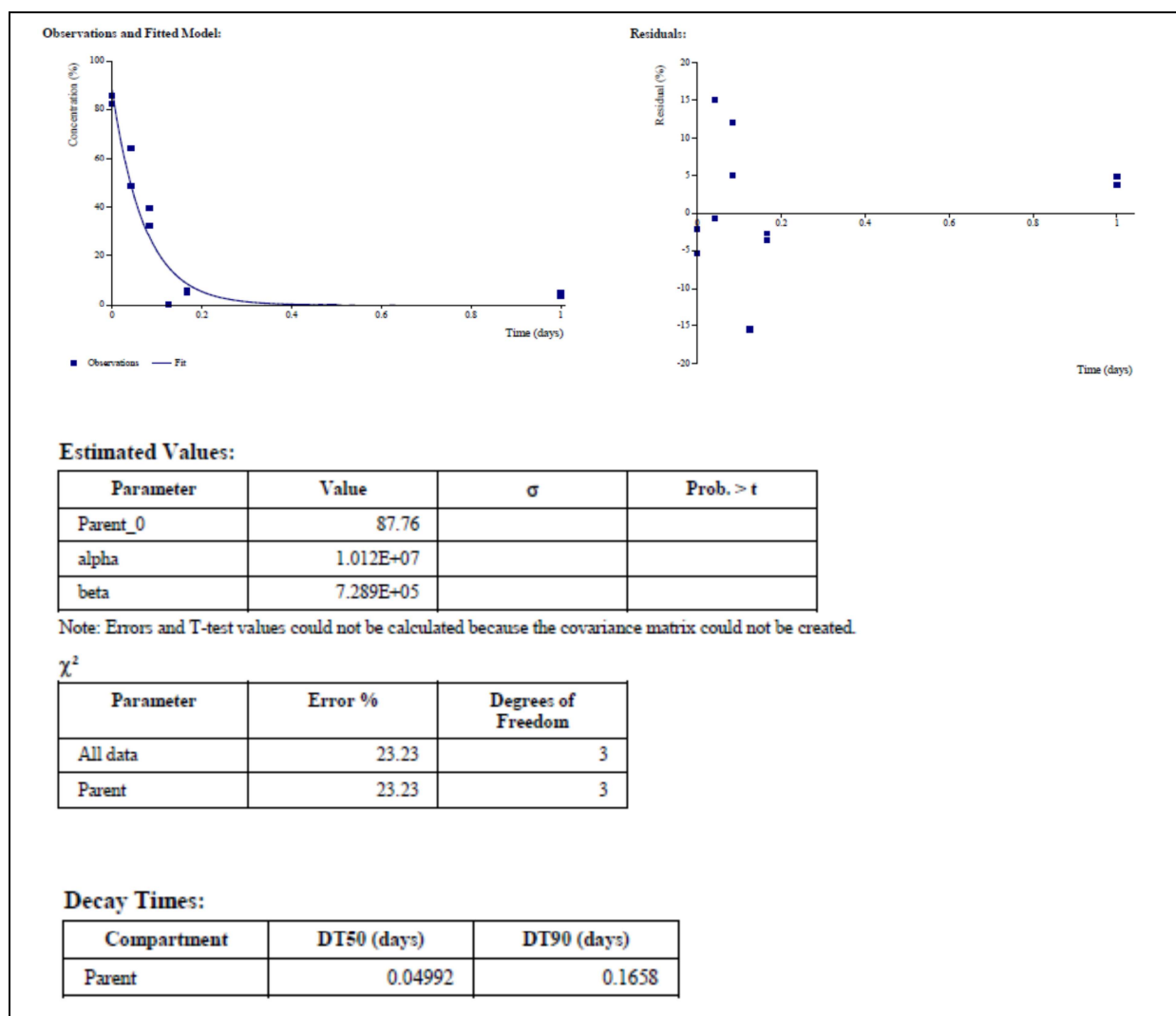


Table 8-61: Calculated half-lives for Ethofumesate metabolite NC8493

| Soil | Model | DT ₅₀ [days] | DT ₉₀ [days] | Chi-Squared (χ^2) |
|----------------------|-------|----------------------------|----------------------------|--------------------------|
| Fislis (silt loam) | SFO | 0.05 | 0.18 | 27.7 |
| Horn (loam) | SFO | 0.07 | 0.24 | 10.5 |
| Sevelen (sandy loam) | SFO | 0.05 | 0.17 | 21.1 |

III. CONCLUSIONS

The aerobic degradation of NC8493 in soil was assessed in three representative European soils (Fislis, Horn and Sevelen) at $20 \pm 2^\circ\text{C}$ in dark. The NC8493 was applied at rate of 0.5 mg/kg, corresponding to an application rate of 500 g/ha.

Concentrations of NC8493 declined very rapidly and the calculated DT₅₀ values ranged from 1.2 to 1.7 hours (SFO).

Comments RMS

The aerobic rate of degradation of NC8493 was studied in three soils under aerobic conditions in the dark at $20 \pm 2^\circ\text{C}$ and a moisture level of pF2.5. The metabolite of Ethofumesate NC8493 was applied at rate of 0.5 mg/kg, corresponding to an expected field concentration of 500 g/ha. In all tested soils, microbial biomass is low at study end (consistently < 1% TOC). At study beginning, microbial biomass is <1% OC in 2 of 3 soils (Fislis and Sevelen). Since the test substance was dissolved in methanol, negative effects on microbial biomass could have occurred. This is reflected by comparison with the results of the parent degradation study (McLaughlin, 2012), where the same soils have been tested (Fislis, Sevelen, Horn). Microbial biomass was twice as high whereas the OC was approximately the same. Nevertheless, the impact on DT50 might be negligible, since the compound degrades very rapidly.

The study is acceptable.

Degradation parameters were checked and confirmed by the RMS

The regulatory endpoints are:

| Soil | Model | DT ₅₀ [days] | DT ₉₀ [days] | Chi-Squared (χ^2) |
|----------------------|-------|----------------------------|----------------------------|--------------------------|
| Fislis (silt loam) | SFO | 0.05 | 0.18 | 27.7 |
| Horn (loam) | SFO | 0.07 | 0.24 | 10.5 |
| Sevelen (sandy loam) | SFO | 0.05 | 0.17 | 21.1 |

| | |
|---------------------|--|
| Reference: | AE C508493 (ethofumesate-2-hydroxy): Aerobic degradation in four European soils |
| Notifier: | Taskforce |
| Author(s), year: | Traub, M.; 2011 |
| Report/Doc. number: | S11-00957 / M-431094-01 |
| Guideline(s): | OECD Guideline 307 |
| GLP: | Yes |
| Deviations: | |
| Validity: | Valid |
| Status: | New study. |

MATERIALS AND METHODS

Materials :

Test Material :

Report name : AE C508493 (=NC 8493)

Certificate No. : AZ 14277

Chem. Purity : 98.8%

Soils :

Table 8-62: Soil characteristics

| Parameter | Results | | | |
|---|--|---|--|---|
| Soil Designation | Laacher Hof AXXA (AX) | Höfchen am Hohenseh 4a (HH) | Dollendorf II (DD) | Wurmwiese (WW) |
| Geographic Location (City / State / Country) | Bayer Field Station "Laacher Hof" Field Plot: "AXXA" D-40789 Monheim am Rhein / Germany | Bayer Field Research Station "Höfchen" Field Plot "Am Hohenseh 4a" D-51399 Burscheid / Germany | Field Plot: "Dollendorf II" D-53945 Blankenheim / Germany | Bayer Field Station "Laacher Hof" Field Plot: "Wurmwie se" D-40789 Monheim am Rhein / Germany |
| Soil Taxonomic Classification (USDA) | Sandy, mixed, mesic typic Argudalfs | Loamy, mixed, mesic typic Argudalfs | N/A | Loamy, mixed, mesic typic Argudalfs |
| Texture Class | Sandy Loam | Silt Loam | Clay Loam | Sandy Loam |
| Sand | 75 % | 23 % | 27 % | 55 % |
| Silt | 16 % | 60 % | 42 % | 30 % |
| Clay | 9 % | 17 % | 31 % | 15 % |
| pH in 0.01 M CaCl ₂ (1/2) | 5.5 5.7 | 6.1 5.8 | 7.2 6.9 | 5.0 4.7 |
| pH in 1 N KCl (1/1) | 5.9 | 6.4 | 7.3 | 5.2 |
| pH in Soil/Water (1/1) | 6.0 | 6.4 | 7.3 | 5.3 |
| pH in Water (Saturated Paste) | | | | |

| Parameter | Results | | | |
|---|---|---|---|---|
| Organic Matter | 3.3 % | 3.1 % | 826 % | 3.6 % |
| Organic Carbon | 1.9 % | 1.8 % | 5.0 % | 2.1 % |
| Soil Microbial Biomass after arrival start end | 174.2 mg C/100g TS 402.9 mg C/100g TS 324.0 mg C/100g TS | 189.8 mg C/100g TS 389.5 mg C/100g TS 297.1 mg C/100g TS | 439.3 mg C/100g TS 331.2 mg C/100g TS 354.2 mg C/100g TS | 197.1 mg C/100g TS 371.3 mg C/100g TS 283.9 mg C/100g TS |
| Cation Exchange Capacity (CEC) | 9.8 meq/100 g | 11.8 meq/100g | 22.0 meq/100g | 11.0 meq/100g |
| Maximum Water Holding Capacity (MWHC) | 49.4 g H ₂ O <i>ad</i> 100 g DW | 55.9 g H ₂ O <i>ad</i> 100 g DW | 79.3 g H ₂ O <i>ad</i> 100 g DW | 61.9 g H ₂ O <i>ad</i> 100 g DW |

Methods :

Study design

The glass flasks (300 mL) contained about 100 g soil (dry weight basis). Each flask was closed by cotton wool. The samples were incubated at 20 ± 2 °C under aerobic conditions in the dark.

Experimental Conditions

The soil moisture content was adjusted 55% of the maximum water holding capacity. The incubation was performed at 20 °C in the dark.

Sampling

Soil extracts were analyzed after incubation for 0, 0.5, 1, 3, 6 and 24 hours.

Analytical Procedures :

The study was performed with non-labeled NC 8493. Duplicate test systems were taken per sampling interval. The entire soil per flask was processed three times at ambient temperature and once under hot conditions by microwave extraction. The combined extracts were analyzed for NC 8493 residues by reversed phase high performance liquid chromatography/mass spectrometry (HPLC-MS/MS) in multiple reaction monitoring (MRM) mode using NC 8493 standards in pure solvent for calibration curve.

RESULT AND DISCUSSION

The analytical results were analyzed according to Focus Guidelines by three kinetic models (single first order, double first order, first order multi compartment) using single values.

Figure 8-30: Kinetic evaluation soil AX (SFO)

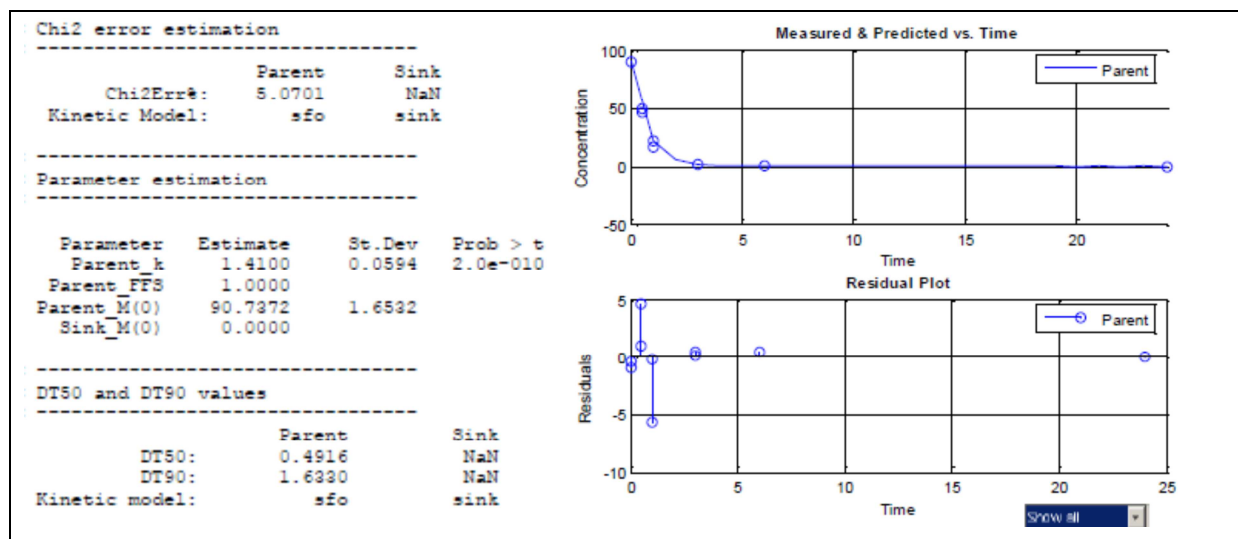


Figure 8-31: Kinetic evaluation soil AX (DFOP)

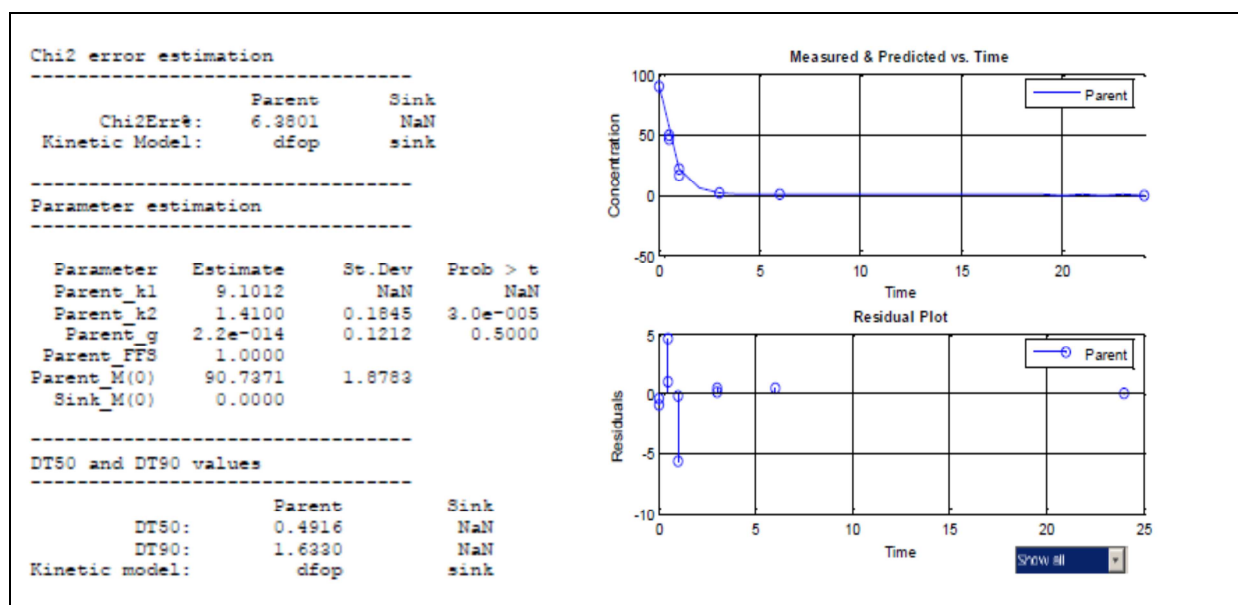


Figure 8-32: Kinetic evaluation soil AX (FOMC)

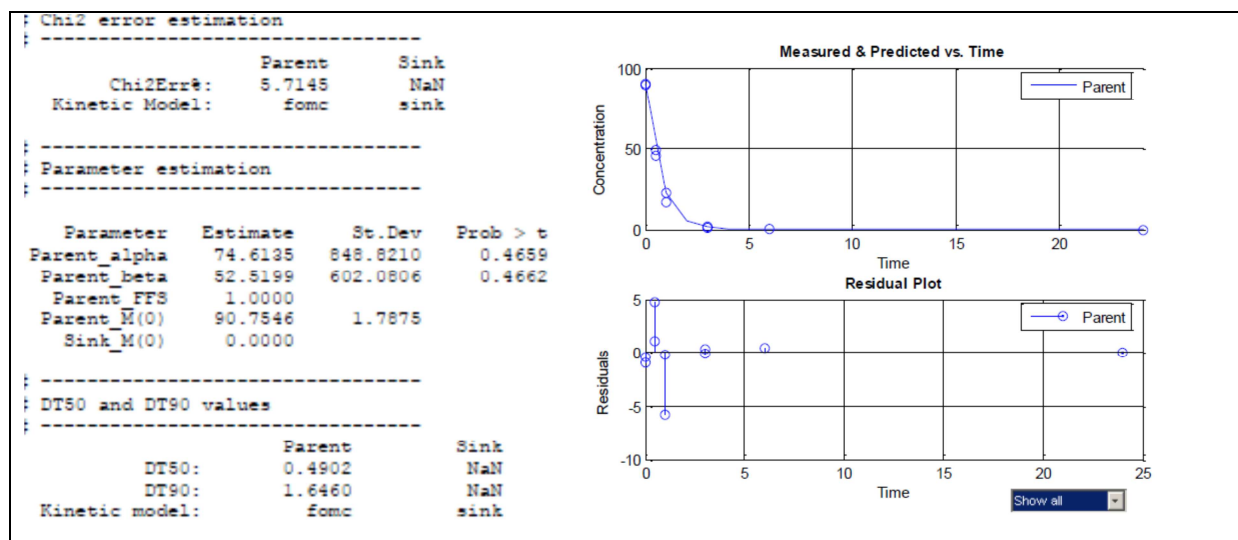


Figure 8-33: Kinetic evaluation soil HH (SFO)

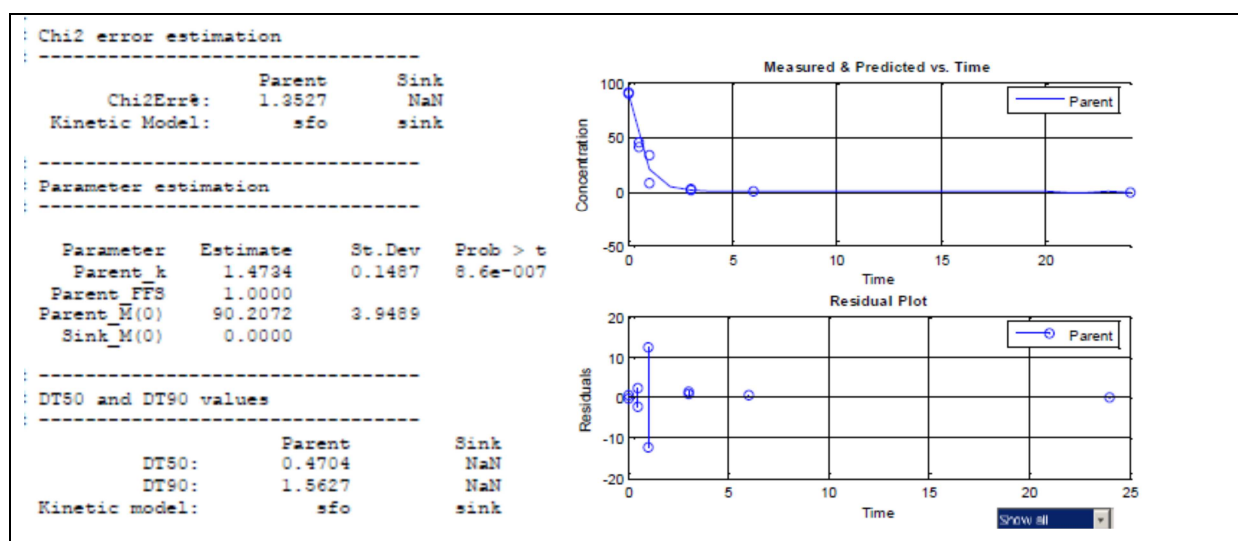


Figure 8-34: Kinetic evaluation soil HH (DFOP)

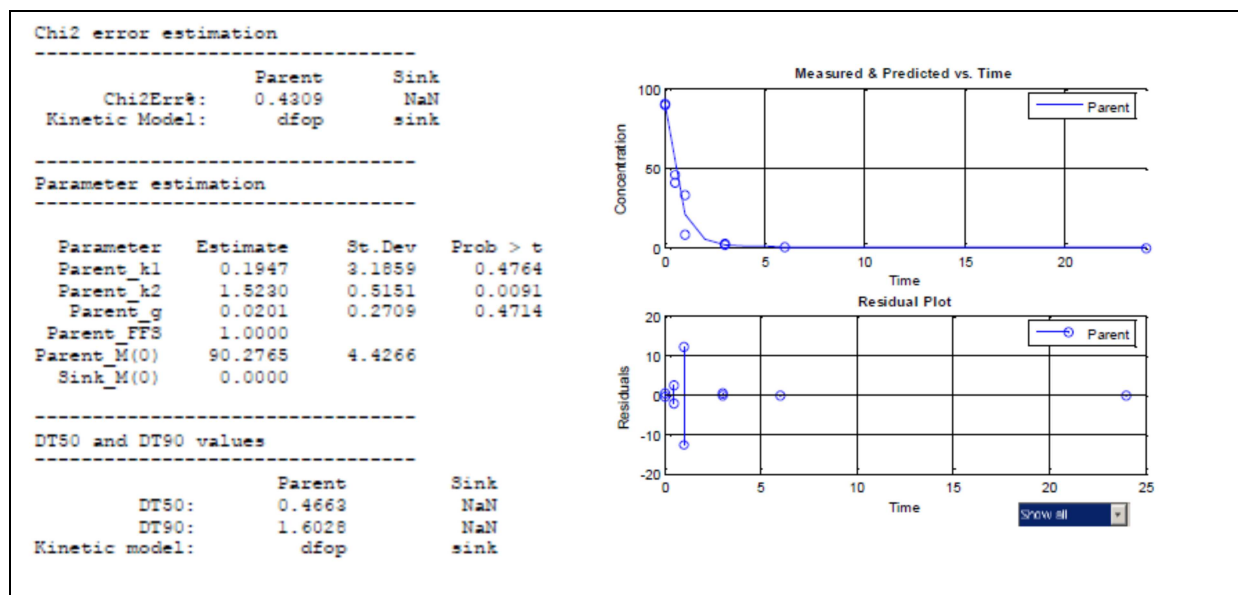


Figure 8-35: Kinetic evaluation soil HH (FOMC)

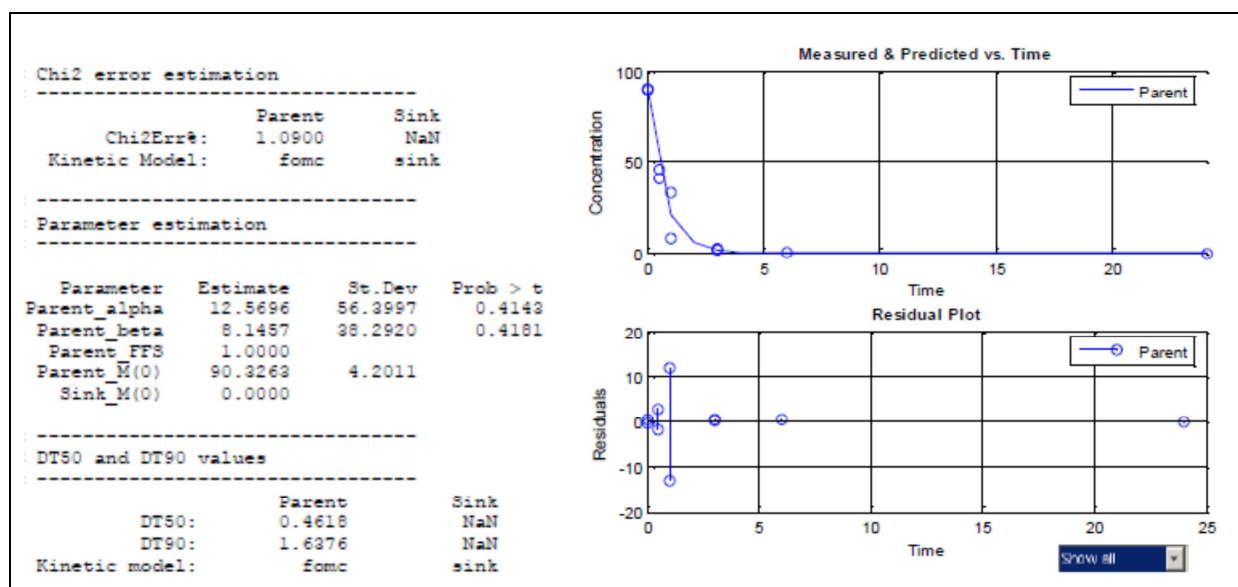


Figure 8-36: Kinetic evaluation soil DD (SFO)

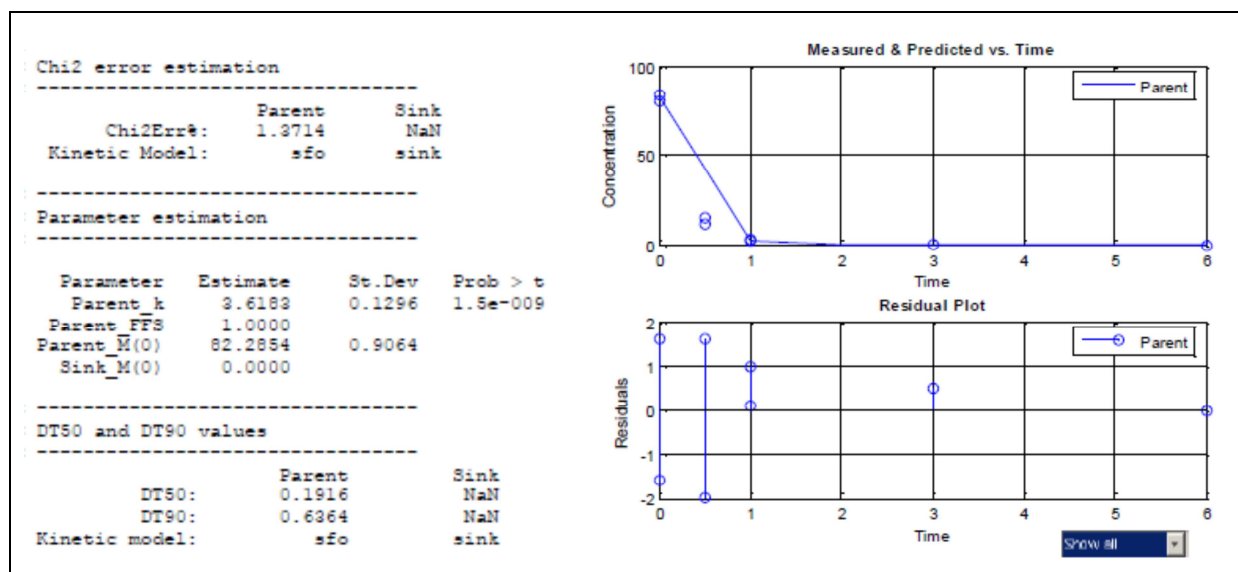


Figure 8-37: Kinetic evaluation soil DD (DFOP)

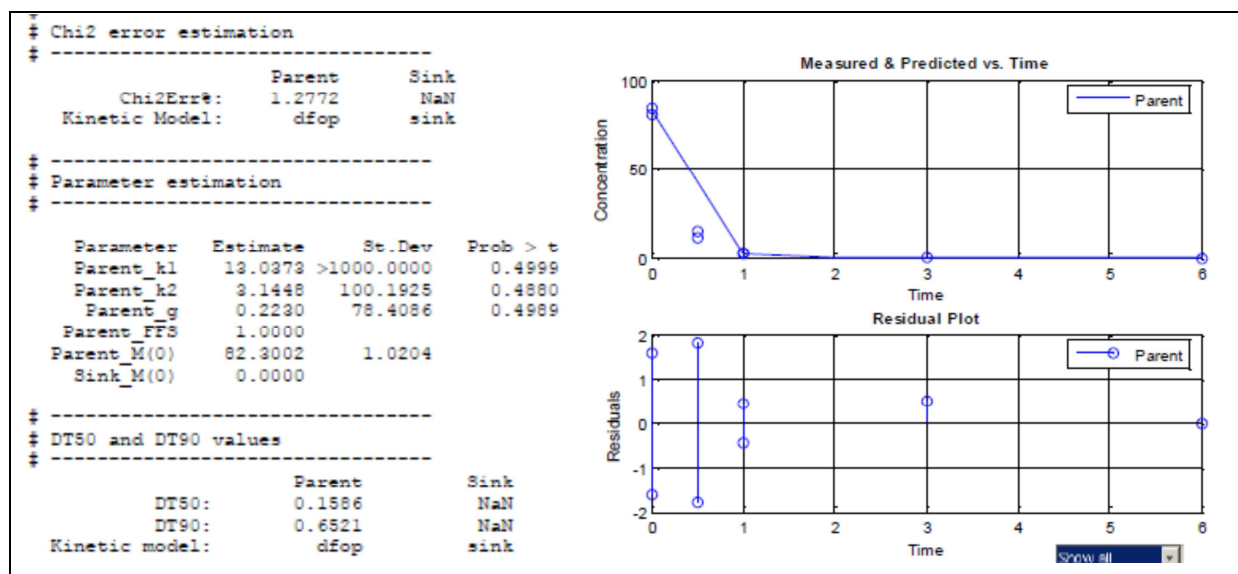


Figure 8-38: Kinetic evaluation soil DD (FOMC)

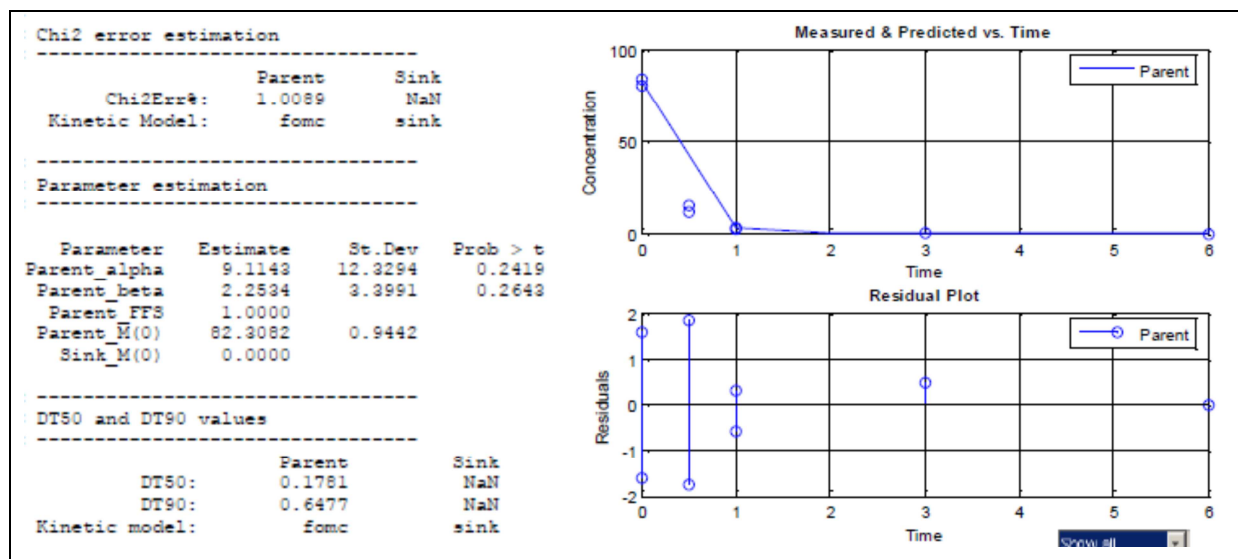


Figure 8-39: Kinetic evaluation soil WW (SFO)

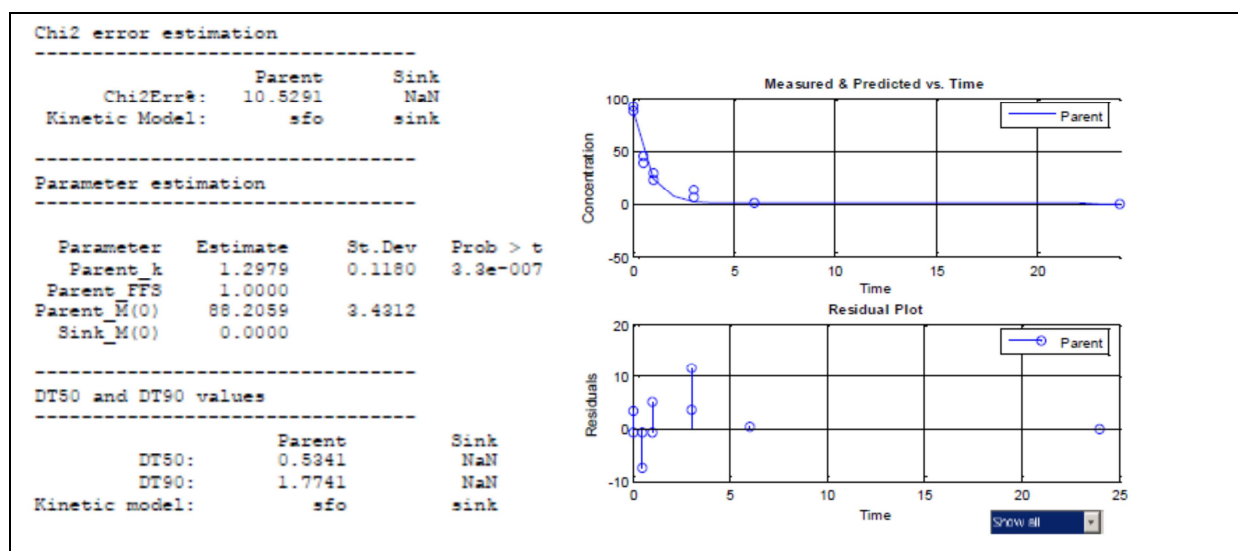


Figure 8-40: Kinetic evaluation soil DD (DFOP)

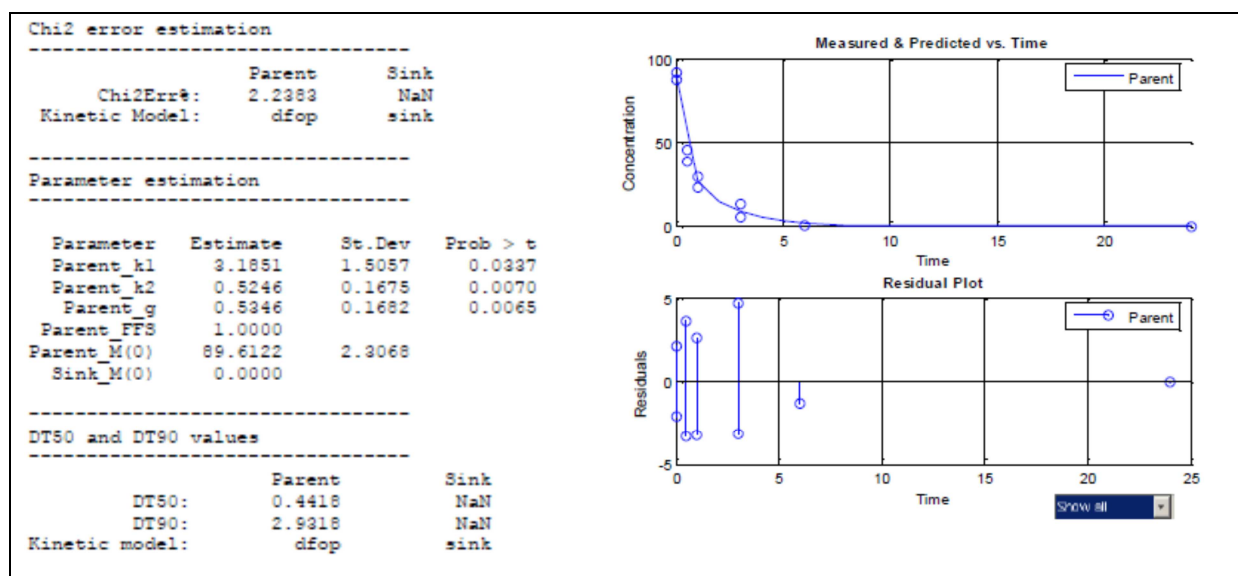


Figure 8-41: Kinetic evaluation soil DD (FOMC)

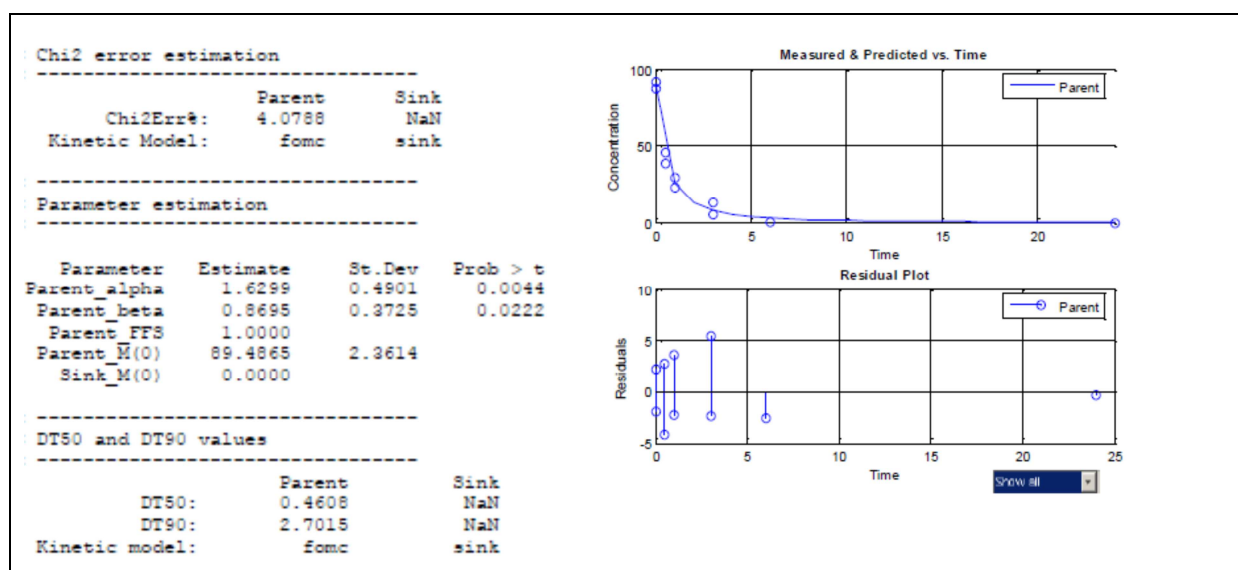


Table 8-63: Degradation of NC 8493 (AE C508493) in soil

| Soil (Soil type) | Best Fit Kinetic Model | DT ₅₀ [hours] | DT ₉₀ [hours] | Chi ² Error [%] | Visual Assessment * |
|---------------------|---------------------------|-----------------------------|-----------------------------|-------------------------------|------------------------|
| Soil 1 (AX) | SFO | 0.5 | 1.6 | 5.07 | + |
| Soil 2 (HH) | DFOP | 0.5 | 1.6 | 0.43 | + |
| Soil 3 (DD) | DFOP | 0.2 | 0.7 | 0.16 | o |
| Soil 4 (WW) | DFOP | 0.4 | 2.9 | 2.24 | + |

Geometric mean: DT₅₀: 0.4 hours (0.016 days)

* Visual Assessment: + = good, o = medium, - = poor

Conclusion:

In conclusion, NC 8493 was found to rapidly degrade in soils under aerobic laboratory conditions, with typical half-lives \ll 1 day for all soils. Therefore, the compound is regarded as transient metabolite and is unlikely to accumulate in a soil environment.

Comments RMS

The degradation of non-labeled NC 8493 was investigated in four soils under aerobic conditions at 20°C in the dark over a period of 24 hours. For the test systems 100 g soil (dry weight basis) were used. The average soil moisture content was 55% of the maximum water holding capacity over the entire period of the study. The biological activity was checked directly after treatment and seven days after application. The application rate of NC 8493 was 21.8 µg per vessel and 100 g air dried soil, which was equivalent to 0.218 mg NC 8493/kg soil (dry weight). The combined ambient temperature and microwave extracts were analyzed by reversed phase high performance liquid chromatography/mass spectrometry (HPLC-MS/MS) in multiple reaction monitoring (MRM) mode using NC 8493 standards in pure solvent for calibration curve. The details on the validation method are not available.

For kinetic evaluation, concentrations below LOD were set to zero, nevertheless the impact is marginal.

The RMS does not agree with DFOP being the best fit for soils HH and DD. For soil DD, all three fitted parameters (k_1 , k_2 , g), for the soil HH two fitted parameters (k_1 , g) exceed the trigger for the t-test ($p < 0.05$) defined in FOCUS, 2006.

The endpoints are:

| Soil | Kinetic Model | DT ₅₀ [d] | DT ₉₀ [d] | Chi ² Error [%] | Visual Assessment * |
|------|---------------|-------------------------|-------------------------|-------------------------------|------------------------|
| AX | SFO | 0.02 | 0.07 | 5.1 | + |
| HH | SFO | 0.02 | 0.07 | 1.4 | + |
| DD | SFO | 0.01 | 0.03 | 1.4 | o |
| WW | DFOP | 0.02 | 0.06 | 2.2 | + |

* Visual Assessment: + = good, o = medium, - = poor

| | |
|---------------------|---|
| Reference: | AE C509607: Aerobic degradation in four European soils |
| Notifier: | Taskforce |
| Author(s), year: | Traub, M.; (2012) |
| Report/Doc. number: | S11-00958 / M-431784-01 |
| Guideline(s): | OECD Test Guideline No. 307 |
| GLP: | yes |
| Deviations: | |
| Validity: | Valid |
| Status: | New study |
| Justification: | The degradation rate of the soil metabolite was investigated in order to assess the leaching behavior of the metabolite NC 20645. |

MATERIALS AND METHODS

Materials :

Test Material :

Report name : AE C509607 (= NC 9607)

Certificate No. : AZ 14966

Chem. Purity : 99.8%

Soils :

Table 8-64: Soil characteristics

| Parameter | Results | | | |
|---|---|---|---|--|
| Soil Designation | Laacher Hof AXXA (AX) | Höfchen am Hohenseh 4a (HH) | Dollendorf II (DD) | Wurmwiese (WW) |
| Geographic Location (City / State / Country) | Bayer Field Station “Laacher Hof“ Field Plot:“AXXA“ D-40789 Monheim am Rhein / Germany | Bayer Field Research Station “Höfchen” Field Plot “Am Hohenseh 4a” D-51399 Burscheid / Germany | Field Plot:”Dollendorf II” D-53945 Blankenheim / Germany | Bayer Field Station “Laacher Hof” Field Plot:”Wurmwie se” D-40789 Monheim am Rhein / Germany |
| Soil Taxonomic Classification (USDA) | Sandy, mixed, mesic typic Argudalfs | Loamy, mixed, mesic typic Argudalfs | N/A | Loamy, mixed, mesic typic Argudalfs |
| Texture Class | Sandy Loam | Silt Loam | Clay Loam | Loam |
| Sand | 73 % | 17 % | 25 % | 49 % |
| Silt | 20 % | 66 % | 42 % | 34 % |
| Clay | 7 % | 17 % | 33 % | 17 % |

| Parameter | Results | | | |
|---------------------------------------|--|--|--|--|
| pH in 0.01 M CaCl ₂ (1/2) | 6.0 | 6.2 | 7.3 | 5.3 |
| pH in 1 N KCl (1/1) | 5.8 | 5.9 | 7.1 | 5.0 |
| pH in Soil/Water (1/1) | 6.2 | 6.5 | 7.4 | 5.5 |
| pH in Water (Saturated Paste) | 6.3 | 6.6 | 7.4 | 5.6 |
| Organic Matter | 3.4 % | 3.1 % | 9.1 % | 3.3 % |
| Organic Carbon | 2.0 % | 1.8 % | 5.3 % | 1.9 % |
| Soil Microbial Biomass after arrival | 220.1 mg C/100g TS | 275.0 mg C/100g TS | 489.2 mg C/100g TS | 275.2 mg C/100g TS |
| start | 294.8 mg C/100g TS | 333.2 mg C/100g TS | 536.5 mg C/100g TS | 324.2 mg C/100g TS |
| end | n.a. | n.a. | n.a. | n.a. |
| Cation Exchange Capacity (CEC) | 9.5 meq/100 g | 11.4 meq/100g | 21.1 meq/100g | 10.5 meq/100g |
| Maximum Water Holding Capacity (MWHC) | 46.9 g H ₂ O <i>ad</i> 100 g DW | 52.4 g H ₂ O <i>ad</i> 100 g DW | 75.1 g H ₂ O <i>ad</i> 100 g DW | 54.4 g H ₂ O <i>ad</i> 100 g DW |

Methods :

Study design

The glass flasks (300 mL) contained about 100 g soil (dry weight basis). Each flask was closed by cotton wool. The samples were incubated at 20 ± 2 °C under aerobic conditions in the dark.

Experimental Conditions

The soil moisture content was adjusted 55% of the maximum water holding capacity. The incubation was performed at 20 °C in the dark.

Sampling

Soil extracts were analyzed after incubation for 0, 0.5, 1, 3, hours after treatment. For soil 4 (WW) an additional sampling after 1d was performed

Analytical Procedures :

The study was performed with non-labeled NC 9607. Duplicate test systems were taken per sampling interval. The entire soil per flask was processed three times at ambient temperature and once under hot conditions by microwave extraction. The combined extracts were analyzed for NC 9607 residues by reversed phase high performance liquid chromatography/mass spectrometry (HPLC-MS/MS) in multiple reaction monitoring (MRM) mode using NC 9607 standards in pure solvent for calibration curve.

RESULT AND DISCUSSION

The analytical results were analyzed according to Focus Guidelines by three kinetic models (single first order, double first order, first order multi compartment) using single values.

Figure 8-42: Kinetic evaluation soil AX (SFO)

```

Chi2 error estimation
-----
Number of data sets :      parent      All
Number of parameters :      2          2
Degrees of Freedom :      2          2
RMSE :                   parent      All
Chi2Sigma :              4.632      4.632
Chi2Err% :               14.36     14.36
-----
Parameter estimation
-----
Degrees of Freedom : 6
Parameter      Estimate      Lower CI      Upper CI      St.Dev      Prob > t
M(0) parent :   95.8158      87.5493      104.082      4.2177      2.38e-07
k parent :      3.4549       2.3546       4.555       0.5614      0.000422
-----
DT50 and DT90 values
-----
DT50 :          parent
DT90 :          0.2006
          0.6665
Kinetic model :   SFO

```

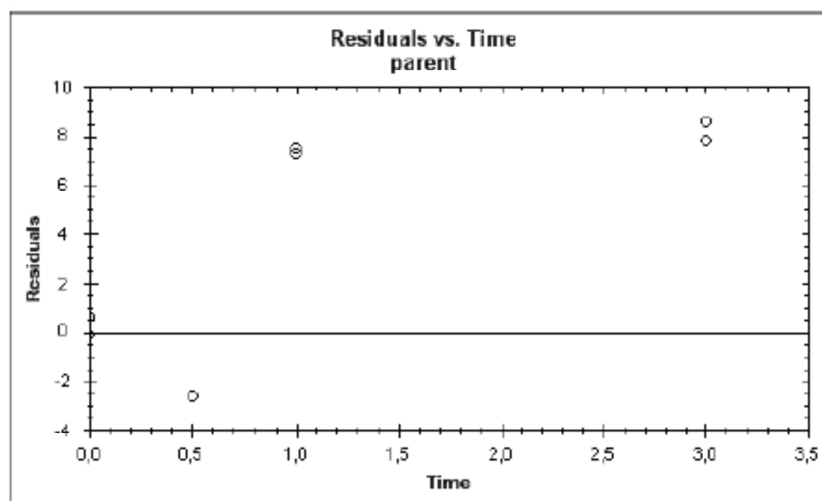
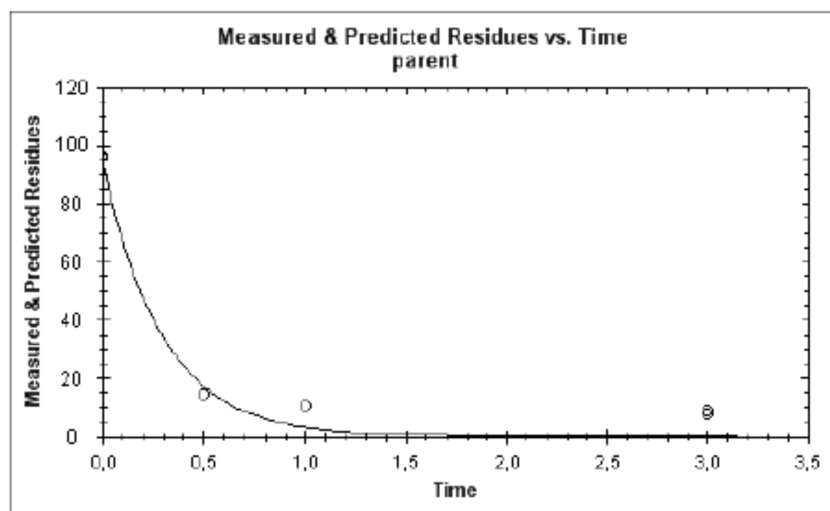


Figure 8-43: Kinetic evaluation soil AX (DFOP)

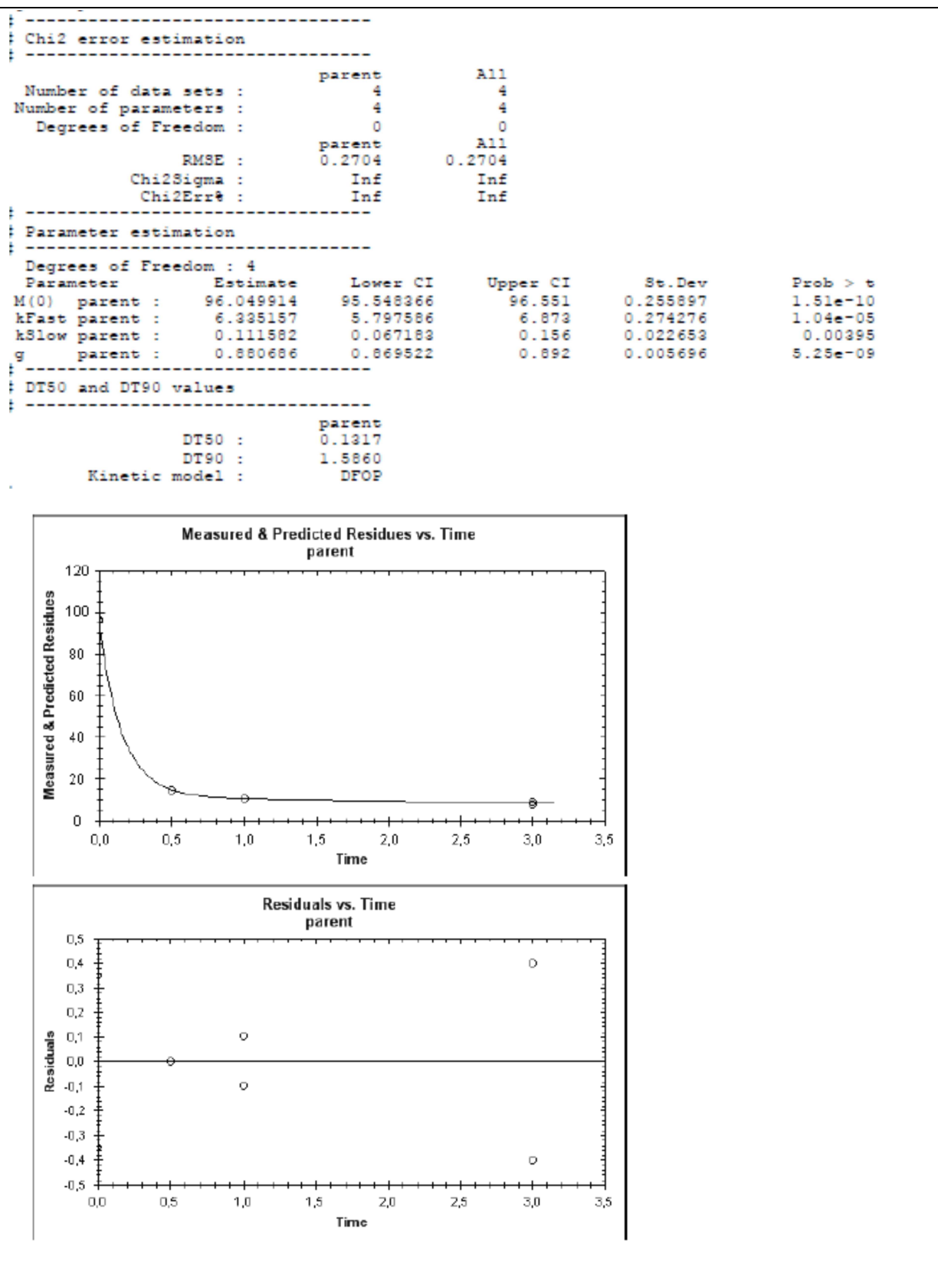


Figure 8-44: Kinetic evaluation soil AX (FOMC)

```

Chi2 error estimation
-----
Number of data sets :      parent      All
Number of parameters :      3          3
Degrees of Freedom :      1          1

RMSE :      parent      All
Chi2Sigma : 0.5476      0.5476
Chi2Err% :   1.506      1.506
-----

Parameter estimation
-----
Degrees of Freedom : 5
Parameter      Estimate      Lower CI      Upper CI      St.Dev      Prob > t
f(0) parent :   96.0474988    95.1807657    96.914      0.4422189    1.96e-11
alpha parent :    0.3289378     0.2457238     0.412      0.0424569    0.000286
beta parent :    0.0014438    -0.0009272     0.004      0.0012097    0.143111
-----

DT50 and DT90 values
-----
DT50 :      parent
DT90 :      0.0104
Kinetic model : FOMC

```

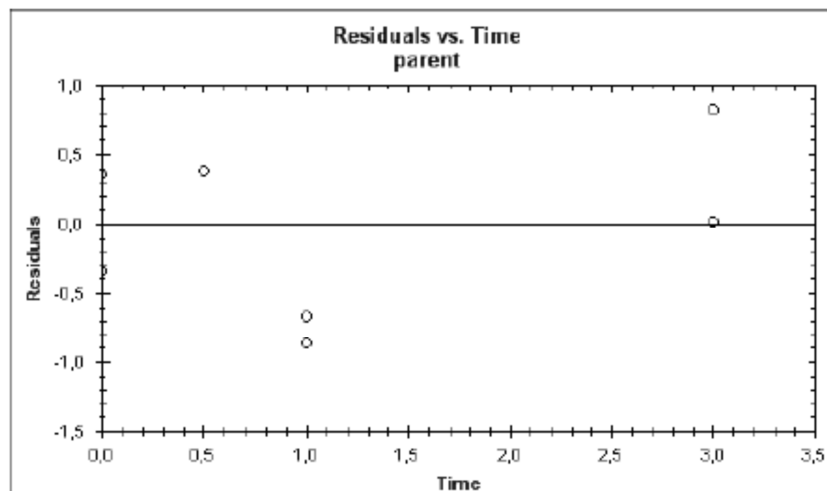
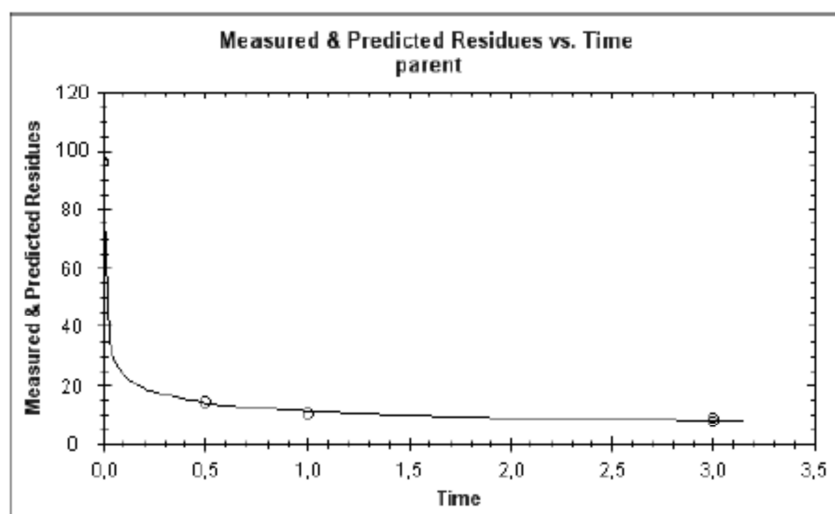


Figure 8-45: Kinetic evaluation soil HH (SFO)

```

-----
Chi2 error estimation
-----
Number of data sets :      parent      All
Number of parameters :      2          2
Degrees of Freedom :      2          2
      RMSE :      parent      All
      Chi2Sigma :      2.281    2.281
      Chi2Err% :      9.345    9.345
-----
Parameter estimation
-----
Degrees of Freedom : 6
Parameter      Estimate      Lower CI      Upper CI      St.Dev      Prob > t
M(0) parent :      83.2729    78.3099      88.236      2.5322      2.63e-08
k parent :      5.0472      3.5098      6.585      0.7844      0.000333
-----
DT50 and DT90 values
-----
      DT50 :      parent
      DT90 :      0.1373
      DT90 :      0.4562
Kinetic model :      SFO

```

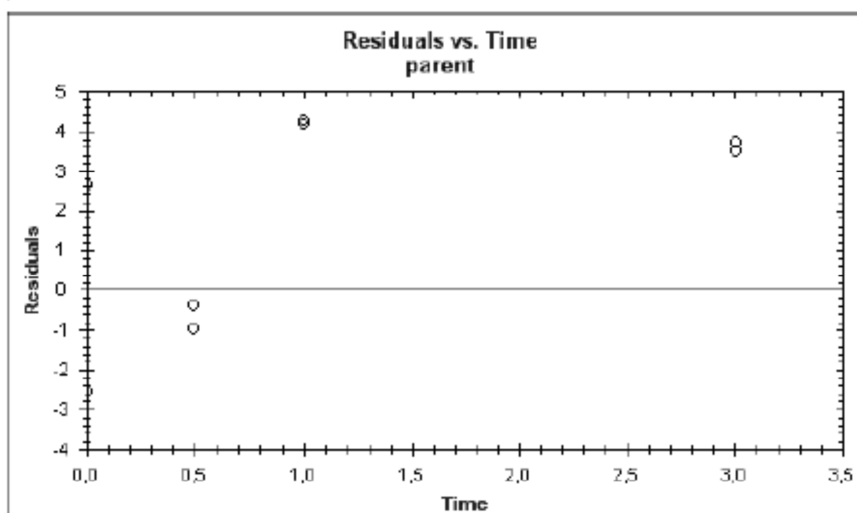
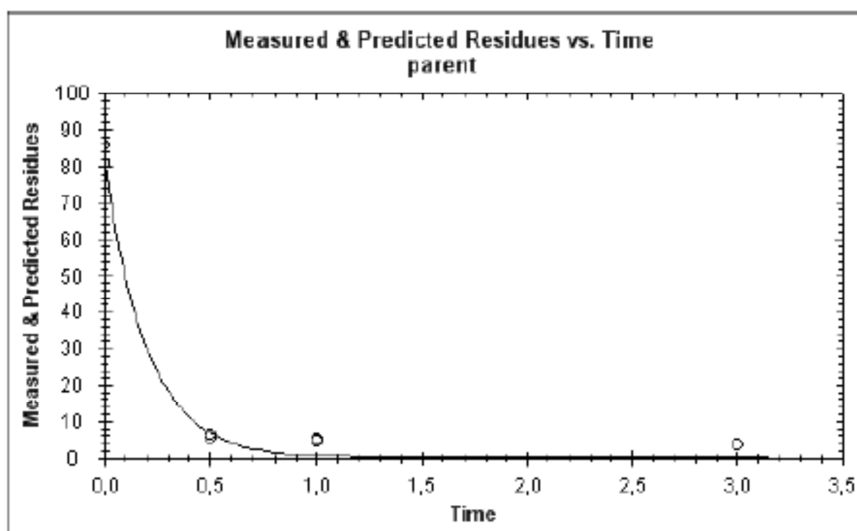


Figure 8-46: Kinetic evaluation soil HH (DFOP)

```

-----
Chi2 error estimation
-----
Number of data sets :      parent      All
                        4              4
Number of parameters :      4              4
Degrees of Freedom :      0              0
RMSE :      parent      All
           1.310      1.310
Chi2Sigma :      Inf      Inf
Chi2Err% :      Inf      Inf
-----
Parameter estimation
-----
Degrees of Freedom : 4
Parameter      Estimate      Lower CI      Upper CI      St.Dev      Prob > t
M(0) parent :    83.30000    80.87285    85.727    1.23837    1.46e-07
kFast parent :     8.86889    -0.40459    18.142    4.73146    0.0671
kSlow parent :     0.13748    -0.29784     0.573    0.22211    0.2847
g parent :        0.93472     0.87580     0.994    0.03007    3.19e-06
-----
DT50 and DT90 values
-----
DT50 :      parent
           0.0861
DT90 :      parent
           0.3615
Kinetic model :      DFOP

```

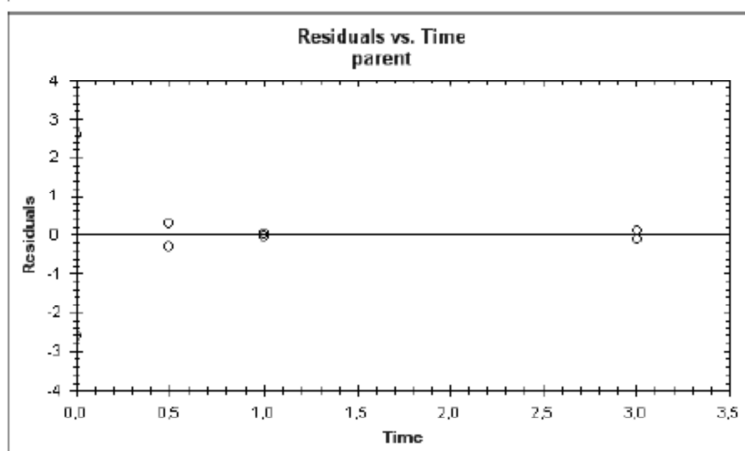
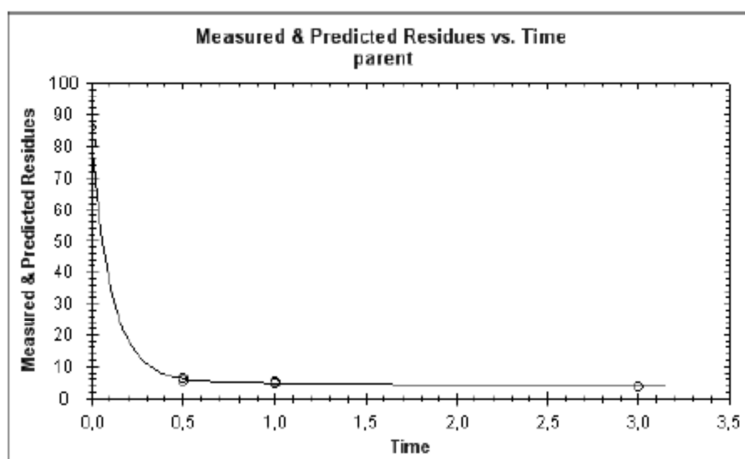


Figure 8-47: Kinetic evaluation soil HH (FOMC)

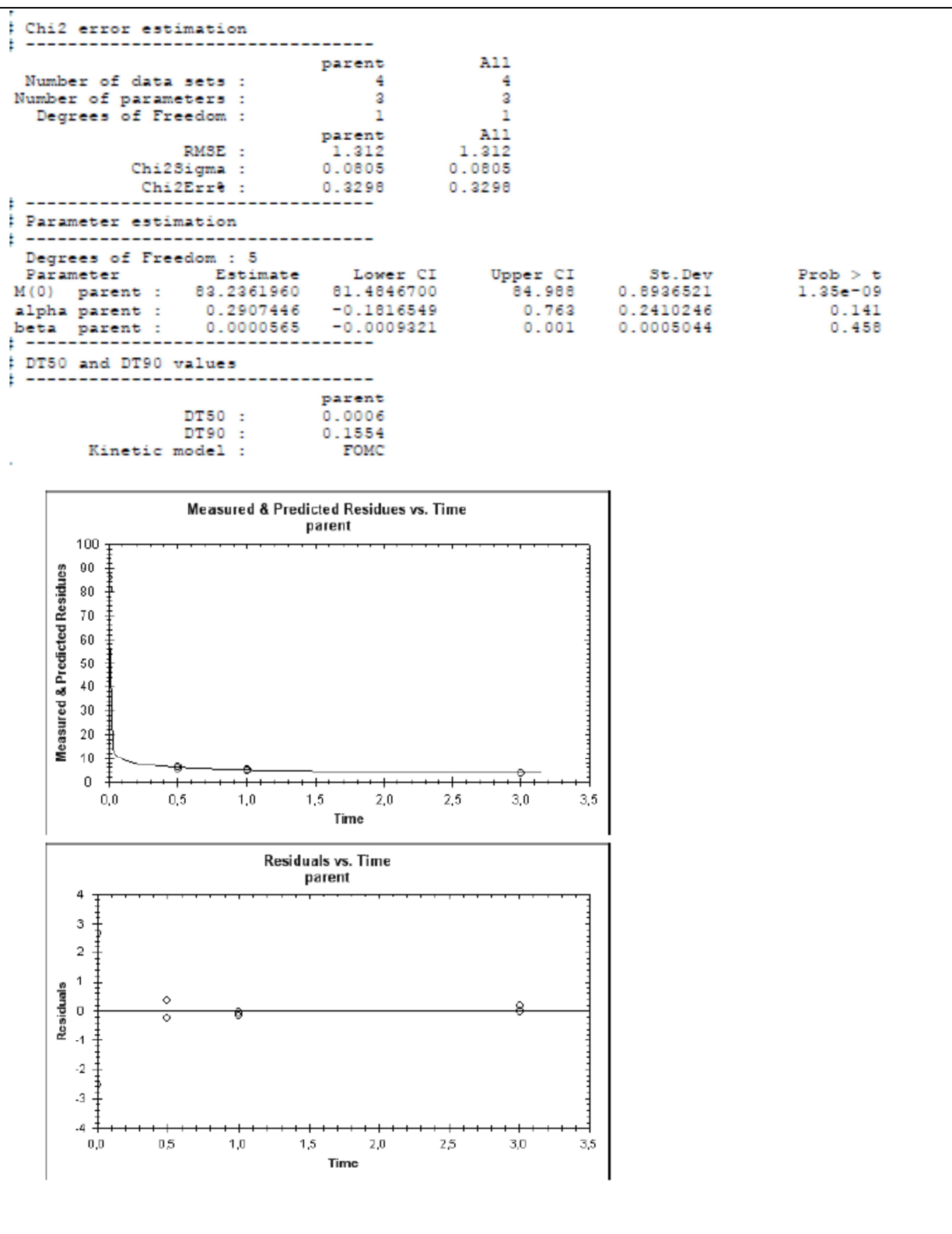


Figure 8-48: Kinetic evaluation soil DD (SFO)

```

Chi2 error estimation
-----
Number of data sets :      parent      All
                        :              4
Number of parameters :      2          2
Degrees of Freedom :      2          2

      RMSE :      parent      All
Chi2Sigma :      2.599      2.599
Chi2Err% :      9.107      9.107
-----

Parameter estimation
-----
Degrees of Freedom : 6
Parameter      Estimate      Lower CI      Upper CI      St.Dev      Prob > t
f(0) parent :      98.6308      93.4902      103.771      2.6228      1.18e-08
t parent :      5.3861      3.6648      7.107      0.8782      0.00043
-----

DT50 and DT90 values
-----
      DT50 :      parent
      DT90 :      0.4275
Kinetic model :      SFO

```

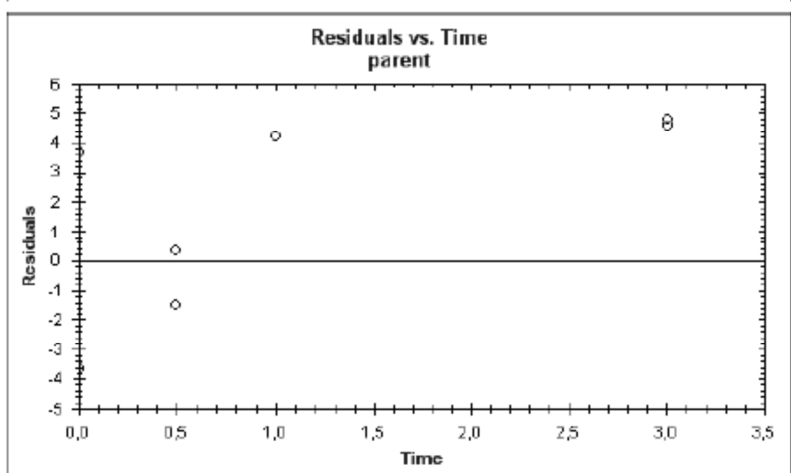
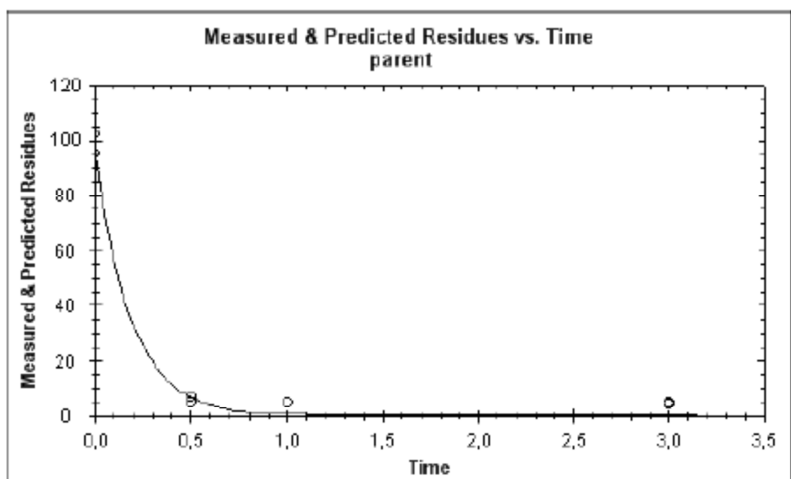


Figure 8-49: Kinetic evaluation soil DD (DFOP)

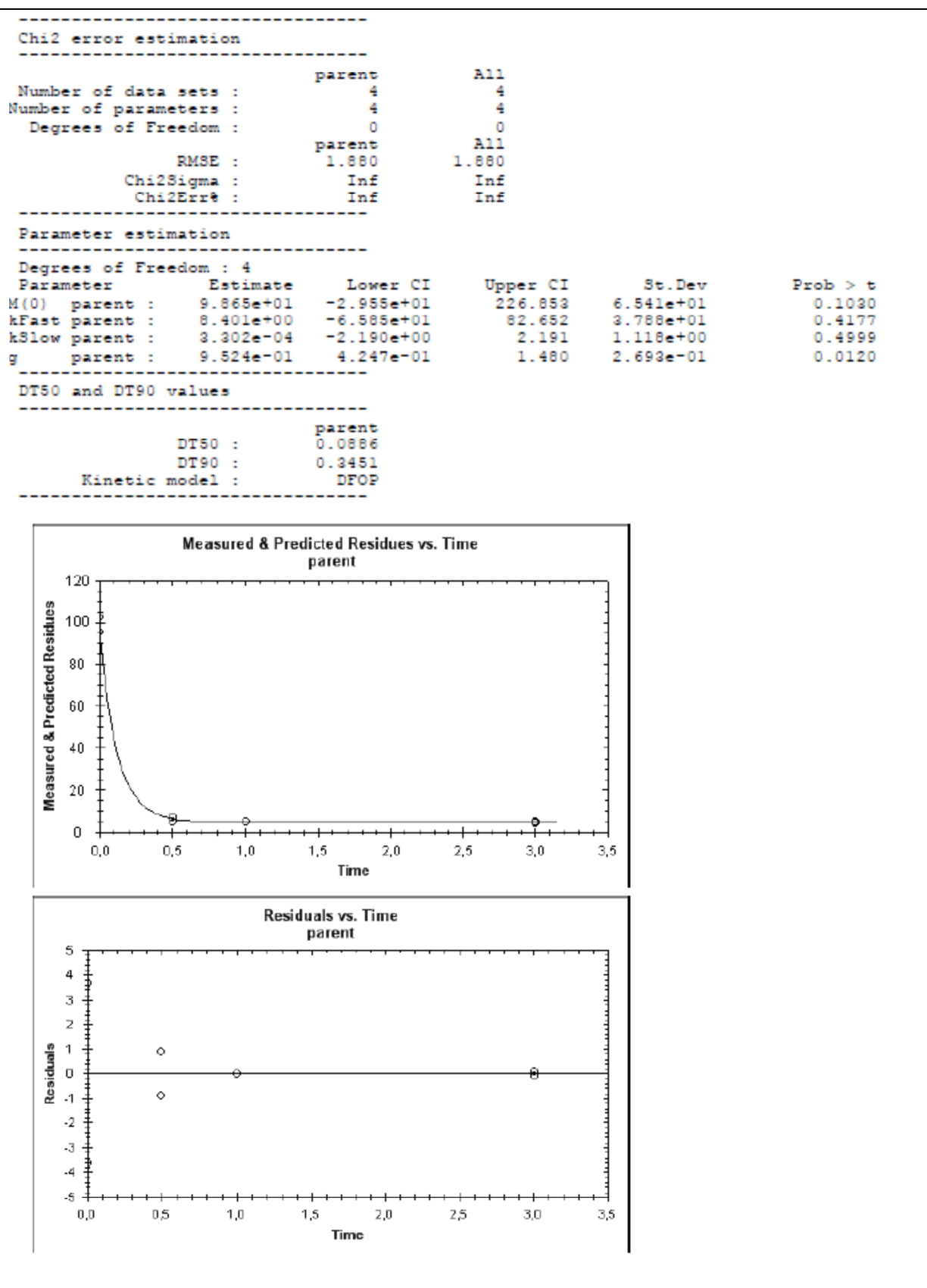


Figure 8-50: Kinetic evaluation soil DD (FOMC)

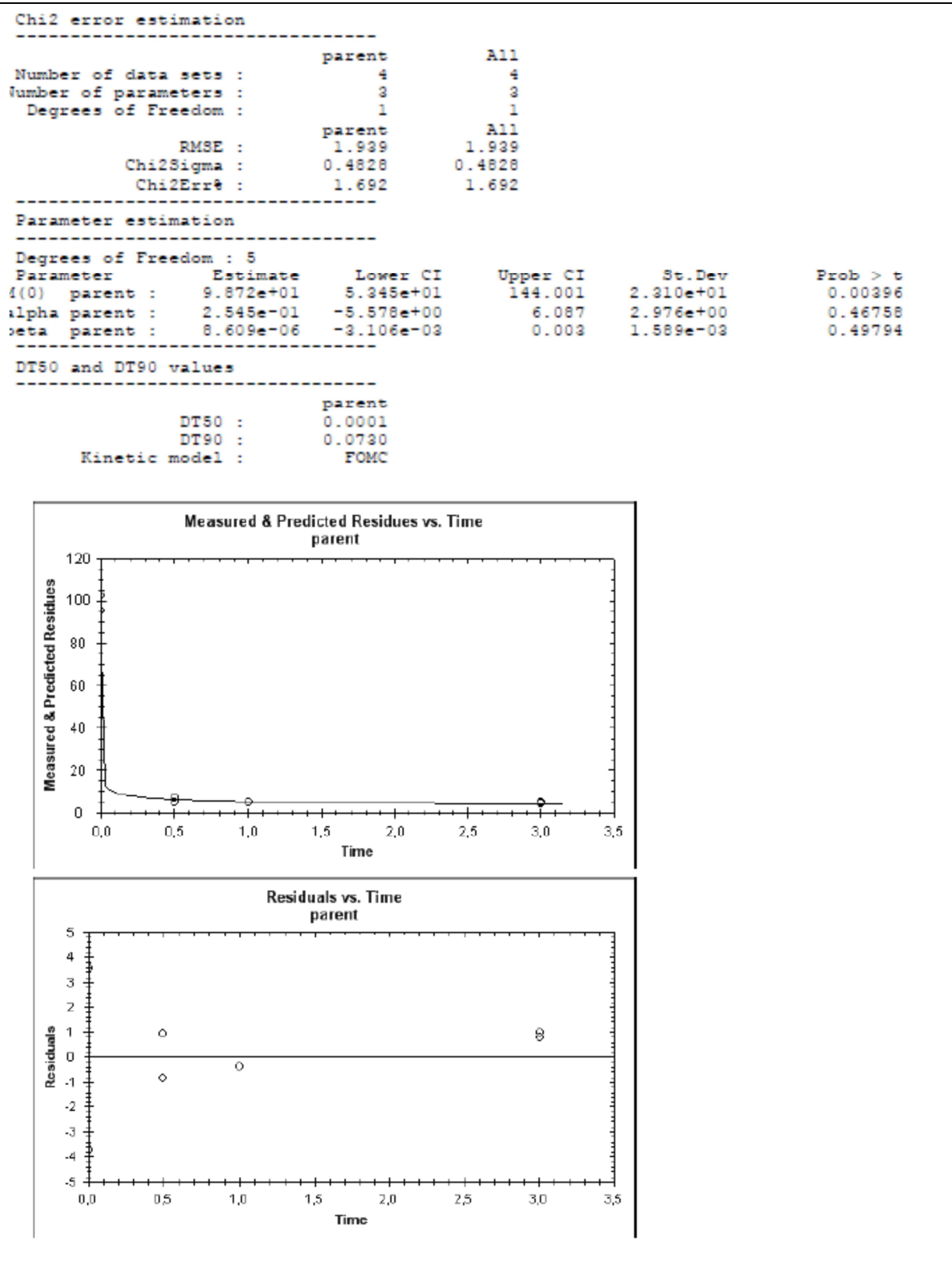


Figure 8-51: Kinetic evaluation soil WW (SFO)

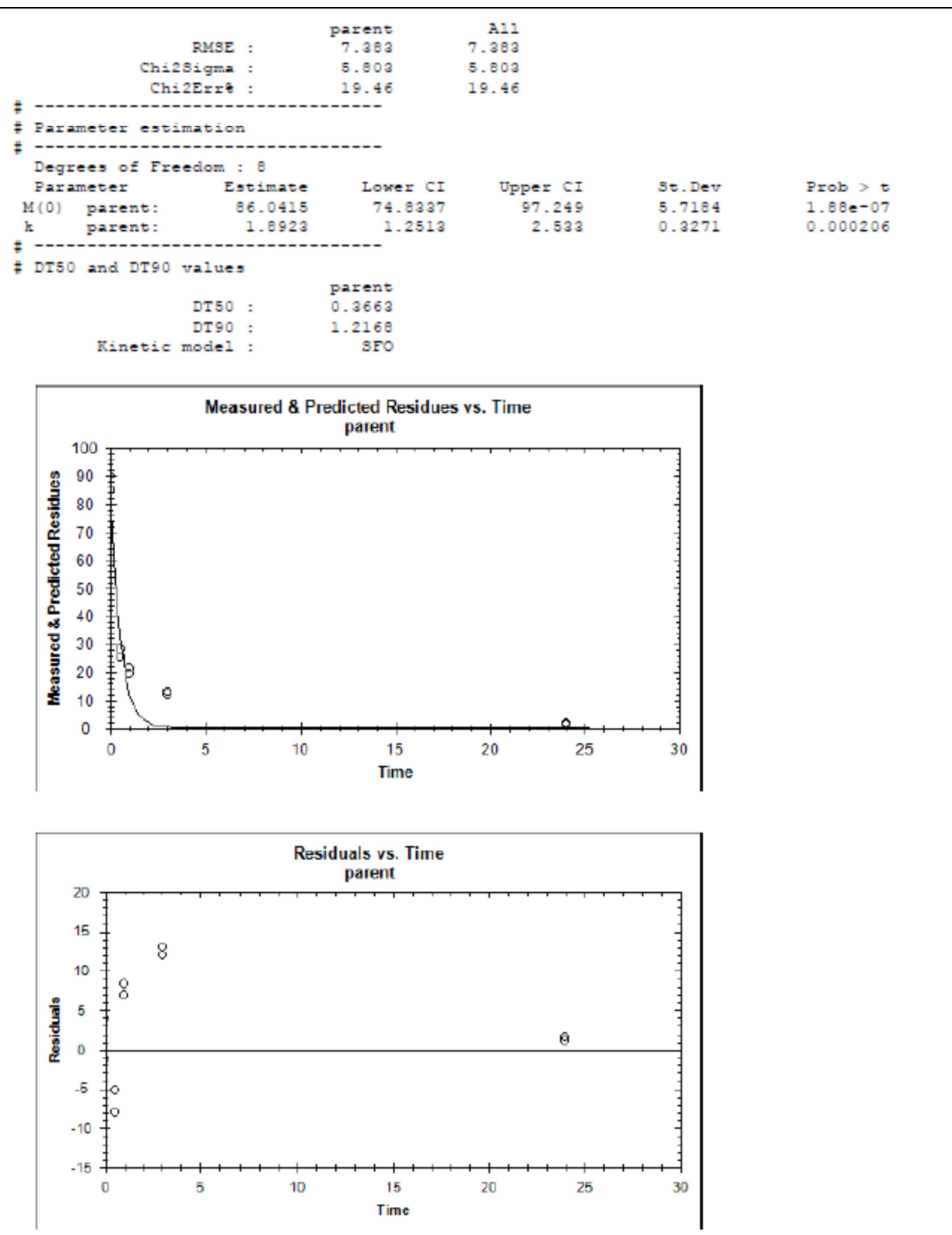


Figure 8-52: Kinetic evaluation soil WW (DFOP)

Chi2 error estimation

| | parent | All |
|------------------------|--------|--------|
| Number of data sets : | 5 | 5 |
| Number of parameters : | 4 | 4 |
| Degrees of Freedom : | 1 | 1 |
| RMSE : | 1.487 | 1.487 |
| Chi2Sigma : | 0.6508 | 0.6508 |
| Chi2Err% : | 2.182 | 2.182 |

Parameter estimation

Degrees of Freedom : 6

| Parameter | Estimate | Lower CI | Upper CI | St.Dev | Prob > t |
|--------------|----------|----------|----------|---------|----------|
| f(0) parent: | 87.39941 | 84.98060 | 89.818 | 1.23411 | 2.67e-10 |
| c1 parent: | 0.21598 | 0.06484 | 0.367 | 0.07711 | 0.015567 |
| c2 parent: | 5.28084 | 2.45777 | 8.104 | 1.44037 | 0.005250 |
| k parent: | 0.28569 | 0.19838 | 0.373 | 0.04454 | 0.000339 |

DT50 and DT90 values

| | parent |
|-----------------|--------|
| DT50 : | 0.2168 |
| DT90 : | 4.8603 |
| Kinetic model : | DFOP |

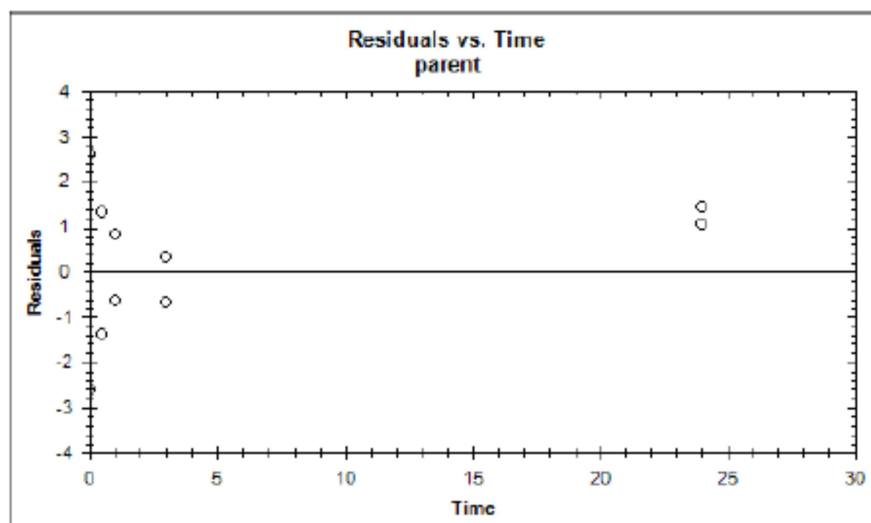
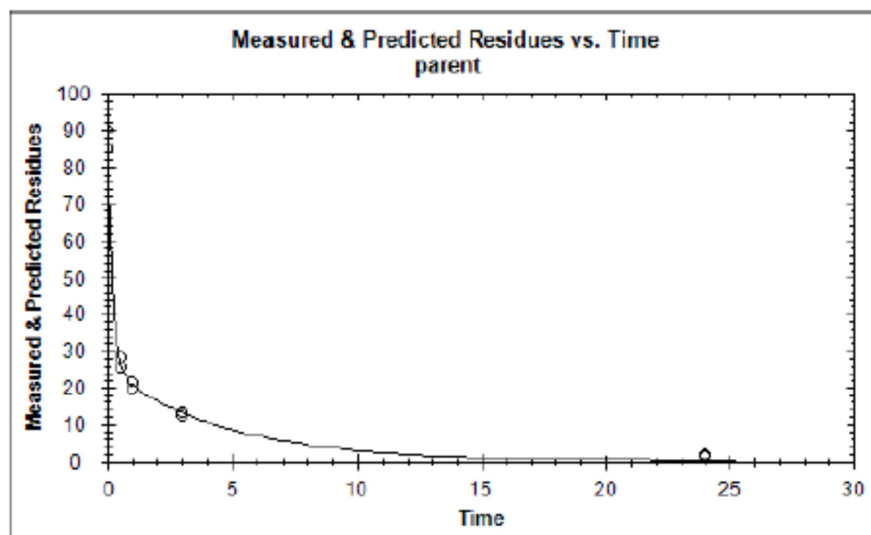


Figure 8-53: Kinetic evaluation soil WW (FOMC)

```

-----
Chi2 error estimation
-----
Number of data sets :      parent      All
                        5              5
Number of parameters :      3              3
Degrees of Freedom :      2              2
RMSE :                  parent      All
                        1.949      1.949
Chi2Sigma :              1.263      1.263
Chi2Err% :                4.236      4.236
-----
Parameter estimation
Degrees of Freedom : 7
Parameter      Estimate      Lower CI      Upper CI      St.Dev      Prob > t
M(0) parent:    87.383045      84.164444      90.602      1.642174      1.08e-10
alpha parent:    0.526107      0.373723      0.678      0.077748      0.000130
beta parent:     0.063482      0.009649      0.117      0.027466      0.027043
-----
DT50 and DT90 values
-----
                        parent
DT50 :              0.1736
DT90 :              4.9878
Kinetic model :      FOMC

```

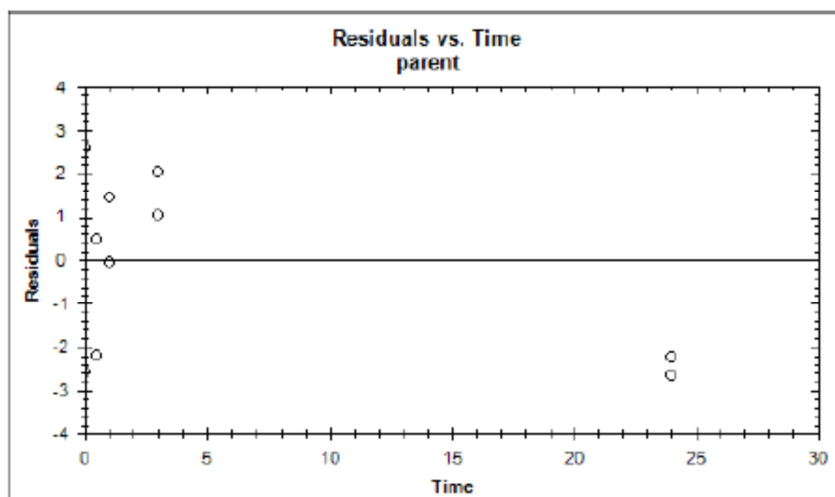
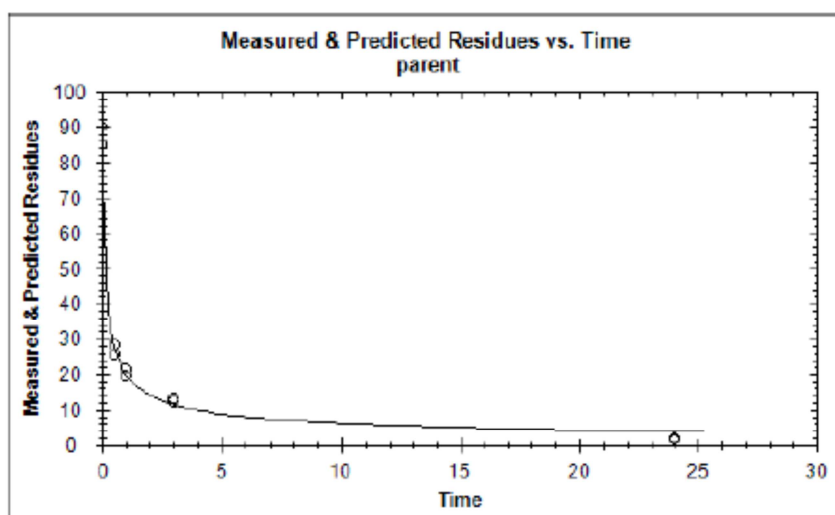


Table 8-65: Degradation of NC 9607 (AE C509607) in soil

| Soil (Soil type) | Best Fit Kinetic Model | DT ₅₀ [hours] | DT ₉₀ [hours] | Chi ² Error [%] | Visual Assessment * |
|---------------------|---------------------------|-----------------------------|-----------------------------|-------------------------------|------------------------|
| Soil 1 (AX) | FOMC | 0.01 | 1.6 | 1.51 | + |
| Soil 2 (HH) | FOMC | 0.6e-3 | 0.2 | 0.33 | + |
| Soil 3 (DD) | FOMC | 0.1e-3 | 0.07 | 1.69 | + |
| Soil 4 (WW) | DFOP | 0.2 | 4.9 | 2.18 | + |

* Visual Assessment: + = good, o = medium, - = poor

Conclusion:

In conclusion, NC 9607 was found to rapidly degrade in soils under aerobic laboratory conditions, with typical half-lives \ll 1 day for all soils. Therefore, the compound is regarded as transient metabolite and is unlikely to accumulate in a soil environment.

Comments RMS

The evaluation of degradation kinetics shows that the p value recommended by FOCUS (2009) is exceeded in soil HH and DD for the fitted DFOP and FOMC parameters. In soil AX, β (FOMC) the p value is > 0.1 . In the soil DD, the p value for k_1 and k_2 (DFOP) and for α and β (FOMC) is > 0.4 . In the soil HH, the p value for k_2 (DFOP) and for α and β (FOMC) was > 0.14 . Therefore, for these two soils the SFO model appears more appropriate despite the higher Chi².

The endpoints are for degradation of metabolite NC 9607 in soil are:

| Soil | | DT50 | DT90 | Chi2 Error |
|------|---------------|---------|---------|------------|
| | Kinetic Model | [hours] | [hours] | [%] |
| AX | DFOP | 0.13 | 1.6 | Inf |
| HH | SFO | 0.1 | 0.5 | 9.34 |
| DD | SFO | 0.1 | 0.4 | 9.11 |
| WW | DFOP | 0.2 | 4.9 | 2.18 |

| | |
|---------------------|---|
| Reference: | Ethofumesate-carboxylic acid (as potassium salt: AE C639175): Aerobic degradation in four European soils |
| Notifier: | Taskforce |
| Author(s), year: | Traub, M.; 2012 |
| Report/Doc. number: | S11-03264 / M-432551-01-1 |
| Guideline(s): | OECD Test Guideline No. 307, 2002 |
| GLP: | yes |
| Deviations: | No |
| Validity: | Valid |
| Status: | New study |

MATERIALS AND METHODS

Materials :

Test Material :

Report name : AE C639175, Potassium salt of ethofumesate carboxylic acid (=NC 20645).
NC 20645 is not stable as acid.

Certificate No. : AZ 17664

Chem. Purity : 94%

Soils :

Table 8-66: Soil characteristics

| Parameter | Results | | | |
|---|--|---|--|---|
| Soil Designation | Laacher Hof AXXA (AX) | Höfchen am Hohenseh 4a (HH) | Dollendorf II (DD) | Wurmweise (WW) |
| Geographic Location (City / State / Country) | Bayer Field Station “Laacher Hof“ Field Plot: “AXXA“ D-40789 Monheim am Rhein / Germany | Bayer Field Research Station “Höfchen” Field Plot “Am Hohenseh 4a” D-51399 Burscheid / Germany | Field Plot: “Dollendorf II” D-53945 Blankenheim / Germany | Bayer Field Station “Laacher Hof” Field Plot: “Wurmwie se” D-40789 Monheim am Rhein / Germany |
| Soil Taxonomic Classification (USDA) | Sandy, mixed, mesic typic Argudalfs | Loamy, mixed, mesic typic Argudalfs | N/A | Loamy, mixed, mesic typic Argudalfs |
| Texture Class | Loamy sand | Silt Loam | Loam | SandyLoam |
| Sand | 84 % | 28 % | 40 % | 62 % |
| Silt | 10 % | 54 % | 36 % | 22 % |
| Clay | 6 % | 18 % | 24 % | 16 % |

| Parameter | Results | | | |
|---------------------------------------|--|--|--|--|
| pH in 0.01 M CaCl ₂ (1/2) | 5.90 | 6.1 | 7.0 | 5.2 |
| pH in 1 N KCl (1/1) | 5.8 | 5.8 | 6.71 | 4.8 |
| pH in Soil/Water (1/1) | 6.2 | 6.3 | 7.1 | 5.3 |
| pH in Water (Saturated Paste) | 6.2 | 6.4 | 7.1 | 5.4 |
| Organic Matter | 3.3 % | 3.4 % | 8.8 % | 3.1 % |
| Organic Carbon | 1.9 % | 2.0 % | 5.1 % | 1.8 % |
| Soil Microbial Biomass after arrival | 199.9 mg C/100g TS | 291.5 mg C/100g TS | 538.4 mg C/100g TS | 174.2 mg C/100g TS |
| start | 277.8 mg C/100g TS | 292.3 mg C/100g TS | 551.0 mg C/100g TS | 264.6 mg C/100g TS |
| end | 250.9 mg C/100g TS | 248.1 mg C/100g TS | 588.6 mg C/100g TS | 214.8 mg C/100g TS |
| Cation Exchange Capacity (CEC) | 8.8 meq/100 g | 11.4 meq/100g | 20.6 meq/100g | 10.4 meq/100g |
| Maximum Water Holding Capacity (MWHC) | 49.9 g H ₂ O <i>ad</i> 100 g DW | 52.4 g H ₂ O <i>ad</i> 100 g DW | 77.2 g H ₂ O <i>ad</i> 100 g DW | 59.4 g H ₂ O <i>ad</i> 100 g DW |

Methods :

Study design

The glass flasks (300 mL) contained about 100 g soil (dry weight basis). Each flask was closed by cotton wool.

The samples were incubated at 20 ± 2 °C under aerobic conditions in the dark.

Experimental Conditions

The soil moisture content was adjusted 55% of the maximum water holding capacity. The incubation was performed at 20 °C in the dark.

Sampling

Soil extracts were analyzed after incubation for 0, 3, 6 hours, 1, 2 and 7 days after treatment.

Analytical Procedures :

The study was performed with non-labeled NC 20645 (AE C639175 = potassium salt). Duplicate test systems were taken per sampling interval. The entire soil per flask was processed three times at ambient temperature and once under hot conditions by microwave extraction. The combined extracts were analyzed for NC 20645 residues by reversed phase high performance liquid chromatography/mass spectrometry (HPLC-MS/MS) in multiple reaction monitoring (MRM) mode using NC 20645 standards in pure solvent for calibration curve.

RESULT AND DISCUSSION

The analytical results were analyzed according to Focus Guidelines by three kinetic models (single first order, double first order, first order multi compartment) using single values.

Figure 8-54: Kinetic evaluation soil AX (SFO)

```

# -----
# Chi2 error estimation
# -----
#
# parent      All
Number of data sets :      5      5
Number of parameters :      2      2
Degrees of Freedom :      3      3
#
# parent      All
RMSE :      2.858      2.858
Chi2Sigma :      2.208      2.208
Chi2Err% :      7.057      7.057
# -----
# Parameter estimation
# -----
#
Degrees of Freedom : 8
Parameter      Estimate      Lower CI      Upper CI      St.Dev      Prob > t
M(0) parent :      91.82701      87.49617      96.158      2.20965      6.19e-11
k parent :      0.25398      0.22528      0.283      0.01465      6.23e-08
# -----
# DT50 and DT90 values
# -----
#
# parent
DT50 :      2.7291
DT90 :      9.0658
Kinetic model :      SFO
#

```

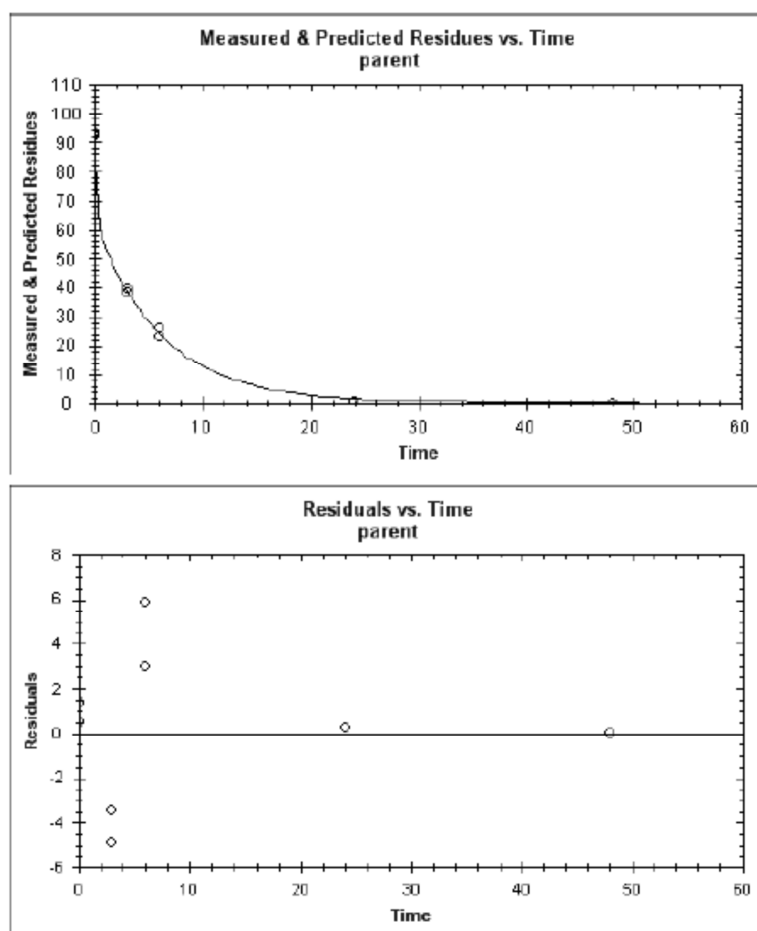


Figure 8-55: Kinetic evaluation soil AX (DFOP)

```

Chi2 error estimation
-----
Number of data sets :      parent      All
Number of parameters :      4          4
Degrees of Freedom :      1          1

RMSE :      parent      All
Chi2Sigma :  0.8555      0.8555
Chi2Err% :   0.4858      0.4858
Chi2Err% :   1.553      1.553
-----

Parameter estimation
-----
Degrees of Freedom : 6
Paramet      Estimate      Lower CI      Upper CI      St.Dev      Prob > t
M(0) parent :      92.80002      91.51580      94.084      0.65522      4.18e-12
kFast parent :      0.15938      0.13780      0.181      0.01101      3.41e-06
kSlow parent :      5.24761      -276.82235      287.318      143.91589      0.486
g parent :      0.67587      0.61123      0.741      0.03298      4.39e-07
-----

DT50 and DT90 values
-----
DT50 :      parent
DT90 :      1.8913
Kinetic model :      DFOF

```

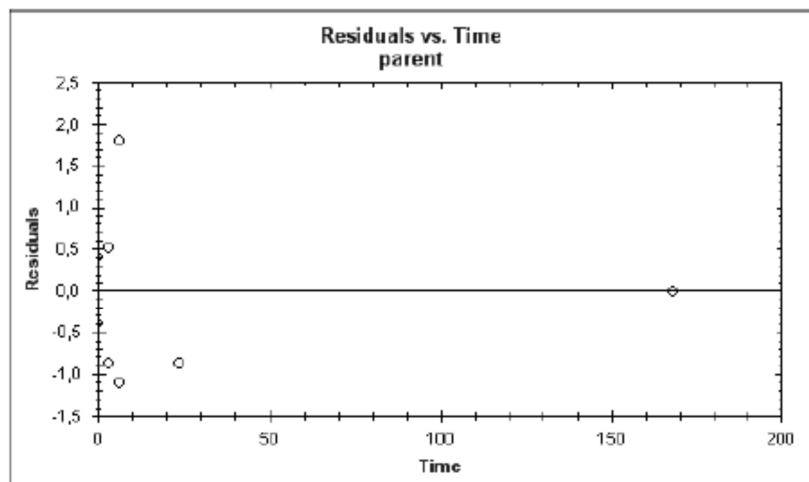
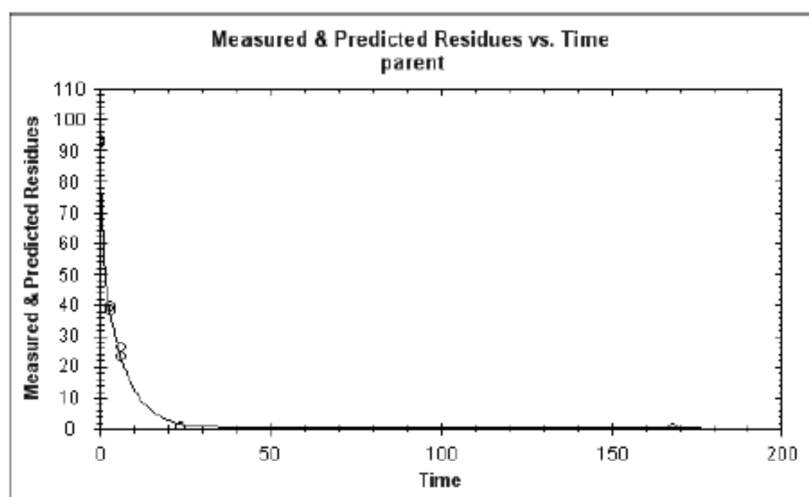


Figure 8-56: Kinetic evaluation soil AX (FOMC)

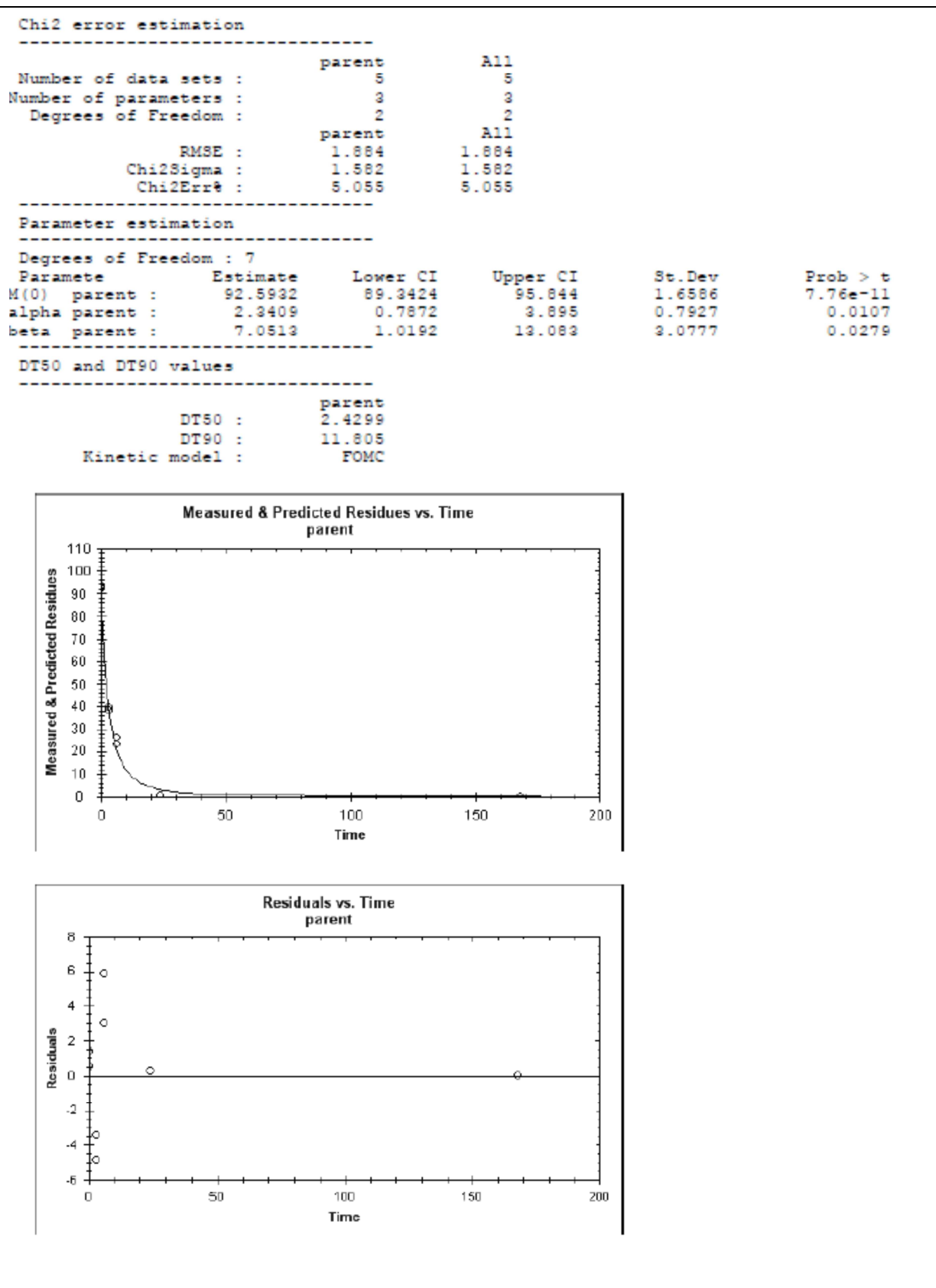


Figure 8-57: Kinetic evaluation soil HH (SFO)

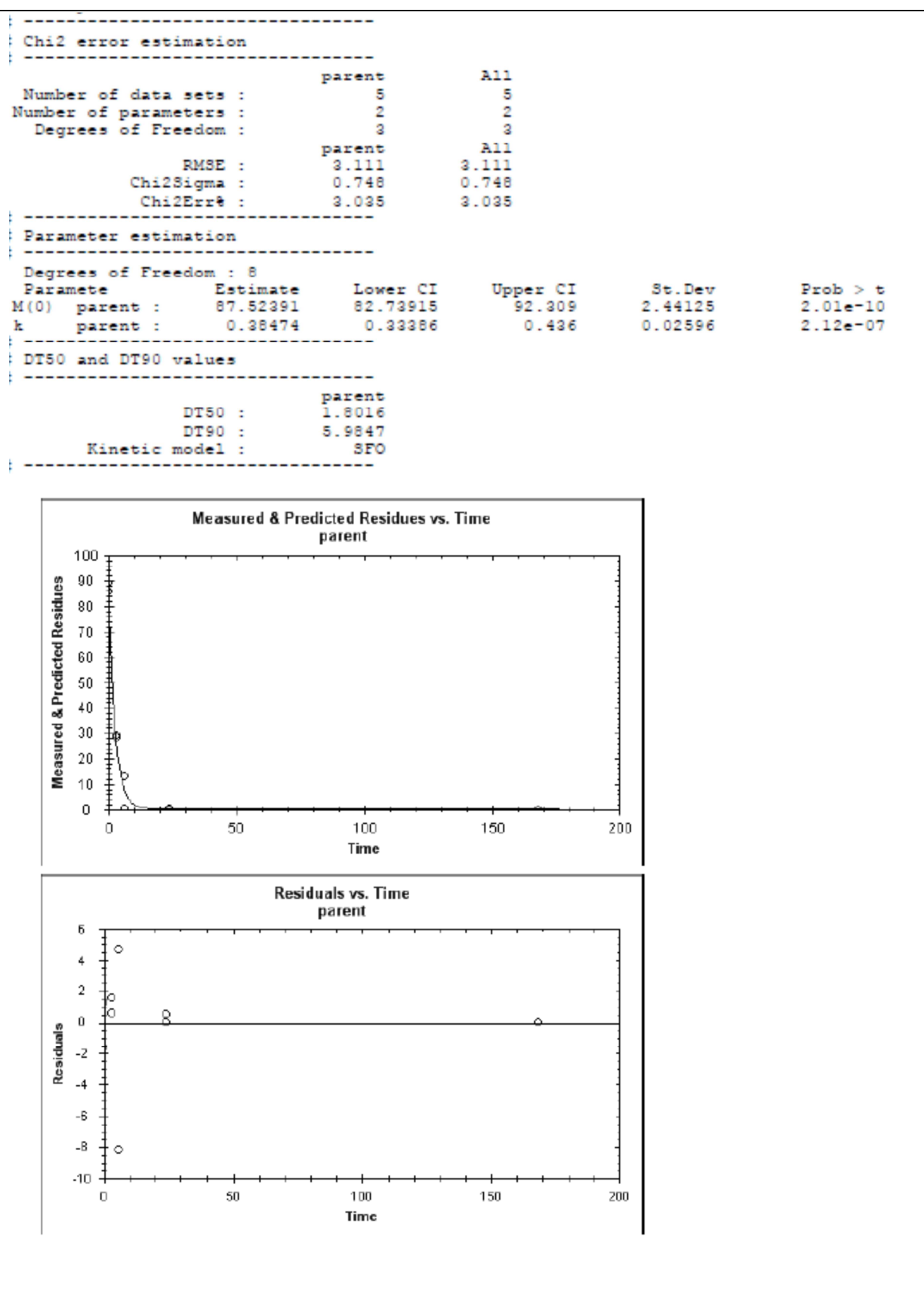


Figure 8-58: Kinetic evaluation soil HH (DFOP)

```

-----
Chi2 error estimation
-----
Number of data sets :      parent      All
                          5              5
Number of parameters :      4              4
Degrees of Freedom :      1              1
                          parent      All
RMSE :                   3.111         3.111
Chi2Sigma :              1.067         1.067
Chi2Err% :               4.328         4.328
-----
Parameter estimation
-----
Degrees of Freedom : 6
Parameter      Estimate      Lower CI      Upper CI      St.Dev      Prob > t
M(0) parent :   87.52391      74.99349      100.054      6.39319      4.72e-06
kFast parent :   0.38474       0.08654       0.683       0.15214      0.02238
kSlow parent :   0.06407      -7.47002       7.598       3.84399      0.49362
g parent :       1.00000       0.56001       1.440       0.22449      0.00215
-----
DT50 and DT90 values
-----
                          parent
DT50 :              1.8016
DT90 :              5.9847
Kinetic model :      DFOP
-----

```

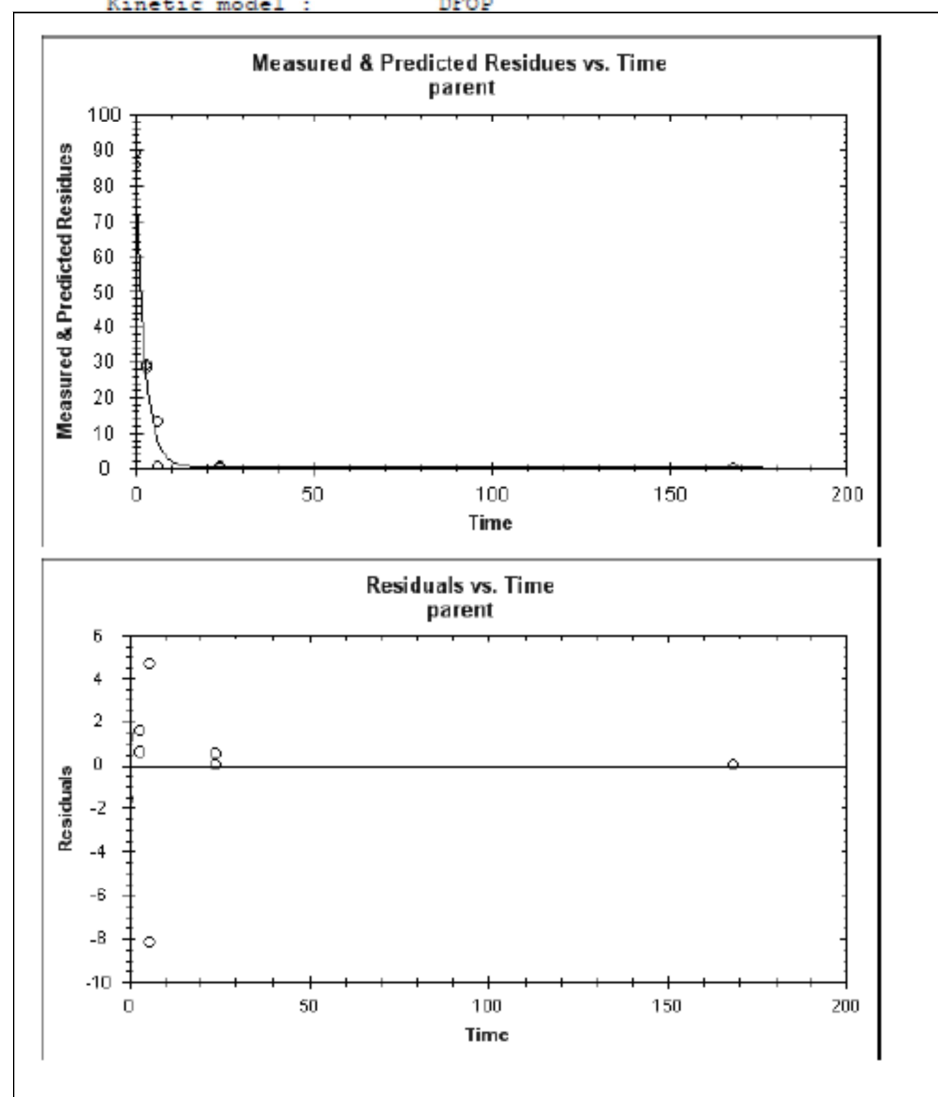


Figure 8-59: Kinetic evaluation soil HH (FOMC)


```

-----
Chi2 error estimation
-----
Number of data sets :      parent      All
Number of parameters :      3          3
Degrees of Freedom :      2          2

RMSE :      parent      All
Chi2Sigma :    1.102    1.102
Chi2Err% :     4.47     4.47
-----
Parameter estimation
-----
Degrees of Freedom : 7
Parameter      Estimate      Lower CI      Upper CI      St.Dev      Prob > t
M(0) parent :    88.002      82.900      93.1        2.603      2.57e-09
alpha parent :  1861.864    -14501.318    18225.0     8348.715    0.415
beta parent :   4615.773    -35967.811    45199.4     20706.291    0.415
-----
DT50 and DT90 values
-----
DT50 :      parent
DT90 :      1.7187
        5.7119
Kinetic model :      FOMC
-----

```

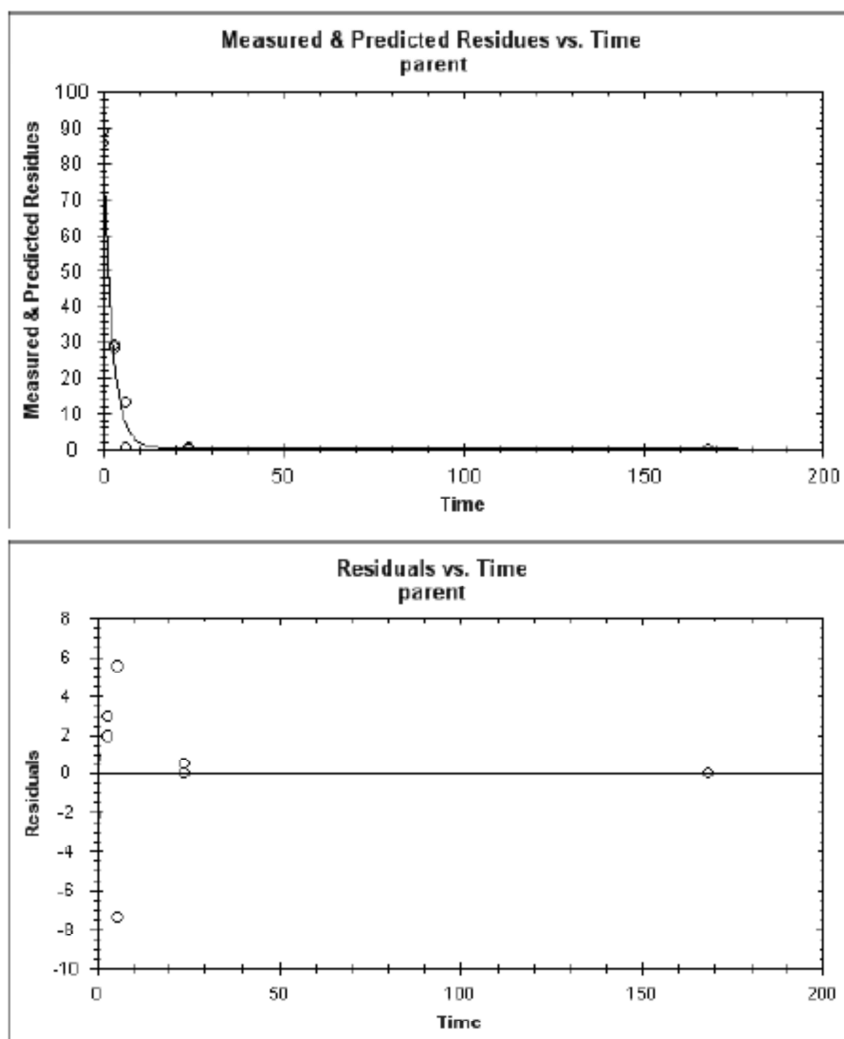


Figure 8-60: Kinetic evaluation soil DD (SFO)

```

-----
Chi2 error estimation
-----
Number of data sets :      parent      All
Number of parameters :      6          6
Degrees of Freedom :      2          2
RMSE :      parent      All
Chi2Sigma :      2.580    2.580
Chi2Err% :      1.681    1.681
          :      5.322    5.322
-----
Parameter estimation
-----
Degrees of Freedom : 10
Parameter      Estimate      Lower CI      Upper CI      St.Dev      Prob > t
M(0) parent :   97.599645     93.793048     101.406     1.942177     1.18e-13
k      parent :    0.186103     0.169303      0.203     0.008572     4.80e-10
-----
DT50 and DT90 values
-----
          :      parent
DT50 :      3.7245
DT90 :      12.373
Kinetic model :      SFO
-----

```

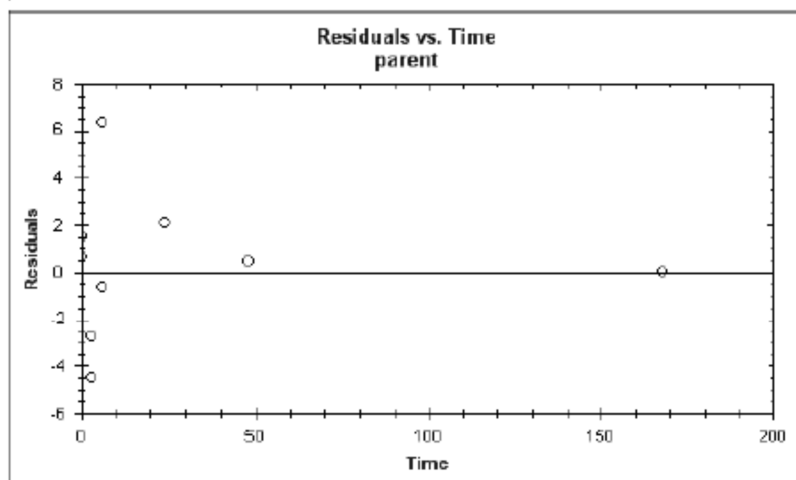
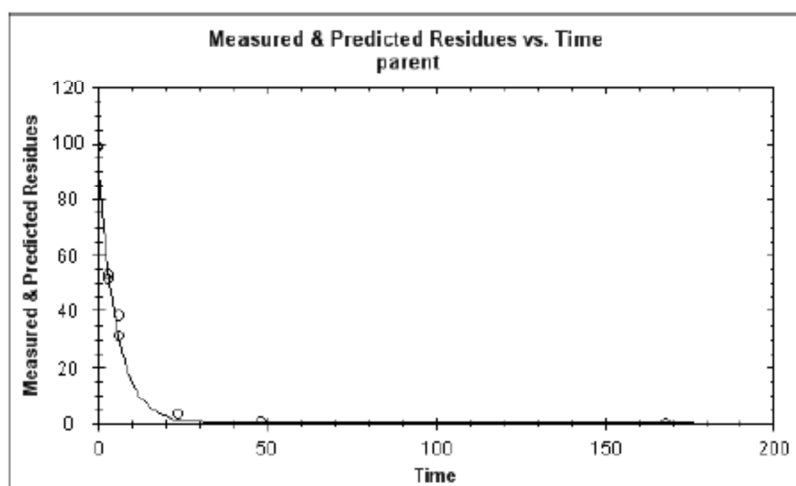


Figure 8-61: Kinetic evaluation soil DD (DFOP)

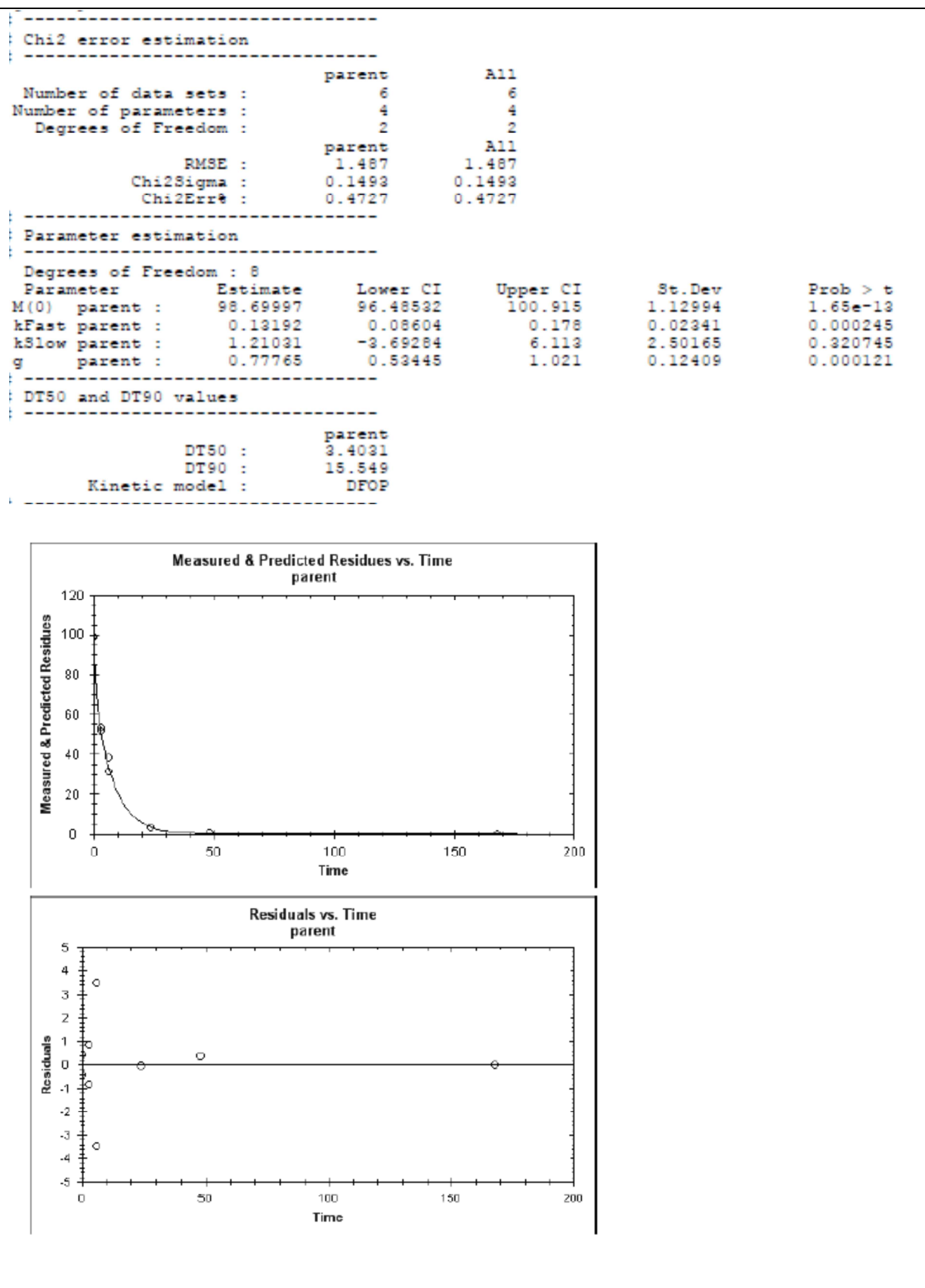


Figure 8-62: Kinetic evaluation soil DD (FOMC)

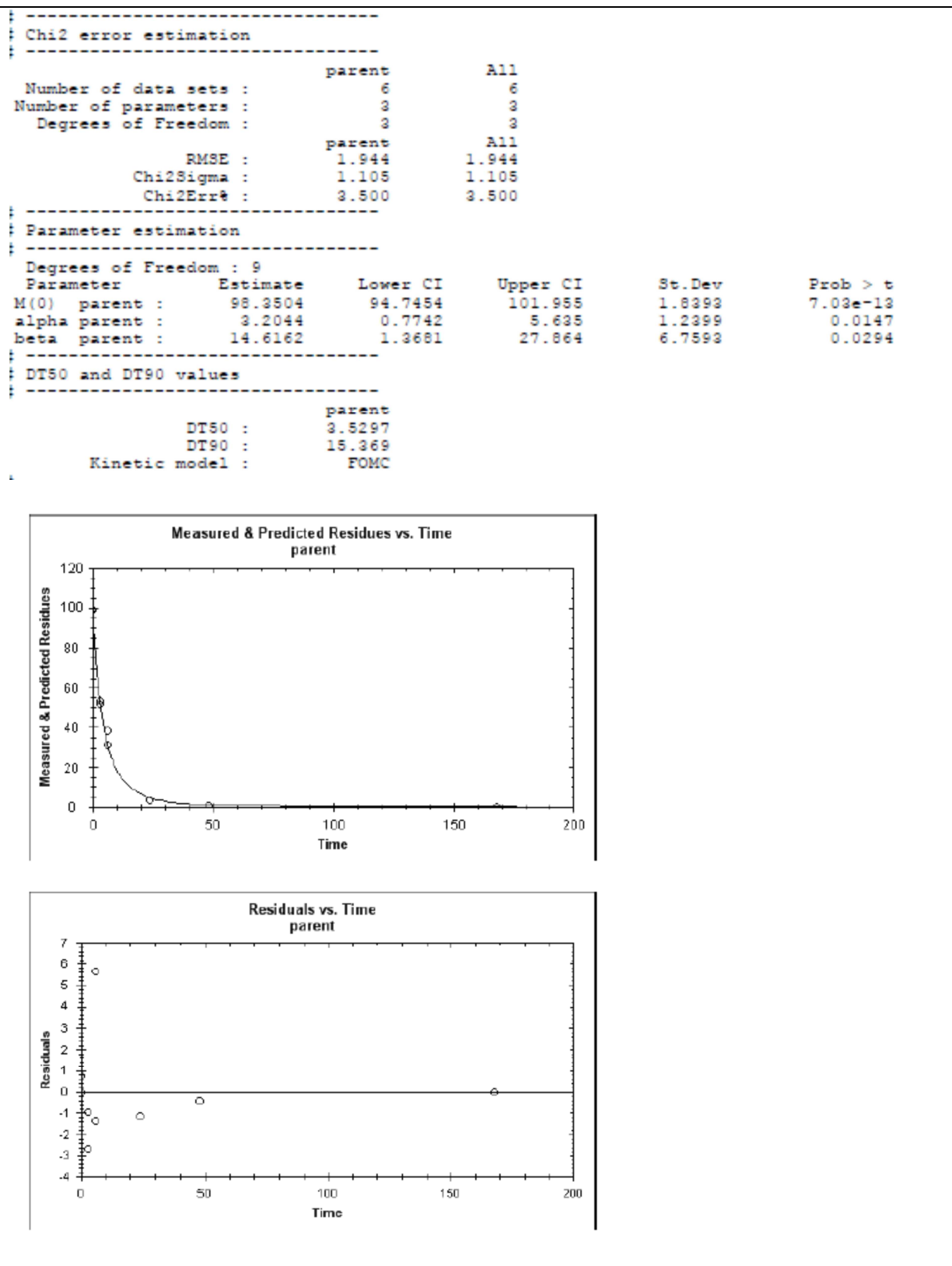


Figure 8-63: Kinetic evaluation soil WW (SFO)

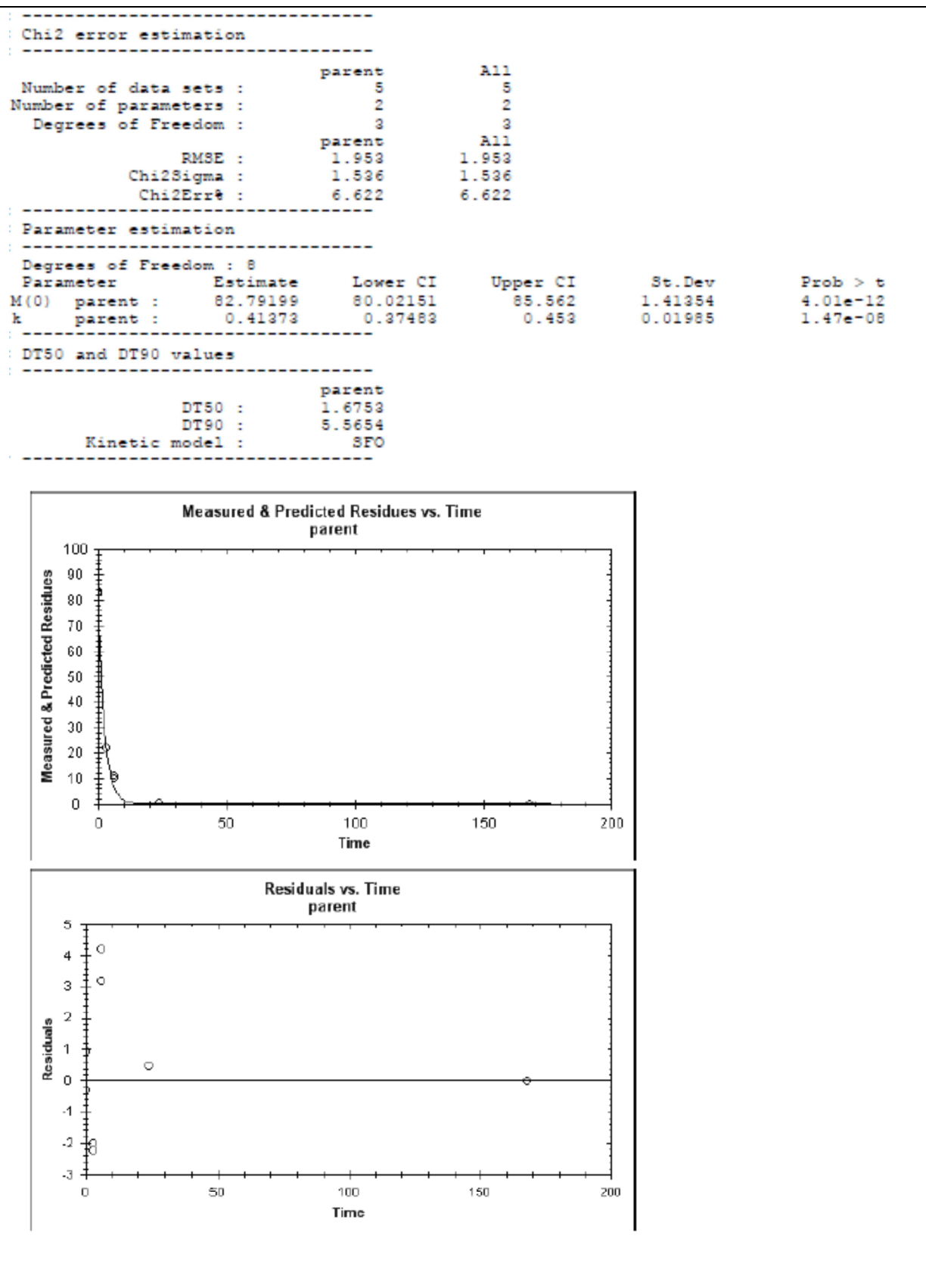


Figure 8-64: Kinetic evaluation soil WW (DFOP)

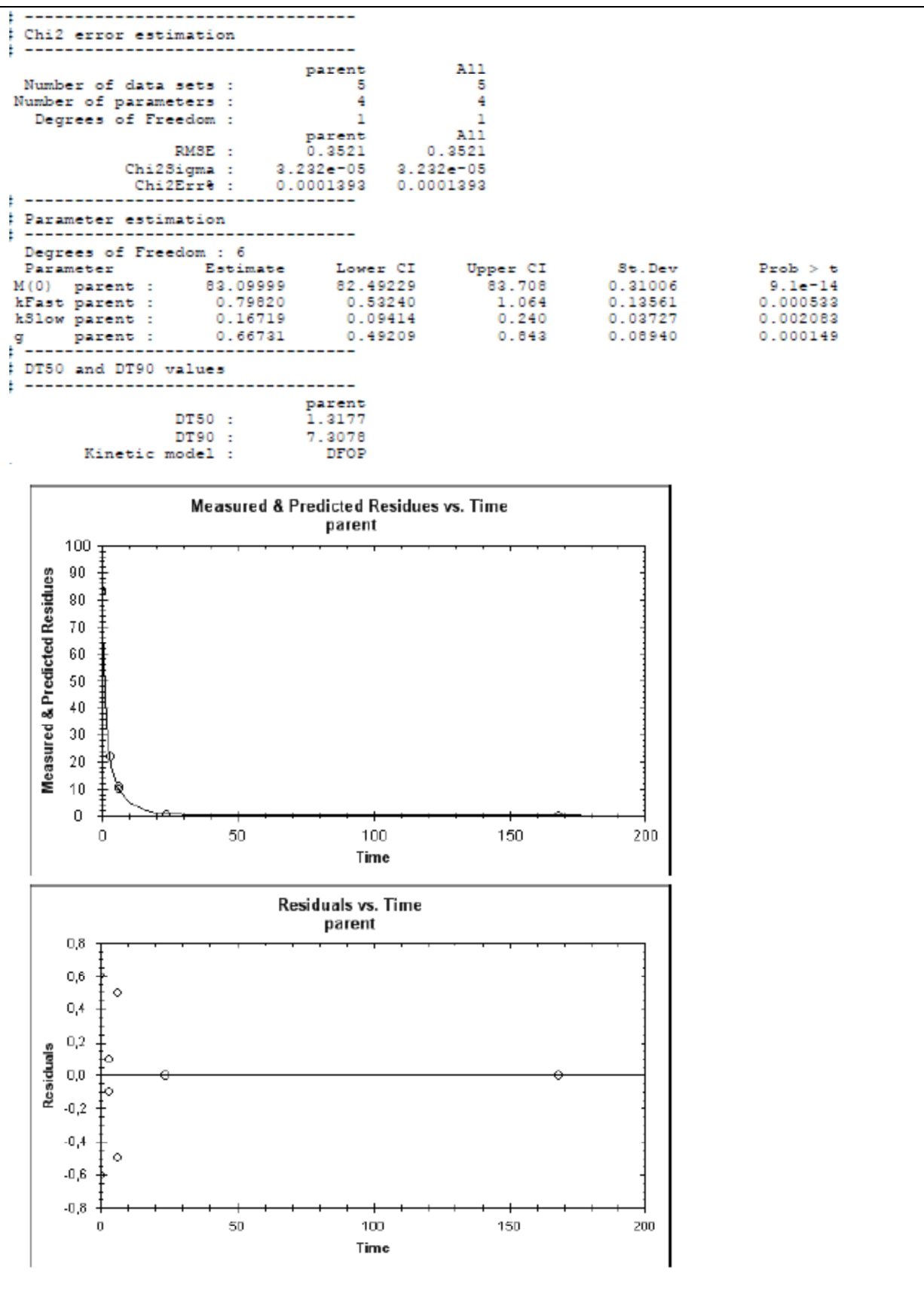


Figure 8-65: Kinetic evaluation soil WW (FOMC)

```

-----
Chi2 error estimation
-----
Number of data sets :      parent      All
                        :           5           5
Number of parameters :      3           3
Degrees of Freedom :      2           2

RMSE :      parent      All
Chi2Sigma : 0.5353      0.5353
Chi2Err% :   1.587      1.587
-----

Parameter estimation
-----
Degrees of Freedom : 7
Parameter      Estimate      Lower CI      Upper CI      St.Dev      Prob > t
M(0) parent :   83.0885      82.1589      84.018      0.4743      2.61e-14
alpha parent :    1.9258      1.4711      2.380      0.2320      3.60e-05
beta parent :    3.0226      1.9687      4.076      0.5377      0.000399
-----

DT50 and DT90 values
-----
DT50 :      parent
DT90 :      1.3095
        6.9693
Kinetic model :      FOMC

```

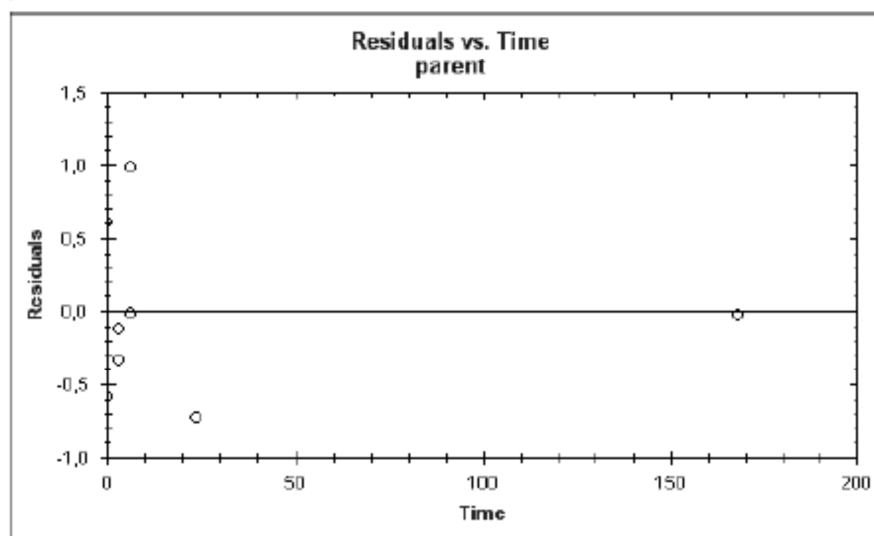
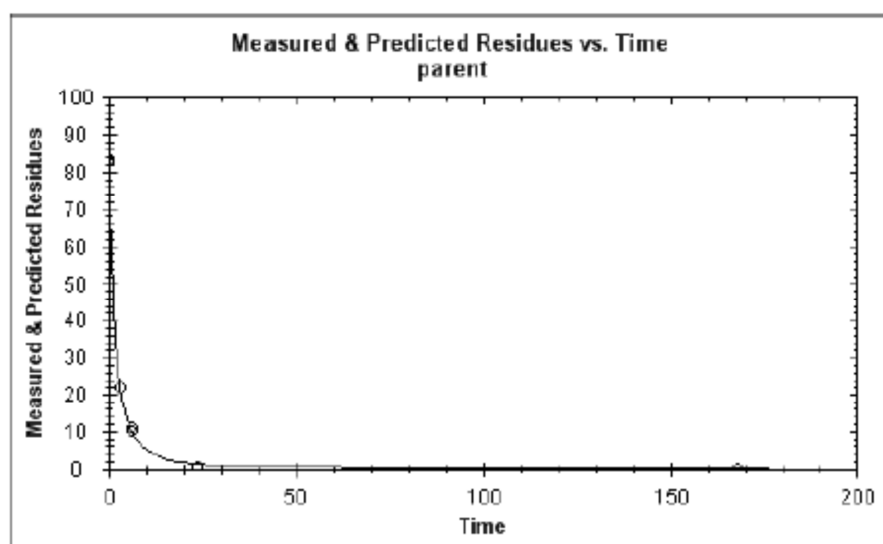


Table 8-67: Degradation of NC 20645 (AE C639175 = potassium salt of NC 20645 , ethofumesate-carboxylic acid) in soil

| Soil (Soil type) | Best Fit Kinetic Model | DT ₅₀ [h] | DT ₉₀ [h] | Chi ² Error [%] | Visual Assessment * |
|---------------------|---------------------------|-------------------------|-------------------------|-------------------------------|------------------------|
| Soil 1 (AX) | DFOP | 1.9 | 12.0 | 1.55 | + |
| Soil 2 (HH) | SFO | 1.8 | 6.0 | 3.04 | + |
| Soil 3 (DD) | DFOP | 3.4 | 15.5 | 0.47 | + |
| Soil 4 (WW) | DFOP | 1.3 | 7.3 | 1.4 e-4 | + |

Geometric mean: DT₅₀ 2hours (0.083 days), for SFO only DT₅₀ 2.4 hours (0.098 days)

* Visual Assessment: + = good, o = medium, - = poor

In theory an intramolecular cyclisation reaction to the respective ethofumesate-lactone NC 9607 is possible. In order to evaluate the overall degradation behavior selected extracts from soil, which was incubated with the metabolites NC 8493, NC 9607 and NC 20645 were analyzed and the metabolites were quantified. The result shows that the back-reaction is only a very minor contributor to the total degradation and that after 24 hours the sum of NC 9607 and NC 20645 (AE C 639175 =potassium salt of NC 20645) is < 5% of the applied NC 20645.

Table 8-68: Additional orientating test: Detection of AE C508493, AE C509607 and AE C639175 in representative samples

Appendix 12: Additional orientating test: Detection of AE C508493, AE C509607 and AE C639175 in representative samples

| Sample | AE C508493 | AE C509607 | AE C639175 |
|--------------------------------|------------|------------|------------|
| | [mg/kg] | | |
| AE C508493 application 0 h | 0.222 | 0.016 | 0.007 |
| AE C508493 application 3 h | 0.004 | 0.030 | 0.196 |
| | | | |
| AE C509607 application 0 h | - | 0.248 | 0.004 |
| AE C509607 application 3 h | - | 0.018 | 0.195 |
| | | | |
| AE C639175 application 0 h | - | 0.024 | 0.247 |
| AE C639175 application 24 h | - | 0.005 | 0.002 |

Conclusion:

In conclusion, NC 20645 (ethofumesate-carboxylic acid), in this study tested as potassium salt AE C639175 was found to rapidly degrade in soils under aerobic laboratory conditions, with typical half-lives << 1 day for all

soils. A back-reaction to the respective ethofumesate- lactone NC 9607 did not influence the overall degradation behavior. Therefore, the compound will not accumulate in a soil environment.

Comments RMS

The degradation of non-labeled NC 20645 (AE C639175 = potassium salt of NC 20645, ethofumesate-carboxylic acid) was investigated in four soils under aerobic conditions at 20°C in the dark. 100 g soil (dry weight basis) were used and the average soil moisture content was 55% of the maximum water holding capacity over the entire period of the study. The biological activity of the soils was checked directly after treatment and sixteen days after application. The application rate of NC 20645 was 29.1 µg per vessel and 100 g air dried soil. The combined ambient temperature and microwave extracts were analyzed for NC 20645 residues by reversed phase high performance liquid chromatography/mass spectrometry (HPLC-MS/MS) in multiple reaction monitoring (MRM) mode using NC 20645 standards in pure solvent for calibration curve.

The selected sampling intervals should demonstrate the degradation of the test item within 7 days. Due to the rapid degradation of approximately 50% of the test item within 6 hours there are not five accurately defined data points > LOD for evaluation of the DT50 value available. The accuracy and repeatability was assessed on the basis of a set of recovery samples. For this purpose, 100 g untreated soil (calculated as dry matter) was adjusted with water to 55% MWHC and fortified at LOQ level (1.5 µg in 205 µL methanol/water 1/1, v/v; = 0.015 mg/kg) and at 22xLOQ level (32.0 µg in 438 µL methanol/water 1/1, v/v; = 0.307 mg/kg) with test item solution. During method validation, recoveries of AE C639175 in soil were between 89.4 - 112.8% (with mean values of 95.4% at LOQ level and 99.6% at 22xLOQ level), 82.3 - 115.8% (with mean values of 98.0% at LOQ level and 85.9% at 22xLOQ level), 82.8 - 92.2% (with mean values of 91.0% at LOQ level and 84.1% at 22xLOQ level), and 82.3 - 96.3% (with mean values of 93.9% at LOQ level and 84.6% at 22xLOQ level) for soils AX, HH, DD and WW, respectively.

The degradation study is fully reliable and the relevant endpoints are:

| Soil | Kinetic Model | DT50 [d] | DT90 [d] | Chi2 Error [%] |
|------|---------------|-------------|-------------|-------------------|
| AX | SFO | 0.11 | 0.40 | 7.1 |
| HH | SFO | 0.08 | 0.25 | 3.0 |
| DD | SFO | 0.15 | 0.52 | 5.3 |
| WW | DFOP | 0.05 | 0.30 | <0.1 |

In an additional study, the potential back reaction of the test item to the NC9607 was investigated. Samples from soil AX treated with AE C508493, soil AX treated with AE C509607 and soil AX treated with AE C639175 were re-analysed regarding their amount of NC 8493, NC 9607 and the potassium salt of NC20645. The results from this orientating test show that 24 hours after application of AE C639175 the sum of AE C639175 and NC 9607 is less than 5% of the applied substance. Based on these results it appears that the back reaction does not contribute significantly to the overall degradation.

B.8.1.1.2.1.3. Anaerobic degradation of the metabolites

| | |
|---------------------|--|
| Reference: | ANAEROBIC SOIL METABOLISM (14C)-Ethofumesate |
| Notifier: | Taskforce |
| Author(s), year: | Waring, A. R.;1992 |
| Report/Doc. number: | A83390 / W 135 / M-155658-01-1 |
| Guideline(s): | None |
| GLP: | yes |
| Deviations: | |
| Validity: | Valid |
| Status: | Previous evaluation in DAR for original approval / baseline dossier. |

Comments RMS

The study was submitted also as an anaerobic route study. Please refer to the respective section.

B.8.1.1.2.2. Field studies**B.8.1.1.2.2.1. Soil dissipation studies**

| | |
|---------------------|---|
| Reference: | DISSIPATION OF ETHOFUMESATE IN SOIL FOLLOWING TREATMENT OF A WP CO-FORMULATION WITH PHENMEDIPHAM IN THE FEDERAL REPUBLIC OF GERMANY. |
| Notifier: | Taskforce |
| Author(s), year: | Straszewski, A.; 1990 |
| Report/Doc. number: | A89473 / W 106 / M-164840-01-1 |
| Guideline(s): | None |
| GLP: | no |
| Deviations: | |
| Validity: | Not valid |
| Status: | Previous evaluation in DAR for original approval / baseline dossier. |
| Reference: | DISSIPATION OF ETHOFUMESATE IN SOIL FOLLOWING TREATMENT OF A WP CO-FORMULATION WITH PHENMEDIPHAM IN THE FEDERAL REPUBLIC OF GERMANY. ADDENDUM (DEUTSCHE ZUSAMMENFASSUNG) |
| Notifier: | Taskforce |
| Author(s), year: | Straszewski, A.; 1990 |
| Report/Doc. number: | A83362 / W 106 addendum / M-155631-01-1 |
| Guideline(s): | None |
| GLP: | no |
| Deviations: | |
| Validity: | Not valid |
| Status: | Previous evaluation in DAR for original approval / baseline dossier. |

Study summary based on previous draft assessment report**Materials and Methods**

The dissipation of ethofumesate from soil following treatment with a WP co-formulation with phenmedipham (present at 20 and 30% as active ingredients, respectively) was investigated under field conditions at four sites (for soil properties, see table below) in Germany in 1989.

Table 8-69: Soil characteristics

| Site | OC (%) | pH | sand (%) | silt (%) | clay (%) | MHC (%), | CEC meq/100 g | Biomass mg/100 g dw |
|-----------------------------------|--------|-----|----------|----------|----------|----------|---------------|---------------------|
| Thann/Dienhart sandy loam-loam | 1.5 | 7.1 | 55 | 24 | 21 | 45 | n.r. | 12 |
| G. Nierswalde/Dittrich sandy loam | 3.7 | 6.0 | 63 | 22 | 15 | 60 | n.r. | 39 |

| | | | | | | | | |
|---------------------------------|------|-----|------|------|------|----|------|----|
| Niederkirchen/Fusser sandy loam | n.r. | 6.9 | n.r. | n.r. | n.r. | 49 | n.r. | 68 |
| Langförden/Jende humous sand | 6.4 | 5.0 | 84 | 0 | 16 | 49 | n.r. | 18 |

Bare soil plots were treated with 6.5 kg formulation/ha, corresponding to 1.3 kg ethofumesate/ha. Twenty soil cores (30 cm depth) were taken for analysis from each treated and control plot at regular intervals for 12 months following application. The cores were divided into 10 cm segments, which were combined prior to soxhlet extraction with acetone, followed by partition into hexane and analysis with GC. No weather data were reported.

Results

The mean recovery efficiency of the method of analysis was determined to $92\pm 7\%$. The dissipation half-lives were assuming first order kinetics, and based on the residue levels immediately after application (soil depth 10 cm, density 1.5 g/cm³).

Table 8-70: Recovery of applied ethofumesate immediately after treatment and dissipation data on treated plots.

| Trial site | Recovery on day 0 ¹ | DT50 | DT90 |
|------------------------|--------------------------------|----------|-----------|
| Thann/Dienhart | 66% | 46 days | 153 days |
| G. Nierswalde/Dittrich | <0.05 ppm | -- | -- |
| Niederkirchen/Fusser | 21% | 19 days | 83 days |
| Langförden/Jende | 62% | 397 days | not given |

-- no residues recovered at this site (detection limit 0.05 mg/kg)

¹... Percent of theoretical initial amounts (=0.86 mg/kg, assuming soil depth 10 cm, soil density 1.5 kg/L)

Comments RMS

The field dissipation of ethofumesate from soil following treatment with a WP co-formulation with phenmedipham (present at 20 and 30% as active ingredients, respectively) was investigated at four sites in Germany in 1989. Weather data were not reported. Bare soil plots were treated with 6.5 kg formulation/ha, corresponding to 1.3 kg ethofumesate/ha. Twenty soil cores (30 cm depth) were taken for analysis from each treated and control plot at regular intervals for 12 months following application. The cores were divided into 10 cm segments, which were combined prior to soxhlet extraction with acetone, followed by partition into hexane and analysis with GC.

The mean recovery efficiency of the method of analysis was determined to be $92\pm 7\%$, however day-zero recovery was very low (21 - 66%) indicating that other losses might have occurred. For instance, at the site Niederkirchen, (where no texture was reported) only a maximum of 21% of expected loading could be found in the soil samples. At the site Nierswalde, ethofumesate residues were below LOD in every analysed sample. Due to the low recoveries at day zero, all the sites were excluded from further considerations.

The study is considered not valid.

| | |
|---------------------|---|
| Reference: | DISSIPATION OF ETHOFUMESATE IN SOIL FOLLOWING USE OF NORTRON EC IN SUGAR BEET CULTIVATION USA 1989 |
| Notifier: | Taskforce |
| Author(s), year: | Castro, L. E.; 1991. Amended: 1991-08-23 |
| Report/Doc. number: | A83366 / W110 / M-155634-02-1 |
| Guideline(s): | None |
| GLP: | yes |
| Deviations: | |
| Validity: | Valid |
| Status: | Previous evaluation in DAR for original approval / baseline dossier. |

Study summary based on previous draft assessment report

Materials and Methods

The dissipation of ethofumesate from soil following treatment with the formulation Nortron EC (19% ethofumesate) was investigated under field conditions in two sugar beet cultivations (for soil properties, see table below) situated in California and North Dakota, USA in 1989. The study was performed according to US EPA Guidelines 164-1.

Table 8-71: Soil characteristics for the upper 7.5 cm horizon.

| Soil | OM (%) | pH | sand (%) | silt (%) | clay (%) | MHC (%), @ 1/3 bar | CEC meq/100 g |
|---------------------|-----------|-----|-------------|-------------|-------------|-----------------------|------------------|
| Fresno sandy loam | 0.5 | 6.5 | 67 | 26 | 7 | 8.2 | 7.0 |
| Northwood clay loam | 4.9 | 7.3 | 30 | 41 | 29 | 34.3 | 20 |

Nortron EC was sprayed pre-emergence onto the 24 x 24 m plots in April and May 1989, at the rates of 2.1 kg as/ha in Fresno and 4.2 kg as/ha in Northwood. Samples were taken at various intervals for 18 months following application. At each sampling time, five soil cores (to a depth of 86 cm) were taken from each of three sub-plots. The cores were sectioned and combined into 7.5 (upper two) and 15 cm horizons. Analysis of ethofumesate was performed in triplicate by GC after soxhlet extraction with acetone and partition into hexane. The limit of detection was 0.01 mg/kg. Monthly average soil temperature at 50 mm depth ranged between 8 and 29°C in Fresno, and between -10 and 24°C (below zero for 5 months) in Northwood during the study period. The sum of total rainfall and irrigation was 4308 mm in Fresno, and 766 mm in Northwood.

Results

The mean recovery of the method of analysis was 102±10%, and no corrections were made. The residue levels were based on the total dry weight content in the soil columns. The half-lives of ethofumesate were 75 days

($r^2=0.76$) in Fresno and 150 days ($r^2=0.28$) in Northwood during the first four months after application, based on first order kinetics. During the following 14 months, the half-lives were 120 days ($r^2=0.93$) in Fresno and 95 days ($r^2=0.93$) in Northwood. At soil temperatures below zero (only in Northwood), no declination of ethofumesate levels was observed. Residues were found mainly to 15 cm depth, but were also sporadically detected to a depth of 30 cm.

Table 8-72: Ethofumesate concentrations (mg/kg) in the Fresno field trial.

| Site | Interval (days) | Rep | Corrected Residues (ppm) in Soil Horizons | | | | |
|--|-----------------|-----|---|--------|----------|----------|----------|
| | | | 0-3 in | 3-6 in | 6-12 in | 12-18 in | 18-24 in |
| F r e s n o C A | -1 | 1 | <0.01 | <0.01 | <0.01 | | |
| | | 2 | <0.01(a) | <0.01 | | | |
| | | 3 | <0.01 | <0.01 | <0.01 | | |
| | 0 | 1 | 1.2 | 0.06 | <0.01 | <0.01 | |
| | | 2 | 1.5 | 0.05 | <0.01 | <0.01 | |
| | | 3 | 1.1 | 0.06 | <0.01 | <0.01 | |
| | 1 | 1 | 1.4 | 0.04 | <0.01 | <0.01 | |
| | | 2 | 1.5 | 0.02 | <0.01 | <0.01 | |
| | | 3 | 0.30(b) | <0.01 | <0.01 | <0.01 | |
| | 14 | 1 | 0.66 | <0.01 | <0.01 | <0.01 | |
| | | 2 | 0.67 | <0.01 | <0.01 | <0.01 | |
| | | 3 | 0.69 | <0.01 | <0.01 | <0.01 | |
| | 28 | 1 | 0.74 | <0.01 | <0.01 | | |
| | | 2 | 1.2 | <0.01 | <0.01 | | |
| | | 3 | 0.94 | <0.01 | <0.01 | | |
| | 61 | 1 | 0.61 | 0.10 | <0.01 | <0.01 | |
| | | 2 | 0.85 | 0.07 | <0.01 | <0.01 | |
| | | 3 | 0.87 | 0.12 | <0.01 | <0.01 | |
| | 120 | 1 | 0.16 | 0.02 | <0.01(u) | <0.01 | <0.01 |
| | | 2 | 0.35 | 0.07 | <0.01 | <0.01 | <0.01 |
| | | 3 | 0.30 | 0.07 | <0.01 | <0.01 | <0.01 |
| | 186 | 1 | 0.18 | 0.02 | <0.01 | <0.01 | |
| | | 2 | 0.34 | 0.04 | <0.01 | <0.01 | |
| | | 3 | 0.09 | 0.03 | <0.01 | <0.01 | |
| | 281 | 1 | 0.09 | 0.04 | <0.01 | <0.01 | <0.01 |
| | | 2 | 0.07 | 0.04 | 0.02 | <0.01 | <0.01 |
| | | 3 | 0.09 | 0.07 | 0.01 | <0.01 | <0.01 |
| | 364 | 1 | 0.06 | 0.04 | <0.01 | <0.01 | <0.01 |
| | | 2 | 0.08 | 0.05 | 0.01 | <0.01 | <0.01 |
| | | 3 | 0.08 | 0.07 | <0.01 | <0.01 | |
| | 456 | 1 | 0.02 | 0.02 | <0.01 | <0.01 | |
| | | 2 | 0.02 | <0.01 | <0.01 | <0.01 | |
| | | 3 | 0.03 | 0.02 | <0.01 | <0.01 | |
| | 546 | 1 | 0.02 | 0.01 | <0.01 | <0.01 | <0.01 |
| | | 2 | 0.02 | <0.01 | <0.01 | <0.01 | <0.01 |
| | | 3 | 0.02 | 0.02 | <0.01 | <0.01 | <0.01 |

Comments RMS

The dissipation of ethofumesate from soil following treatment with the formulation Nortron EC (19% ethofumesate) was investigated under field conditions in two sugar beet cultivations situated in California and North Dakota, USA in 1989. Nortron EC was sprayed pre-emergence onto bare plots in April and May 1989, at

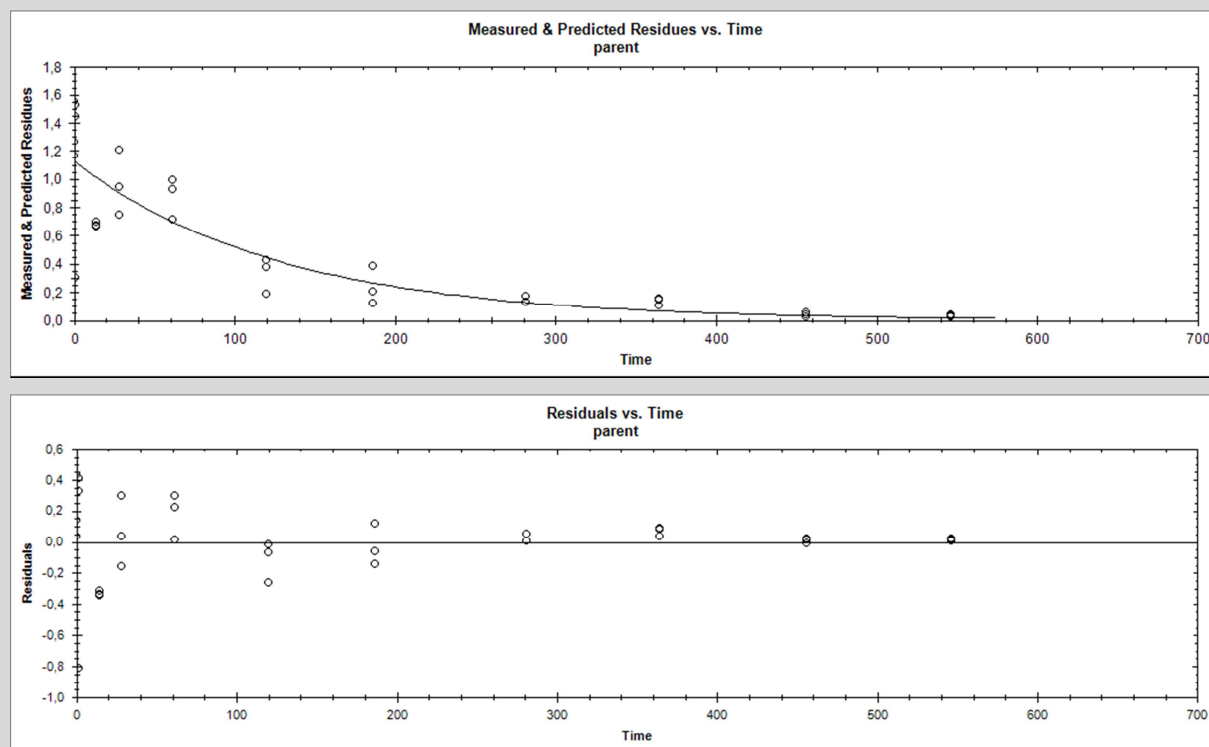
the rates of 2.1 kg as/ha in Fresno and 4.2 kg as/ha in Northwood. Soils were not cultivated afterwards. Soil samples were collected at various intervals, using two cores to a depth of 6 inches (approx. 15 cm) and then from 6 to 36 inches (approx. 15 to 90 cm), the latter split into five equal sections. Analysis of ethofumesate was performed in triplicate by GC after soxhlet extraction with acetone and partition into hexane. The limit of detection was 0.01 mg/kg. A fortified control sample was analysed with each set of samples (yielding a total of 92 samples). Mean recovery through the method was $(102 \pm 10\%)$, the limit of quantification was 0.01 mg/kg.

Weather data are generally adequately reported. However, the weather conditions in North Dakota appear not to be representative for European sugar beet scenarios, especially as highlighted by the notifier in Schmitt (2008) the calculated soil temperature fell below -20° . Therefore, the North Dakota trial was excluded from further considerations. The RMS agrees with the notifier, whereas the Co-RMS considers the North Dakota field trial representative for European sugar beet scenarios.

Degradation kinetics for the non-normalized Fresno study were recalculated by RMS with all samples below LOD set to $1/2$ LOD or - after the first non-detect (time and depth) – set to zero in case no detects appeared later on. Values between LOD and LOQ were set to $0.5 \times (\text{LOQ} + \text{LOD})$.

The kinetic evaluation of the non-normalized field study results was carried out by the RMS. The results are in the Figures below.

SFO



```

-----
Child error estimation
-----
ChildErr% :      parent      All
Kinetic model :      SFO
-----

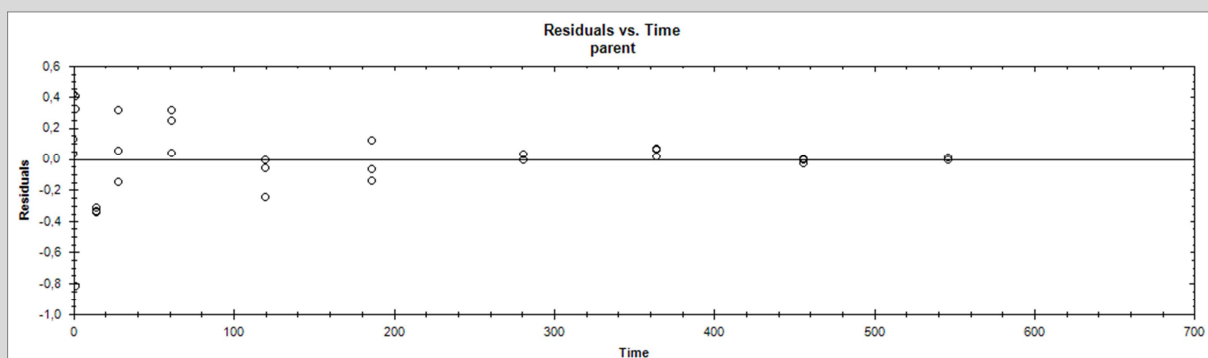
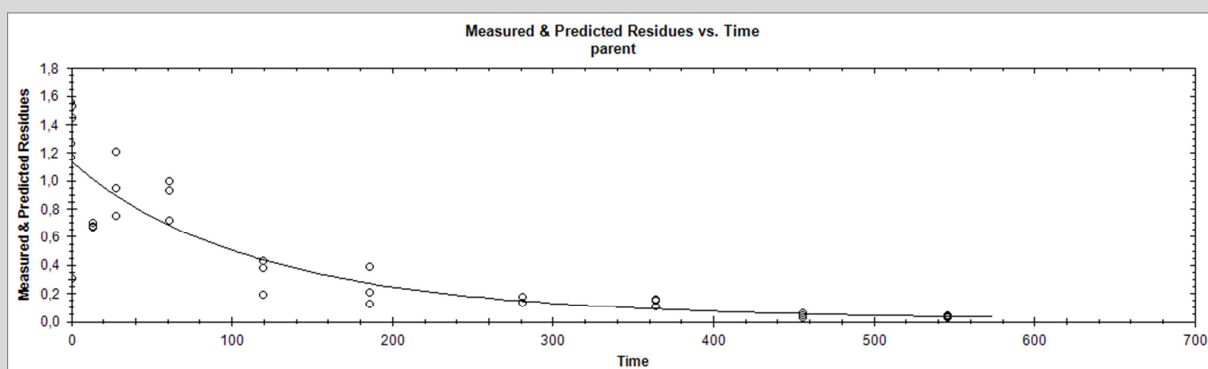
Parameter estimation
-----

Degrees of Freedom : 31
Parameter      Estimate      Lower CI      Upper CI      St.Dev      Prob > t
M(0) parent    :      1.124925      0.965222      1.295        0.081482      4.39e-15
k parent       :      0.007798      0.004487      0.011        0.001689      3.22e-05
-----

DT50 and DT90 values
-----
DT50 :      parent
DT90 :      295.27
Kinetic model :      SFO

```

FOMC



```

-----
Child error estimation
-----
ChildErr% :      parent      All
Kinetic model :      FOMC
-----

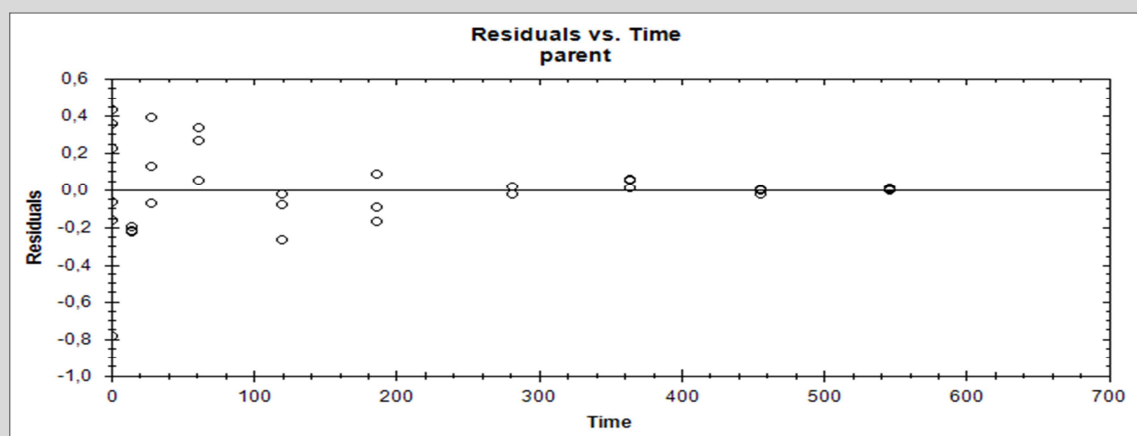
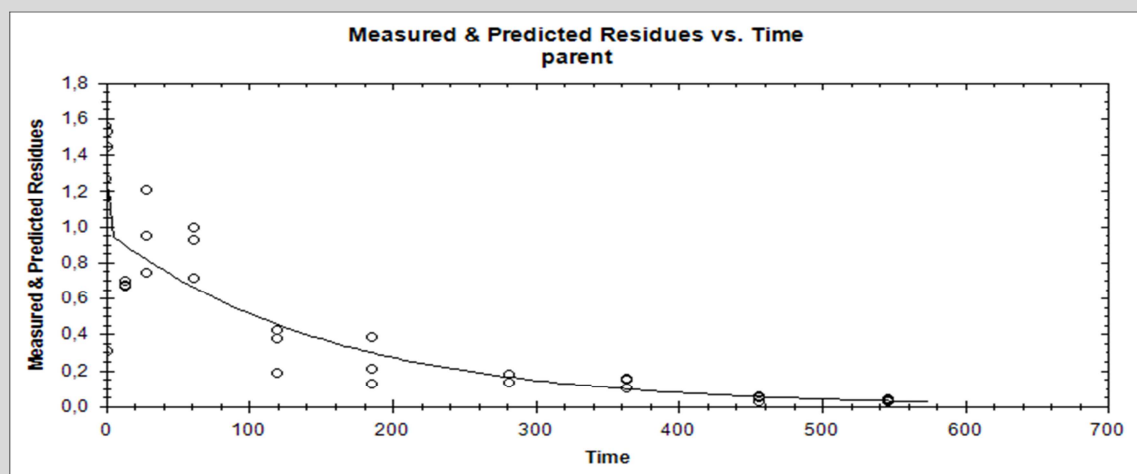
Parameter estimation
-----

Degrees of Freedom : 30
Parameter      Estimate      Lower CI      Upper CI      St.Dev      Prob > t
M(0) parent    :      1.136e+00      9.473e-01      1.305        9.644e-02      4.4e-13
alpha parent   :      6.079e+00      -3.387e+01      46.031      2.039e+01      0.384
beta parent    :      6.931e+03      -4.406e+03      5792.966      2.602e+03      0.394
-----

DT50 and DT90 values
-----
DT50 :      parent
DT90 :      319.20
Kinetic model :      FOMC

```


DFOP



| Chi2 error estimation | | | | | | |
|-------------------------|--------|----------|-----------|----------|----------|----------|
| | | parent | All | | | |
| Chi2Err% | | 18.46 | 18.46 | | | |
| Kinetic model : | | DFOP | | | | |
| Parameter estimation | | | | | | |
| Degrees of Freedom : 25 | | | | | | |
| Parameter | | Estimate | Lower CI | Upper CI | St.Dev | Prob > t |
| H(0) | parent | 1.328339 | 1.071921 | 1.585 | 0.130808 | 2.33e-11 |
| k1 | parent | 1.066879 | -1.500834 | 3.635 | 1.310692 | 0.2119 |
| k2 | parent | 0.006403 | 0.003671 | 0.009 | 0.001394 | 3.30e-05 |
| g | parent | 0.264478 | 0.032146 | 0.507 | 0.123642 | 0.0205 |
| DT50 and DT90 values | | | | | | |
| | | parent | | | | |
| DT50 : | | 60.275 | | | | |
| DT90 : | | 311.41 | | | | |
| Kinetic model : | | DFOP | | | | |

The endpoints are:

| Site | DT50 | DT90 | Chi² | t-test | Kinetic model |
|--------|------|------|------|--------|---------------|
| | [d] | [d] | [%] | | |
| Fresno | 89 | 295 | 20.7 | < 0.01 | SFO |

| | |
|---------------------|---|
| Reference: | DECLINE OF ETHOFUMESATE RESIDUES IN SOIL FOLLOWING APPLICATION WITH A 50 SC FORMULATION IN THE FEDERAL REPUBLIC OF GERMANY 1988/89 |
| Notifier: | Taskforce |
| Author(s), year: | Snowdon, P. J.;1991 |
| Report/Doc. number: | A83344 / W 85 / M-155613-01-1 |
| Guideline(s): | None |
| GLP: | yes |
| Deviations: | |
| Validity: | Not valid |
| Status: | Previous evaluation in DAR for original approval / baseline dossier. |

Study summary based on previous draft assessment report

Materials and Methods

The dissipation of ethofumesate from soil following treatment with a 50 SC formulation (50% ethofumesate) was investigated under field conditions on four plots (for soil properties, see table below) situated in the Federal Republic of Germany in 1988/89.

Table 8-73: Soil characteristics

| Site/soil | OC (%) | pH | sand (%) | silt (%) | clay (%) | MHC (%), | CEC meq/100 g | Biomass mg/100 g dw |
|-----------------------------|-----------|-----|-------------|-------------|-------------|-------------|------------------|------------------------|
| Thann sandy loam/loam | 2.0 | 6.6 | 60 | - | - | 47 | n.r | 18 |
| Niederkirchen sandy loam | 0.6 | 6.8 | 44 | - | - | 33 | n.r | 34 |
| Goch-Nierswalde sandy loam | 2.8 | 6.0 | 73 | - | - | 65 | n.r | 33 |
| Langförden-Lohe humous sand | 3.9 | 4.7 | 95 | - | - | 43 | n.r | 16 |

The formulation was sprayed onto the 3200 - 5000 m² plots in May or June, 1988, at the rate of 2.0 kg as/ha. Samples were taken at various intervals for one year following treatment. At each sampling time, twenty soil cores (to a depth of 30 cm) were taken from each plot. The cores were sectioned and combined into 10 cm horizons. Analysis for ethofumesate was performed in duplicate or single samples by GC after soxhlet extraction with acetone followed by partition into hexane. The limit of determination was 0.02 mg as/kg. The air temperature ranged from -6 - 22°C in Thann, -5 - 27°C in Niederkirchen, -1 - 17°C in Goch-Nierswalde, and -4 - 25°C in Langförden-Lohe during the study period. The total rainfall was ca. 750 mm in Thann, 460 mm in Niederkirchen, 740 mm in Goch-Nierswalde, and 680 mm in Langförden-Lohe.

Results

The mean recovery of the method of analysis was $89 \pm 14\%$. The residue levels were corrected for the mean recovery and were based on the total dry weight content in the soil columns. The half-lives of ethofumesate in the upper 10 cm soil layer were calculated using two different models. The results are summarised in the tables below.

Figure 8-66: Ethofumesate residue levels in soil samples from German field trials

| Interval | Residue level (mg/kg) | | | Residue level (mg/kg) | | |
|-----------|-----------------------|------------------------|------------|--------------------------|------------|------------|
| | 0 - 10 cm | 10 - 20 cm | 20 - 30 cm | 0 - 10 cm | 10 - 20 cm | 20 - 30 cm |
| | Trial site Thann | | | Trial site Niederkirchen | | |
| 0 days | 0.82, 0.83 | 0.03, ND, <0.02, <0.02 | ND, <0.04 | 0.36, 0.34 | NM | NM |
| 1 day | ND, ND | <0.02 | ND, ND | 0.45 | NM | NM |
| 3 days | <0.02 | ND, <0.02 | ND, ND | 0.43 | NM | NM |
| 7 days | ND, <0.02 | ND | <0.02 | 0.31 | NM | NM |
| 14 days | ND | ND, <0.02 | ND | 0.30 | NM | NM |
| 28 days | ND, 0.04 | ND, ND, <0.03 | ND | 0.14 | NM | NM |
| 2 months | <0.02 | <0.02 | ND | 0.19, 0.24 | NM | NM |
| 6 months | ND, ND | <0.02 | ND | 0.09, 0.10 | NM | NM |
| 12 months | ND | NM | NM | 0.02 | NM | NM |
| | Trial site Nierswalde | | | Trial site Langförden | | |
| 0 days | 1.2, 1.3 | ND, <0.02 | NM | 0.85, 1.0 | NM | NM |
| 1 day | 0.91, 0.92, 0.92 | ND, 0.03 | NM | 0.84 | NM | NM |
| 3 days | 0.93, 1.2 | ND, <0.02, 0.12 | NM | 0.97, 0.66 | NM | NM |
| 7 days | 1.5, 1.4, 1.1, 1.0 | 0.02 | NM | 0.81 | NM | NM |
| 14 days | 1.1, 1.1, 0.88, 0.86 | ND, ND | NM | 0.34, 0.39 | NM | NM |
| 28 days | 0.88, 1.1 | 0.02 | NM | 0.66, 0.78 | NM | NM |
| 2 months | 0.69, 0.52 | NM | ND | 0.52, 0.88 | NM | NM |
| 6 months | 0.34 | NM | NM | 0.64, 0.64 | NM | NM |
| 12 months | 0.14 | NM | NM | 0.18 | NM | NM |

ND...Not detected

NM...Not measured

Residues were found mainly in the upper 10 cm of the cores but were also detected in lower horizons. In Thann, no measurable residues were found from day 1 onwards.

Comments RMS

The dissipation of ethofumesate from soil following treatment with a 50 SC formulation (50% ethofumesate) was investigated at four sites in Germany (Thann, Niederkirchen, Nierswalde, and Langforden) in 1988/89. The

application (2000 g/ha) was made to bare soil at all sites, on the 13th June, 1988 at Niederkirchen; on 28th May, 1988 at Nierswalde; and on 31st May, 1988 at Langförden. Plots were kept bare. At each sampling time, twenty soil cores (to a depth of 30 cm) were taken from each plot and sectioned into 10 cm horizons.

Information on the soils is not appropriate. Soil data consisted only of an abbreviation for soil classification system (most likely the German classification), and the percentage of soil in size class < 20 µm.

In Niederkirchen and Langförden, only the upper 10 cm horizon were analysed for residues. At Langförden, from day zero to day 28, the upper 20 cm were analysed and after the 28 day sampling date, only the upper 10 cm were analysed. Therefore, potential losses due to leaching of the test substance cannot be ruled out and the studies are excluded from further considerations.

At Thann, no ethofumesate residues could be found in the sampled soils. However, ethofumesate was found at concentrations up to 0.3 mg /kg in control samples from the same site. This leads to the assumption that the analytical method was not appropriate, that samples have been mixed up during preparation or that ethofumesate had been previously applied at the control site.

The study is not valid.

| | |
|---------------------|--|
| Reference: | DECLINE OF ETHOFUMESATE RESIDUES IN SOIL FOLLOWING APPLICATION WITH A 50 SC FORMULATION IN THE UK 1990/91 |
| Notifier: | Taskforce |
| Author(s), year: | Snowdon, P. J.;1991 |
| Report/Doc. number: | A83357 / W 97 / M-155626-01-1 |
| Guideline(s): | None |
| GLP: | yes |
| Deviations: | |
| Validity: | Valid |
| Status: | Previous evaluation in DAR for original approval / baseline dossier. |

Study summary based on previous draft assessment report

Materials and Methods

The dissipation of ethofumesate from soil following treatment with a 50 SC formulation (50% ethofumesate) was investigated under field conditions on two plots (for soil properties, see table below) situated in the United Kingdom in 1990/91.

Table 8-74: Soil characteristics.

| Soil | OC (%) | pH | sand (%) | silt (%) | clay (%) | MHC (%), @ 1/3 bar | CEC meq/100 g |
|----------------------------|--------|-----|----------|----------|----------|-----------------------|------------------|
| Willingham sandy clay loam | 2.0 | 7.5 | 28 | 45 | 27 | n.r | 22 |
| Isleham loamy sand | 12 | 7.5 | 55 | 33 | 9 | n.r | 43 |

The formulation was sprayed onto the 21 x 36 m plots in May 1990, at the rate of 1.5 kg as/ha. The plots were kept weed-free by application of paraquat. Samples were taken at various intervals for 282 and 366 days in Willingham and Isleham, respectively, following treatment with the formulated ethofumesate. At each sampling time, ten soil cores (to a depth of 30 cm) were taken from each plot. The cores were divided into 10 cm sections, and all sections from each depth combined before analysis. Analysis for ethofumesate was performed in single samples by GC after soxhlet extraction with acetone followed by partition into hexane. The limit of determination was 0.05 mg as/kg. The air temperature ranged from -3 to 26°C in Willingham, and between -1 and 25°C in Isleham during the study period. The total rainfall was 301 mm in Willingham and 353 mm in Isleham.

Results

The mean recovery of the method of analysis was 90±16%. The residue levels were corrected for the mean recovery and were based on the total dry weight content in the soil columns. The half-lives of ethofumesate in the upper 30 cm soil layer were calculated to 29 days in Willingham and to 44 days in Isleham using a Topfit model (modified first order kinetics, goodness of fit= 0.059 and 0.026, respectively), and to 12 (6 - 17, 95% CL) and 36 (27 - 45, 95% CL) days using a Timme model (first order kinetics). The corresponding DT₉₀ values were determined to be 121 (Topfit) or 129 (70-188) (Timme) days in Willingham, and 145 or 120 (91-148) days in Isleham. Residues were found mainly in the upper 10 cm of the cores but were also detected in the 20 - 30 cm horizon.

Table 8-75: Decline of Ethofumesate concentrations in the field trials Willingham and Isleham

| Trial site Willingham | | Trial site Isleham | |
|-----------------------|------------------|----------------------|------------------|
| days after treatment | Residues [µg/kg] | days after treatment | Residues [µg/kg] |
| 0 | 0.815 | 0 | 1.115 |
| 1 | 0.685 | 1 | 1.535 |
| 3 | 0.535 | 3 | 1.225 |
| 7 | 0.575 | 7 | 0.955 |
| 14 | 0.875 | 14 | 1.145 |
| 28 | 0.505 | 28 | 0.935 |
| 56 | 0.203 | 56 | 0.715 |
| 91 | 0.165 | 91 | 0.485 |
| 197 | 0.025 | 190 | 0.025 |
| 289 | NA | 282 | NA |
| 366 | 0.025 | | |

Comments RMS:

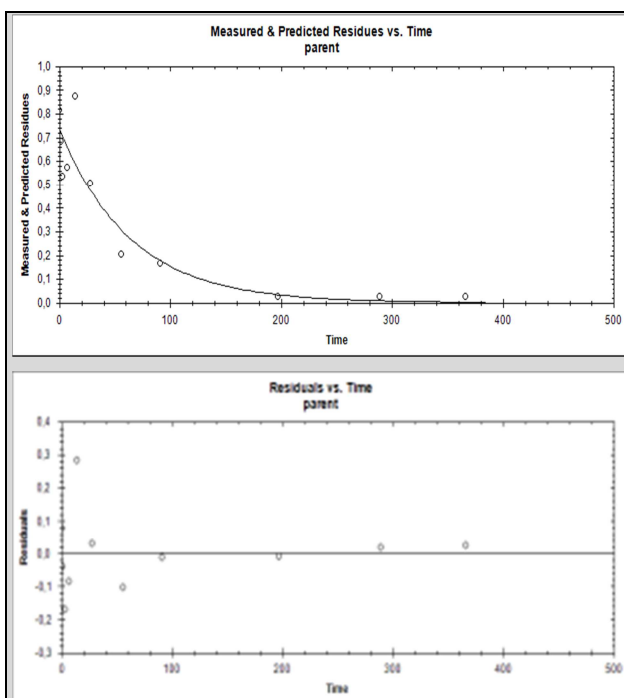
The field dissipation of ethofumesate from soil following treatment with a 50 SC formulation (50% ethofumesate) was investigated at two bare plots in the United Kingdom in 1990/91. The formulation was applied at a rate of 1.5 kg as/ha. The plots were kept bare by application of paraquat. Samples were taken at various intervals for 282 and 366 days in Willingham and Isleham, respectively. At each sampling time, ten soil cores (to a depth of 30 cm) were taken from each plot. The cores were split into 10 cm sections, and the sections from each depth combined before analysis. Analysis for ethofumesate was performed in single samples by GC after soxhlet extraction with acetone followed by partition into hexane. The reported LOQ was 0.05 mg/kg, which was deemed not acceptable in the previous evaluation as it corresponds to 2.5% of the nominally applied test substance (based on the 0-5 cm soil horizon and a bulk density of 1.5 g cm⁻³). The method was cross referenced to Manley, J.D.(1974; Registration reference NC 8438/W 59). Nevertheless, the RMS considers the LOQ acceptable albeit higher than the LOQ of the other studies (0.01 – 0.04 mg/kg).

Degradation kinetics for the non-normalized trials were recalculated by RMS with all samples below LOD set to 1/2 LOD or - after the first non-detect (time and depth) – set to zero in case no detects appeared later on. Values between LOD and LOQ were set to 0.5 x (LOQ + LOD). The results are shown in the figures below.

| Site | DT50 | DT90 | Chi ² | t-test | Kinetic model |
|------------|------|------|------------------|--------|---------------|
| Willingham | 44 | 147 | 22.26 | < 0.01 | SFO |
| Isleham | 59 | 196 | 12.32 | < 0.01 | SFO |

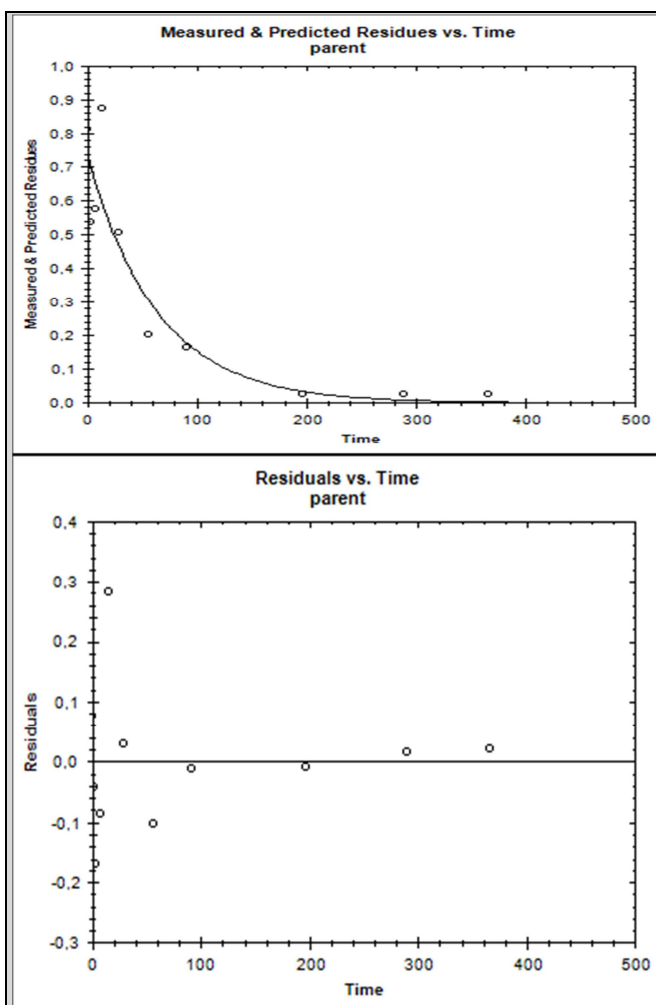
Kinetic evaluation field trial Willingham, non-normalized (SFO)

| | | | | | | |
|------------------------|-----------------|------------|----------|----------|----------|----------|
| Chi2 error estimation | | | | | | |
| ----- | | | | | | |
| | | parent | All | | | |
| | Chi2Err4 : | 22.26 | 22.26 | | | |
| | Kinetic model : | SFO | | | | |
| ----- | | | | | | |
| Parameter estimation | | | | | | |
| ----- | | | | | | |
| Degrees of Freedom : 9 | | | | | | |
| Parameter | | Estimate | Lower CI | Upper CI | St.Dev | Prob > t |
| M(0) | parent | : 0.737475 | 0.614073 | 0.861 | 0.062961 | 4.73e-07 |
| k | parent | : 0.015692 | 0.006702 | 0.025 | 0.004587 | 0.00381 |
| ----- | | | | | | |
| DT50 and DT90 values | | | | | | |
| ----- | | | | | | |
| | | parent | | | | |
| | DT50 : | 44.171 | | | | |
| | DT90 : | 146.73 | | | | |
| | Kinetic model : | SFO | | | | |



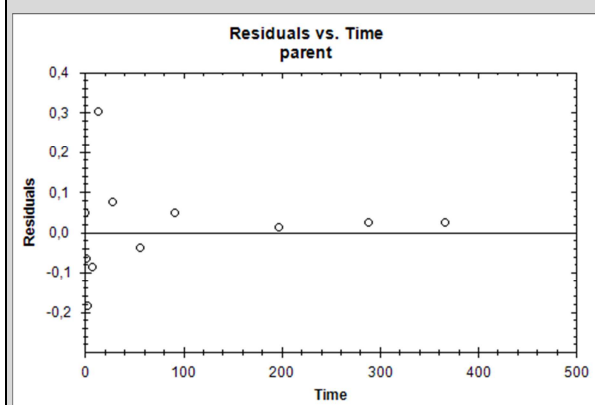
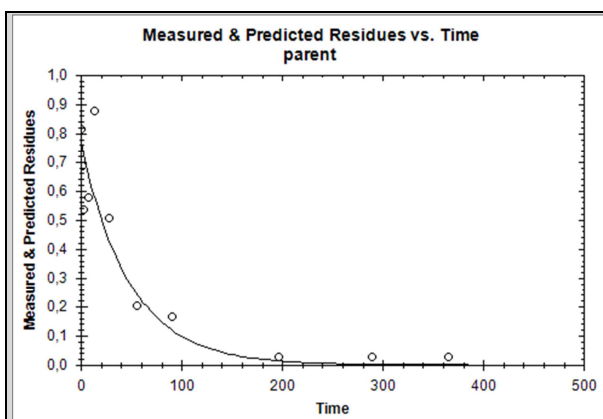
Kinetic evaluation field trial Willingham (DFOP)

```
# Chi2 error estimation
#
#      parent      All
#      Chi2Err% :    24.41    24.41
#      Kinetic model :      DFOP
#
# Parameter estimation
#
# Degrees of Freedom : 7
#
# Parameter      Estimate      Lower CI      Upper CI      St.Dev      Prob > t
#-----
M(0) parent      1      0.7374731    0.5974470    0.877    0.0714432    8.67e-06
x1 parent        1      0.0156955    -0.0807472    0.112    0.0492064    0.3795
x2 parent        1      0.0156906    0.0006161    0.031    0.0076912    0.0404
q parent         1      0.1035923    -0.8404475    1.048    0.4016618    0.4179
#
# DT50 and DT90 values
#
#      parent
#      DT50 :    44.175
#      DT90 :    146.74
#      Kinetic model :      DFOP
```



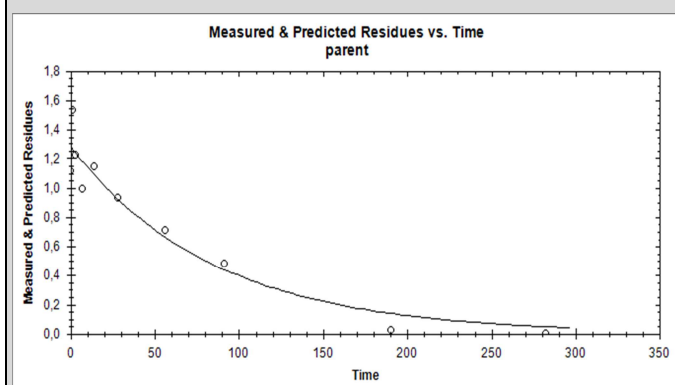
Kinetic evaluation field trial Willingham (FOMC)

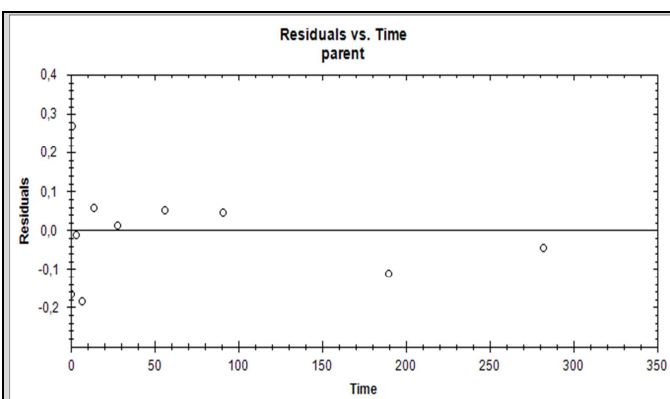
| | | | | | | |
|------------------------|-----------|------------|-----------|-----------|----------|--|
| Chi2 error estimation | | | | | | |
| | parent | All | | | | |
| Chi2Err% | 24.43 | 24.43 | | | | |
| Kinetic model | FOMC | | | | | |
| Parameter estimation | | | | | | |
| Degrees of Freedom : 8 | | | | | | |
| Parameter | Estimate | Lower CI | Upper CI | St.Dev | Prob > t | |
| M(0) parent | 7.455e-01 | 4.397e-01 | 0.892 | 6.442e-02 | 1.15e-06 | |
| alpha parent | 2.410e+02 | -1.419e+03 | 1039.692 | 8.463e+02 | 0.392 | |
| beta parent | 3.164e+04 | -8.861e+04 | 91078.889 | 4.094e+04 | 0.392 | |
| DT50 and DT90 values | | | | | | |
| | parent | | | | | |
| DT50 | 13.507 | | | | | |
| DT90 | 111.68 | | | | | |
| Kinetic model | FOMC | | | | | |



Kinetic evaluation field trial Isleham, non-normalized (SFO)

| | | | | | |
|------------------------|----------|----------|----------|----------|----------|
| Chi2 error estimation | | | | | |
| ----- | | | | | |
| | parent | All | | | |
| Chi2Err% | 12.32 | 12.32 | | | |
| Kinetic model : | SFO | | | | |
| ----- | | | | | |
| Parameter estimation | | | | | |
| ----- | | | | | |
| Degrees of Freedom : 8 | | | | | |
| Parameter | Estimate | Lower CI | Upper CI | St.Dev | Prob > t |
| (0) parent : | 1.281721 | 1.147464 | 1.416 | 0.068508 | 3.44e-08 |
| parent : | 0.611727 | 0.007486 | 0.916 | 0.002164 | 0.000315 |
| ----- | | | | | |
| DT50 and DT90 values | | | | | |
| ----- | | | | | |
| | parent | | | | |
| DT50 : | 59.108 | | | | |
| DT90 : | 196.35 | | | | |
| Kinetic Model : | SFO | | | | |





Kinetic evaluation field trial Isleham, non-normalized (DFOP)

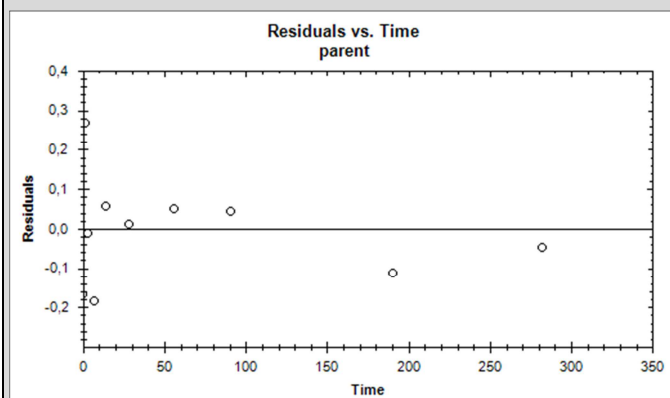
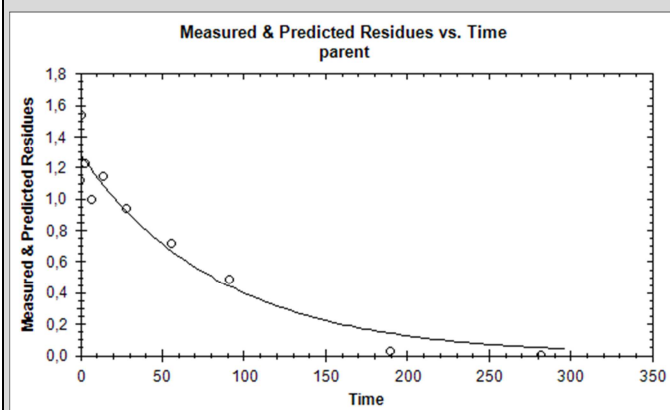
```
Chi2 error estimation
=====
                parent          All
    Chikerr4 :      13.67      13.67
    Kinetic model :      DFOP

=====

Parameter estimation
=====

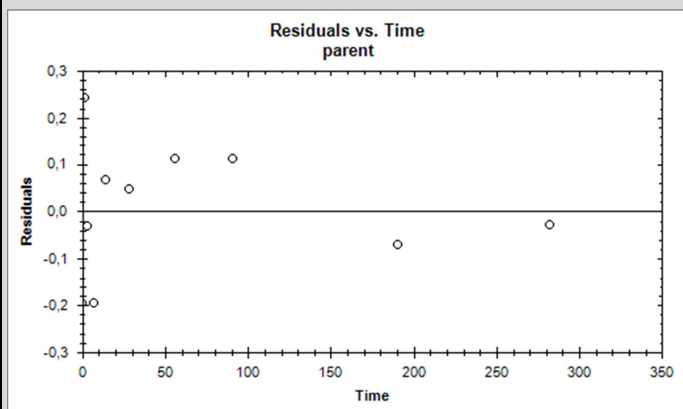
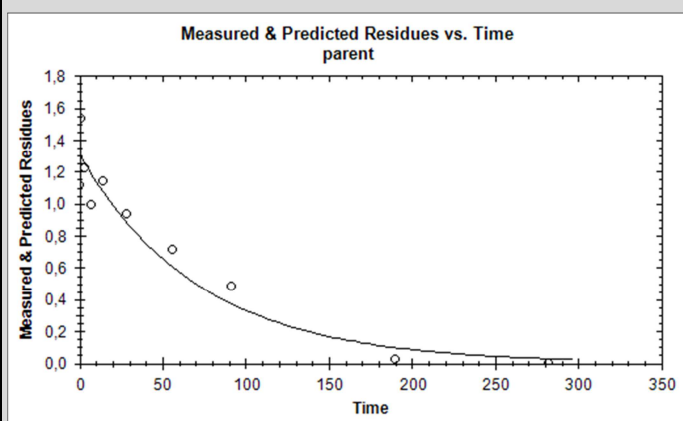
Degrees of Freedom : 6
Parameter
K(0) parent      1      1.281718      1.083459      1.480      0.101155      7.4e-06
k1 parent      1      0.011728      -0.097515      0.121      0.05573E      0.42015
k2 parent      1      0.011728      0.005459      0.018      0.00319E      0.00525
d parent      1      0.036775      -0.380783      0.454      0.213045      0.43432

=====
DT50 and DT90 values
=====
                parent
    DT50 :      59.104
    DT90 :      196.34
    Kinetic model :      DFOP
```



Kinetic evaluation field trial Isleham, non-normalized (FOMC)

| | | | | | |
|------------------------|-----------|------------|-----------|-----------|----------|
| Chi2 error estimation | | | | | |
| | parent | All | | | |
| Chi2Errt : | 13.57 | 13.57 | | | |
| Kinetic model : | FOMC | | | | |
| Parameter estimation | | | | | |
| Degrees of Freedom : 7 | | | | | |
| Parameter | Estimate | Lower CI | Upper CI | St.Dev | Prob > t |
| ((0)) parent : | 1.310e+00 | 1.173e+00 | 1.444e+00 | 6.795e-02 | 1.26e-07 |
| alpha parent : | 1.725e+02 | -1.151e+03 | 1.496e+03 | 6.755e+02 | 0.403 |
| beta parent : | 1.242e+04 | -8.324e+04 | 1.083e+05 | 4.881e+04 | 0.403 |
| DT50 and DT90 values | | | | | |
| | parent | | | | |
| DT50 : | 50.025 | | | | |
| DT90 : | 166.96 | | | | |
| Kinetic model : | FOMC | | | | |



| | |
|---------------------|--|
| Reference: | DISSIPATION OF ETHOFUMESATE IN SOIL FOLLOWING TREATMENT OF AN EC CO-FORMULATION WITH PHENMEDIPHAM AND DESMEDIPHAM IN THE FEDERAL REPUBLIC OF GERMANY 1990 |
| Notifier: | Taskforce |
| Author(s), year: | Moede, J.;1992 |
| Report/Doc. number: | A83378 / W 121 / M-155646-01-1 |
| Guideline(s): | None |
| GLP: | yes |
| Deviations: | |
| Validity: | Valid |
| Status: | Previous evaluation in DAR for original approval / baseline dossier. |

Study summary based on previous draft assessment report

Materials and Methods

The dissipation of ethofumesate from soil following treatment with an EC co- formulation (128 g ethofumesate/l) with phenmedipham (62 g/l) and desmedipham (16 g/l) was investigated under field conditions on four plots (for soil properties, see table below) situated in the Federal Republic of Germany in 1990/91.

Table 8-76: Soil characteristics

| Site/soil | OC (%) | pH | sand (%) | silt (%) | clay (%) | MHC (%), | CEC meq/100 g | Biomass mg/100 g dw |
|-----------------------|-----------|-----|-------------|-------------|-------------|-------------|------------------|------------------------|
| Keeken loam | 4.4 | 6.1 | 32 | 41 | 32 | 87 | n.r | 58 |
| Asperden sand | 2.6 | 6.2 | 85 | 7.9 | 6.9 | 47 | n.r | 13 |
| Weeze sand | 3.8 | 5.8 | 88 | 5.7 | 6.5 | 49 | n.r | 17 |
| Nierswalde sandy loam | 3.5 | 6.2 | 70 | 18 | 12 | 61 | n.r | 36 |

The formulation was sprayed onto bare soil plots in June 1990, at the rate of 6 l product/ha, corresponding to 0.8 kg ethofumesate/ha. Samples were taken at various intervals for one year following treatment with the formulated product. At each sampling time, twenty soil cores (to a depth of 30 cm) were taken from each plot. The cores were sectioned and combined into 10 cm horizons. Analysis for ethofumesate was performed in single samples by GC after soxhlet extraction with acetone following partitioning into hexane. The limit of determination was 0.04 mg as/kg. No weather data were reported.

Results

The mean recovery of the method of analysis was 94±5% and 87±4% (two different sets of recovery determinations). The residue levels were corrected for the mean recovery of 94% in samples from days 0 - 214, and 87% in samples from 12 months. The levels were based on the total dry weight content in the soil columns. The half-lives of ethofumesate in the upper 10 cm soil layer were calculated to 59 days in Keeken, 133 days in

Weeze, and to 355 days in Nierswalde using a Topfit model (first order kinetics, goodness of fit = 0.15, 0.025 and 0.054). The corresponding values assuming a Timme model (1.5th order kinetics) were 94 (38 -150), 105 (31-179) and 253 (122-384) days. The DT₉₀ values ranged between 196 days and >3 years. Residues were found only in the upper 10 cm of the cores. In Asperden, no measurable residues were found from day 7 onwards (only 0.07 mg/kg on day 1).

Table 8-77: Residues of ethofumesate in soil (0-10 cm) in four German field trials

| Days after application | Trial locations | | | |
|------------------------|-------------------|----------|-------|------------|
| | Keeken | Asperden | Weeze | Nierswalde |
| | Residues in mg/kg | | | |
| 0 ¹ | <0.04 | <0.04 | <0.04 | <0.04 |
| 0 ² | 0.08 | 0.06 | 0.39 | 0.22 |
| 1 | 0.41 | 0.07 | 0.32 | 0.28 |
| 7 | 0.41 | <0.04 | 0.36 | 0.19 |
| 14 | 0.39 | 0.04 | 0.36 | 0.25 |
| 28 | 0.39 | <0.04 | 0.19 | 0.20 |
| 61 | 0.05 | <0.04 | 0.24 | 0.34 |
| 122 | 0.07 | <0.04 | 0.18 | 0.23 |
| 214 | 0.05 | <0.04 | 0.17 | 0.18 |
| 12 months ³ | <0.04 | <0.04 | 0.09 | 0.07 |

¹ sampling before application

² sampling after application

³ 361 d after application: Keeken

365 d after application: Asperden

359 d after application: Weeze

366 d after application: Nierswalde

Table 8-78: Residues of ethofumesate in soil (10-20 cm) in four German field trials

| Days after application | Trial locations | | | |
|------------------------|-------------------|----------|-------|------------|
| | Keeken | Asperden | Weeze | Nierswalde |
| | Residues in mg/kg | | | |
| 0 ¹ | <0.04 | <0.04 | <0.04 | <0.04 |
| 0 ² | <0.04 | <0.04 | <0.04 | <0.04 |
| 1 | <0.04 | <0.04 | <0.04 | <0.04 |
| 7 | <0.04 | <0.04 | <0.04 | <0.04 |
| 14 | <0.04 | <0.04 | <0.04 | <0.04 |
| 28 | <0.04 | <0.04 | <0.04 | <0.04 |
| 61 | <0.04 | <0.04 | <0.04 | <0.04 |
| 122 | <0.04 | <0.04 | <0.04 | <0.04 |
| 214 | <0.04 | <0.04 | <0.04 | <0.04 |
| 12 months ³ | <0.04 | <0.04 | <0.04 | <0.04 |

¹ sampling before application

² sampling after application

³ 361 d after application: Keeken

365 d after application: Asperden

359 d after application: Weeze

366 d after application: Nierswalde

Comments RMS:

The trials were located in Germany at Keeken, Asperden, Weeze, and Nierswalde. A single large plot was used at each site, in representative agricultural land for sugarbeet. The application (800 g/ha) was made to bare soil and maintained bare. Soil samples were collected at various intervals, a single core to a depth of 30 cm, split into three 10 cm sections. The sites were maintained as bare ground throughout the assessment period.

The LOQ was 0.04 mg/kg, recovery efficiencies of 94 % and 87 % were reported for the study. For any of the trials, no residues were detected at any of the study site at any time point in the soil horizons below 10 cm.

For the site Asperden, no kinetic evaluation of the data from is possible due to the fact that most of the measured concentrations are at or below the LOD.

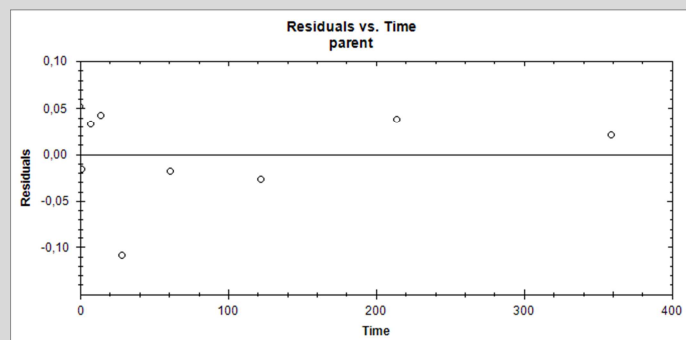
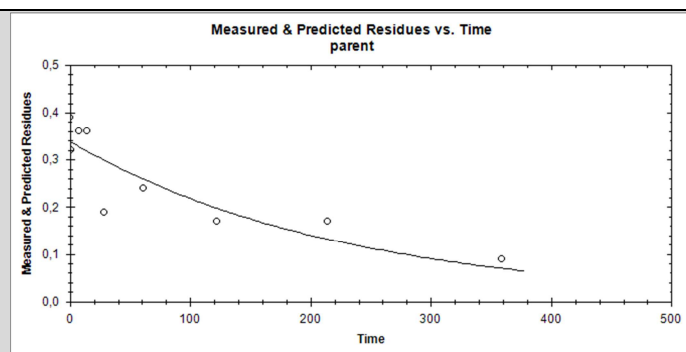
In case of the trial Nierswalde, the previous evaluation gave an $r^2 < 0.5$. Visual inspection showed that the bad fit can be attributed to the very large scatter of the observed data and it was concluded that no reliable evaluation of this dataset can be anticipated, independent of the model used. Therefore this dataset was excluded from the evaluation, because any result obtained from it would be too uncertain.

The RMS has re-evaluated the Weeze and Keeken field studies. The day 0 data point for the Keeken site is a clear outlier, and was therefore excluded from the analysis. A two-compartment model was considered (parent → sink). For the site Weeze, the parameters β (FOMC) and k_1 (DFOP) had a p value > 0.2. Therefore, despite the higher χ^2 , SFO was regarded as the more appropriate model.

The kinetic evaluation was carried out by the RMS. The results are in the tables below.

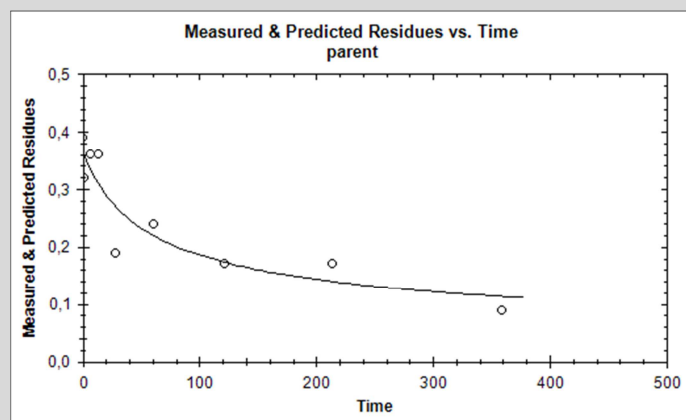
| Site | DT50 | DT90 | χ^2 | Kinetic model |
|--------|------|------|----------|---------------|
| Weeze | 157 | 522 | 15.0 | SFO |
| Keeken | 40 | 134 | 21.1 | SFO |

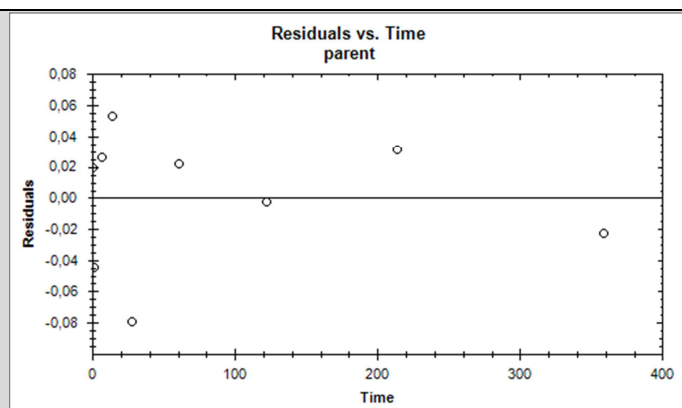
Kinetic evaluation trial Weeze, non-normalized (SFO)



| | | | | | | |
|------------------------|---|----------|----------|----------|----------|----------|
| | | parent | All | | | |
| Chi2Err% | : | 15.04 | 15.04 | | | |
| Kinetic model : | | SFO | | | | |
| ----- | | | | | | |
| Parameter estimation | | | | | | |
| ----- | | | | | | |
| Degrees of Freedom : 7 | | | | | | |
| Parameter | | Estimate | Lower CI | Upper CI | St.Dev | Prob > t |
| M(0) parent | : | 0.337949 | 0.284653 | 0.391 | 0.027090 | 2.45e-06 |
| k parent | : | 0.004410 | 0.001560 | 0.007 | 0.001454 | 0.00952 |
| ----- | | | | | | |
| DT50 and DT90 values | | | | | | |
| ----- | | | | | | |
| | | parent | | | | |
| DT50 : | | 157.17 | | | | |
| DT90 : | | 522.12 | | | | |
| Kinetic model : | | SFO | | | | |

Kinetic evaluation trial Weeze, non-normalized (FOMC)





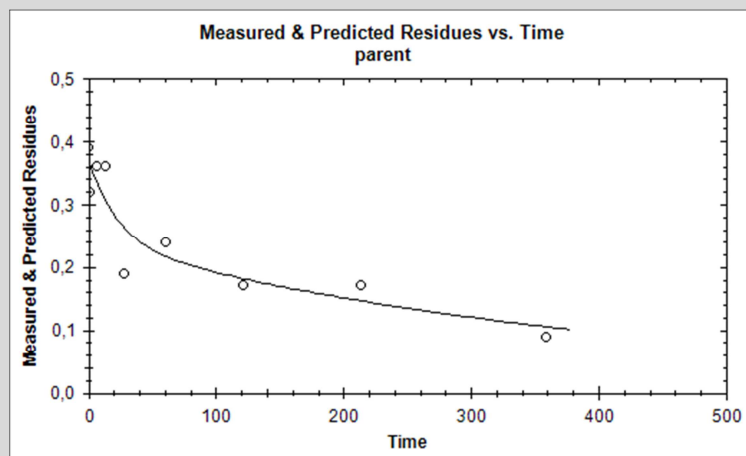
```

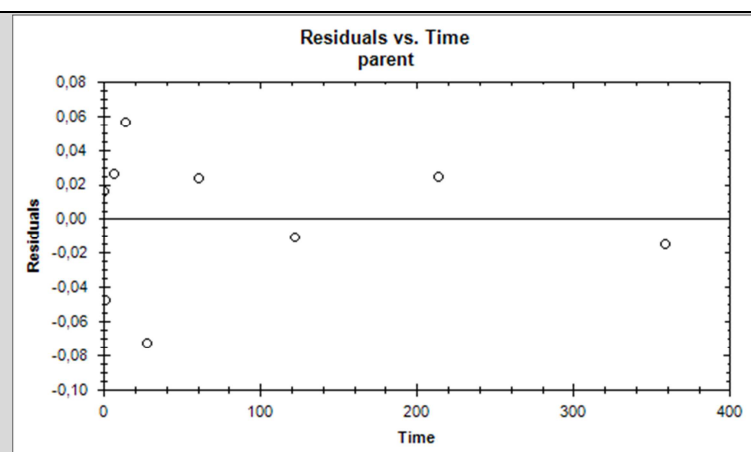
Chi error estimation
-----
      parent      All
ChiErr% :      13.13      13.13
Kinetic model :      FOMC

Parameter estimation
-----
Degrees of Freedom : 6
Parameter      Estimate      Lower CI      Upper CI      St.Dev      Prob > t
M(0) parent :      0.37049      0.30453      0.437      0.03375      1.69e-05
alpha parent :      0.44574      0.04348      0.848      0.20524      0.0364
beta parent :      26.85255      -35.22967      88.935      21.67518      0.2145

DT50 and DT90 values
-----
      parent
DT50 :      100.30
DT90 :      4677.1
Kinetic model :      FOMC
  
```

Kinetic evaluation trial Weeze, non-normalized (DFOP)





Chi2 error estimation

| | | |
|-----------------|--------|-------|
| | parent | All |
| Chi2Err% | 13,53 | 13,53 |
| Kinetic model : | DFOP | |

Parameter estimation

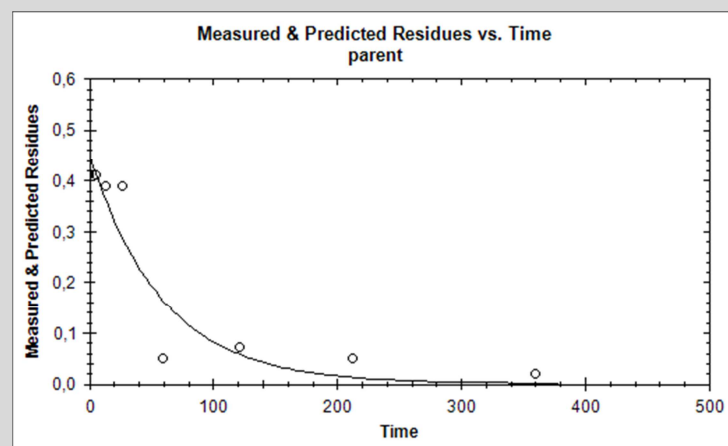
Degrees of Freedom : 5

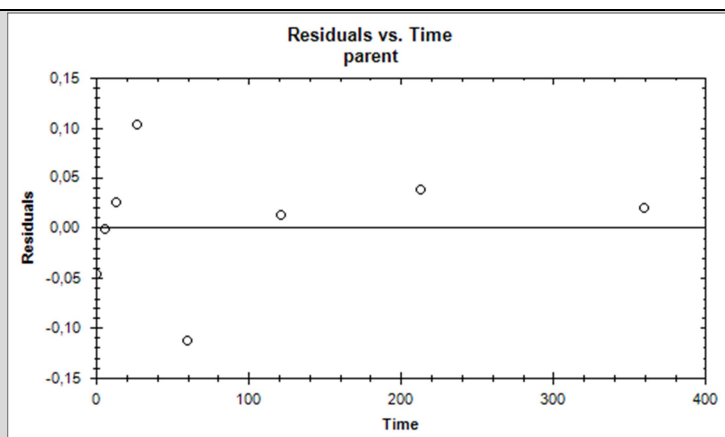
| Parameter | | Estimate | Lower CI | Upper CI | St.Dev | Prob > t |
|-----------|--------|----------|-----------|----------|----------|----------|
| M(0) | parent | 0.373784 | 0.303480 | 0.444 | 0.035870 | 7.01e-05 |
| k1 | parent | 0.043405 | -0.051819 | 0.139 | 0.048625 | 0.2065 |
| k2 | parent | 0.002271 | -0.001189 | 0.006 | 0.001765 | 0.1273 |
| g | parent | 0.364788 | -0.090690 | 0.820 | 0.232391 | 0.0886 |

DT50 and DT90 values

| | |
|-----------------|--------|
| | parent |
| DT50 : | 108.32 |
| DT90 : | 814.08 |
| Kinetic model : | DFOP |

Kinetic evaluation trial Keeken, non-normalized (SFO)





```

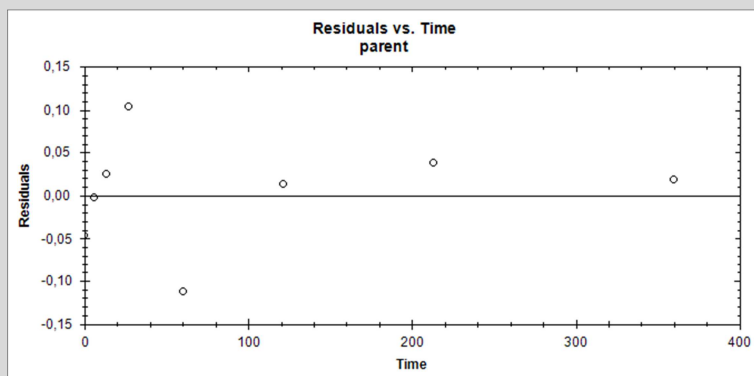
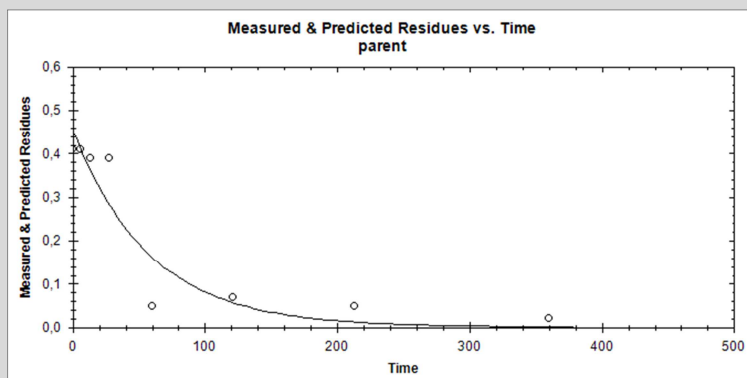
Chi2 error estimation
-----
          parent      All
Chi2Err% :      21.11      21.11
Kinetic model :      SFO

Parameter estimation
-----

Degrees of Freedom : 6
Parameter      Estimate      Lower CI      Upper CI      St.Dev      Prob > t
M(0) parent    :      0.455947      0.361714      0.550      0.048079      3.92e-05
k parent       :      0.017145      0.006785      0.028      0.005285      0.0088

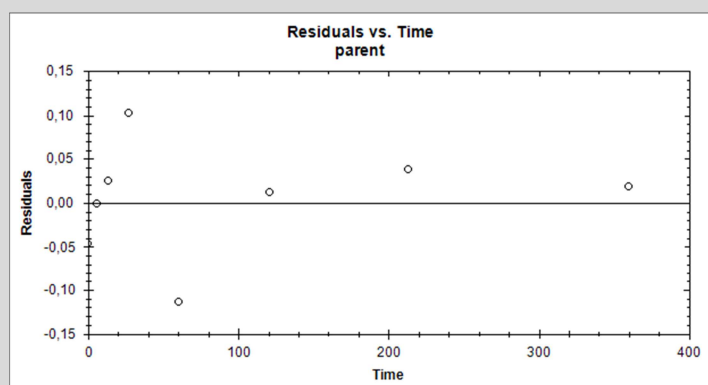
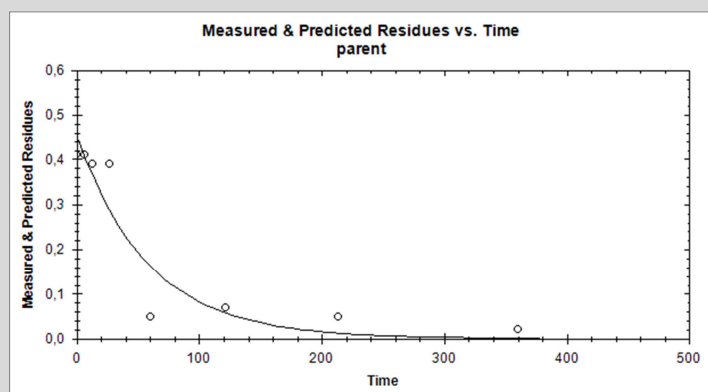
DT50 and DT90 values
-----
          parent
DT50 :      40.430
DT90 :      134.30
Kinetic model :      SFO
  
```

Kinetic evaluation trial Weeze, non-normalized (FOMC)



| | | | | | | | | | |
|------------------------|---|-----------|------------|---|-----------|----------|--|--|--|
| Chi2 error estimation | | | | | | | | | |
| ----- | | | | | | | | | |
| | | parent | All | | | | | | |
| Chi2Err% | : | 22.52 | 22.52 | <div>Right-Click to copy to clipboard</div> | | | | | |
| Kinetic model | : | FOMC | | | | | | | |
| ----- | | | | | | | | | |
| Parameter estimation | | | | | | | | | |
| ----- | | | | | | | | | |
| Degrees of Freedom : 5 | | | | | | | | | |
| Parameter | | Estimate | Lower CI | Upper CI | St.Dev | Prob > t | | | |
| M(0) parent | : | 4.568e-01 | 3.732e-01 | 0.54 | 4.268e-02 | 6.17e-05 | | | |
| alpha parent | : | 2.568e+02 | -3.684e+03 | 4197.47 | 2.011e+03 | 0.452 | | | |
| beta parent | : | 1.481e+04 | -2.129e+05 | 242536.60 | 1.162e+05 | 0.452 | | | |
| ----- | | | | | | | | | |
| DT50 and DT90 values | | | | | | | | | |
| ----- | | | | | | | | | |
| | | parent | | | | | | | |
| DT50 | : | 40.025 | | | | | | | |
| DT90 | : | 133.38 | | | | | | | |
| Kinetic model | : | FOMC | | | | | | | |

Kinetic evaluation trial Weeze, non-normalized (DFOP)



Chi2 error estimation

| | parent | All |
|---------------|--------|-------|
| Chi2Err% | 24.32 | 24.32 |
| Kinetic model | DFOP | |

Parameter estimation

| Degrees of Freedom : 4 | | | | | | |
|------------------------|--------|----------|-----------|----------|----------|----------|
| Parameter | | Estimate | Lower CI | Upper CI | St.Dev | Prob > t |
| M(0) | parent | 0.455953 | 0.341276 | 0.571 | 0.058510 | 0.000731 |
| k1 | parent | 0.017276 | -0.126083 | 0.161 | 0.073144 | 0.412442 |
| k2 | parent | 0.017129 | -0.005683 | 0.040 | 0.011639 | 0.107541 |
| g | parent | 0.072250 | -1.924630 | 2.071 | 1.019855 | 0.473461 |

DT50 and DT90 values

| | parent |
|---------------|--------|
| DT50 | 40.442 |
| DT90 | 134.34 |
| Kinetic model | DFOP |

| | |
|---------------------|--|
| Reference: | TESTS ON THE DEGRADATION OF ETHOFUMESATE IN THE TOPSOIL UNDER FIELD CONDITIONS AT FOUR DIFFERENT LOCATIONS. |
| Notifier: | Taskforce |
| Author(s), year: | Aldag, R.;1992 |
| Report/Doc. number: | A87554 / R 500-1 / M-161457-01-1 |
| Guideline(s): | BBA: IV, 4-1 |
| GLP: | no |
| Deviations: | |
| Validity: | Valid |
| Status: | Previous evaluation in DAR for original approval / baseline dossier. |

Study summary based on previous draft assessment report

Materials and Methods

The dissipation of ethofumesate from soil following treatment with the SC formulation Kemiron flow (500 g as/l) was investigated under field conditions on four plots (for soil properties, see table below) situated in the Federal Republic of Germany in 1990/91. The study was performed according to BBA Guidelines IV 4 - 1.

Table 8-79: Soil characteristics according to USDA classification.

| Site/soil | OC (%) | pH | sand (%) | silt (%) | clay (%) | MHC (%), | CEC meq/100 g | Biomass mg/100 g dw |
|-------------------------------|-----------|-----|-------------|-------------|-------------|-------------|------------------|------------------------|
| Mainz loamy silt | 1.9 | 7.5 | 7.0 | 81 | 12 | n.r. | n.r. | 22 |
| Speyer silty sand | 0.84 | 6.7 | 39 | 53 | 7.8 | n.r. | n.r. | 22 |
| Furth loamy silt | 1.3 | 6.0 | 3.4 | 82 | 14 | n.r. | n.r. | 20 |
| Reichelsheim sandy-loamy silt | 1.4 | 6.0 | 29 | 61 | 10 | n.r. | n.r. | 33 |

The plots were sprayed once with 3 l formulation/ha or twice with 1.5 l formulation/ha onto bare soil plots (50 m²) in April 1991, corresponding to 1.5 kg ethofumesate/ha in total. Samples were taken at various intervals for 9 - 13 months following treatment with the formulated product. At each sampling time, twenty soil cores (to a depth of 30 cm) were taken from each plot. The cores were sectioned and combined into 0 - 5 cm, 5 - 15 cm and 15 - 30 cm horizons. Analysis of ethofumesate was performed in single samples by GC after extraction with methanol and dichloromethane followed by partitioning into acetone. The limit of detection was 0.02 mg/kg. The monthly average temperature ranged from 0.7 - 24°C in Mainz, 0.9 - 20°C in Speyer and 1.5 - 19°C in Reichelsheim/Furth during the study period. The total rainfall was ca. 400 mm in Mainz, 430 mm in Niederkirchen and 650 mm in Reichelsheim/Furth.

Results

The recovery efficiency of the method of analysis ranged between 50 and 119% (mean 77%). The half-lives of ethofumesate in the upper 30 cm soil layer were calculated using a Timme model (1.5th order kinetics). The

results are summarised in the table below. In Mainz, residues were found to 30 cm depth, in Speyer, Furth and Reichelsheim, mainly in the upper 5 cm of the cores.

Table 8-80: Residue results in field trial Mainz (A and B) and Speyer (A and B)

| Mainz-Bretzenheim (A) | | | Mainz-Bretzenheim (B) | | |
|-----------------------|--------------|----------------|-----------------------|--------------|----------------|
| Date | Original DAA | Residues ug/kg | Date | Original DAA | Residues ug/kg |
| 08. Apr 91 | 0 | 2.9 | 15. Apr 91 | 0 | 2.854 |
| 22. Apr 91 | 14 | 1.3 | 06. Mai 91 | 21 | 2.836 |
| 06. Mai 91 | 28 | 2.4 | 03. Jun 91 | 49 | 2.478 |
| 03. Jun 91 | 56 | 2 | 29. Jul 91 | 105 | 1.764 |
| 29. Jul 91 | 112 | 1.33 | 23. Sep 91 | 161 | 0.682 |
| 23. Sep 91 | 168 | 0.53 | 18. Nov 91 | 217 | 0.786 |
| 18. Nov 91 | 224 | 0.82 | 13. Jan 92 | 273 | 0.687 |
| 13. Jan 92 | 280 | 0.72 | 09. Mai 92 | 329 | 0.516 |
| 09. Mrz 92 | 336 | 0.63 | 04. Mai 92 | 385 | 0.308 |
| 04. Mai 92 | 392 | 0.5 | | | |
| Speyer (A) | | | Speyer (A) | | |
| Date | Original DAA | Residues ug/kg | Date | Original DAA | Residues ug/kg |
| 15. Apr 91 | 0 | 2.09 | 22. Apr 91 | 0 | 2.3 |
| 29. Apr 91 | 14 | 1.31 | 13. Mai 91 | 21 | 0.908 |
| 06. Mai 91 | 21 | 0.84 | 10. Jun 91 | 49 | 0.56 |
| 10. Jun 91 | 56 | 0.79 | 06. Aug 91 | 106 | 0.396 |
| 06. Aug 91 | 113 | 0.55 | 30. Sep 91 | 161 | 0.272 |
| 30. Sep 91 | 168 | 0.25 | 25. Nov 91 | 217 | 0.104 |
| 25. Nov 91 | 224 | 0.22 | 20. Jan 92 | 273 | 0.096 |
| 20. Jan 92 | 280 | 0.15 | | | |

Comments RMS

The dissipation of ethofumesate from soil following treatment with the SC formulation Kemiron flow (500 g as/l) was investigated under field conditions in Germany. Four paired trials (referred to as A: single; and B: multiple) were carried out in Germany at Mainz-Bretzenheim, Speyer-Rinkenbergerhof, Furth-Odenwald and Reichelsheim-Odenwald. Two large plots were used at each site, in typical agricultural land. The plots were sprayed once with 3 l formulation/ha or twice with 1.5 l formulation/ha in April 1991, corresponding to 1.5 kg ethofumesate/ha in total. The applications were made to bare soil (and kept bare) at both sites. Soil cores were taken at various intervals for 9-13 months and each core was sectioned and combined into 0 - 5 cm, 5 - 15 cm and 15 - 30 cm horizons. Analysis of ethofumesate was performed in single samples by GC after extraction with methanol and dichloromethane followed by partitioning into acetone. The limit of detection was 0.02 mg/kg. Recovery efficiencies for the residue data at Furth-Odenwald and Reichelsheim-Odenwald were low (65% at Furth-Odenwald and very variable around a mean of 69% at Reichelsheim-Odenwald) and were therefore excluded from further kinetic analysis.

Only the single application trials were considered in the previous evaluation, however the notifier now has included also the multiple application trials for the locations Mainz and Speyer. Although the paired trials had identical soils, the application regimes (single and double applications) and sampling dates were different, so the pairs can be treated as separate. The LOD was 0.02 mg/kg. For Mainz-Bretzenheim (A), the data shows an outlier at day 14, and this was removed from the analysis. The kinetic evaluation was carried out by the RMS.

Based on the visual assessment and Chi² error DFOP represents the best fit for the Speyer A trial. However, zero is included in the confidence interval of k1, which makes this parameter unreliable. As zero is not included in any of the confidence intervals for the parameters of FOMC, FOMC appears more appropriate than DFOP.

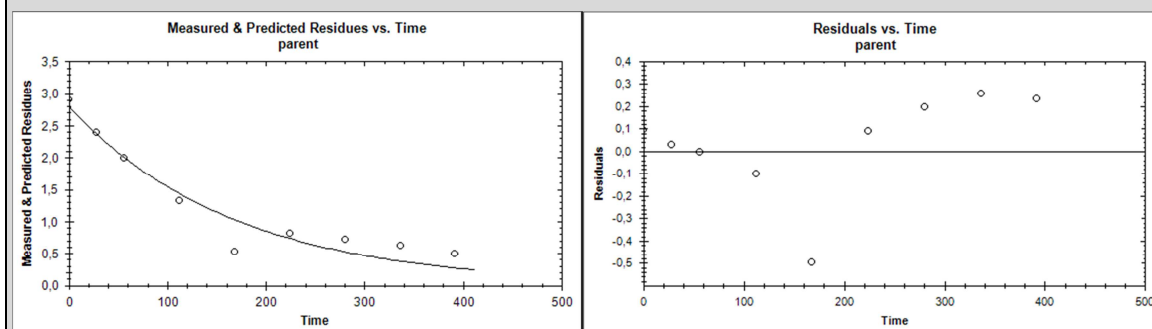
For the results see tables below.

| The endpoints are: | DT50 | DT90 | Chi ² | Kinetic model |
|--------------------|--------|------|------------------|---------------|
| | (d) | (d) | | |
| MainzA | 116 | 384 | 13.3 | SFO |
| MainzB | 114 | 379 | 11.3 | SFO |
| SpeyerA | 21* | 333 | 12.5 | FOMC |
| SpeyerB | 13.6** | 166 | 3.9 | DFOP |

* $\alpha = 0.004$, $\beta = 0.05$

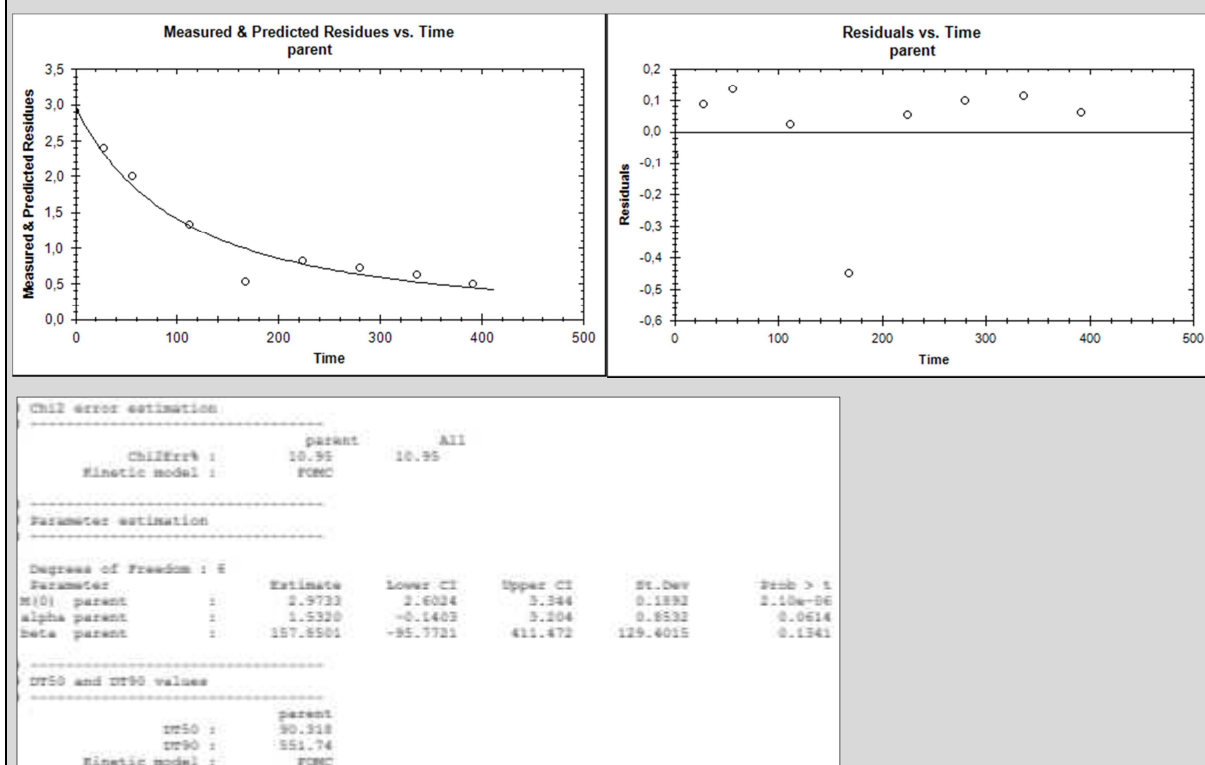
** $k_1 = 0.09528$, $k_2 = 0.00772$, $g = 0.6392$

Kinetic evaluation Mainz A, non normalized (SFO)

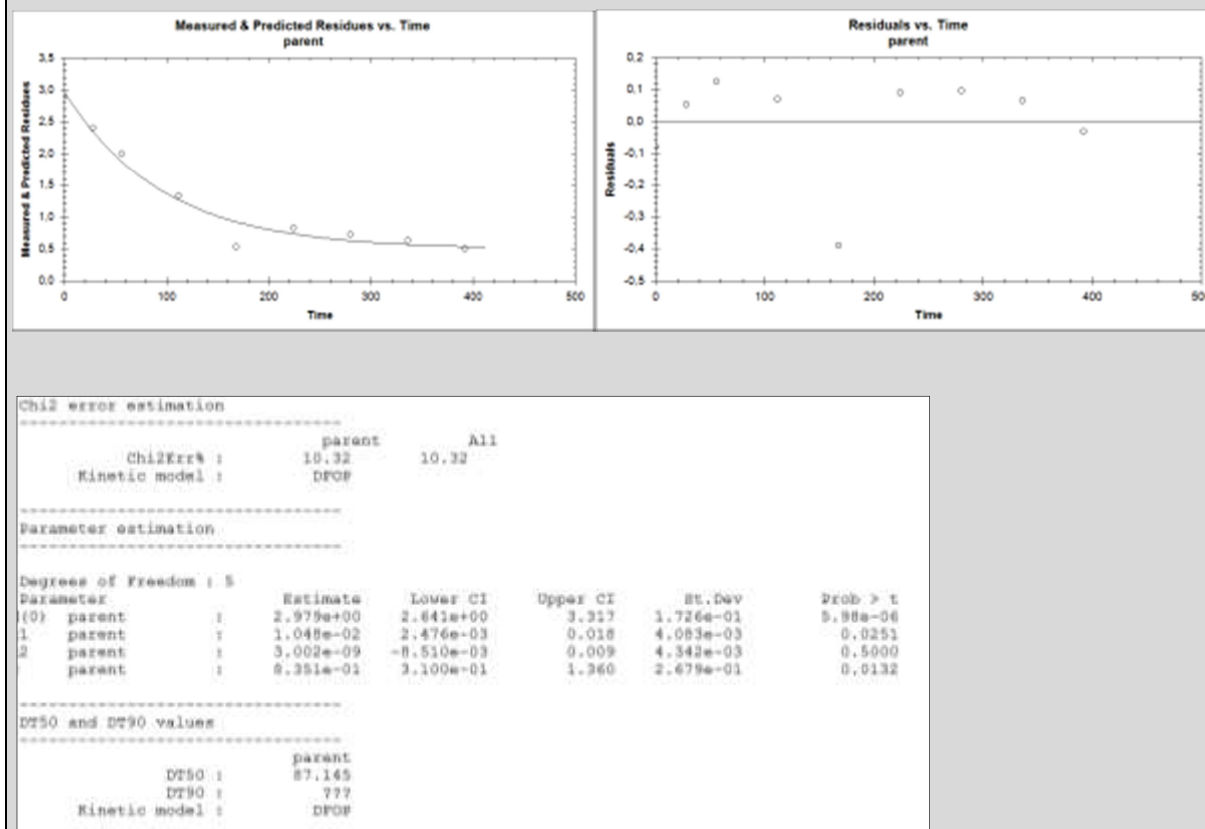


| | | | | | | |
|------------------------|--------|-----------|-----------|----------|-----------|----------|
| Chi2 error estimation | | | | | | |
| ----- | | | | | | |
| | | parent | All | | | |
| Chi2Err% | | 13.31 | 13.31 | | | |
| Kinetic model : | | SFO | | | | |
| ----- | | | | | | |
| Parameter estimation | | | | | | |
| ----- | | | | | | |
| Degrees of Freedom : 7 | | | | | | |
| Parameter | | Estimate | Lower CI | Upper CI | St.Dev | Prob > t |
| M(0) | parent | 2.8047444 | 2.4275907 | 3.182 | 0.1824285 | 5.54e-07 |
| k | parent | 0.0059988 | 0.0042793 | 0.008 | 0.0008773 | 0.000122 |
| ----- | | | | | | |
| DT50 and DT90 values | | | | | | |
| ----- | | | | | | |
| | | parent | | | | |
| DT50 : | | 115.55 | | | | |
| DT90 : | | 383.84 | | | | |
| Kinetic model : | | SFO | | | | |

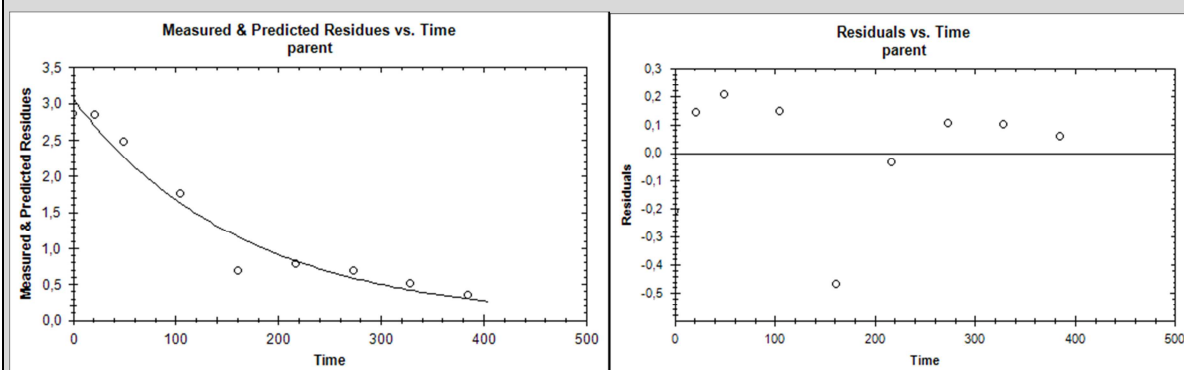
Kinetic evaluation Mainz A, non normalized (FOMC)



Kinetic evaluation Mainz A, non normalized (DFOP)



Kinetic evaluation Mainz B, non normalized (SFO)



```

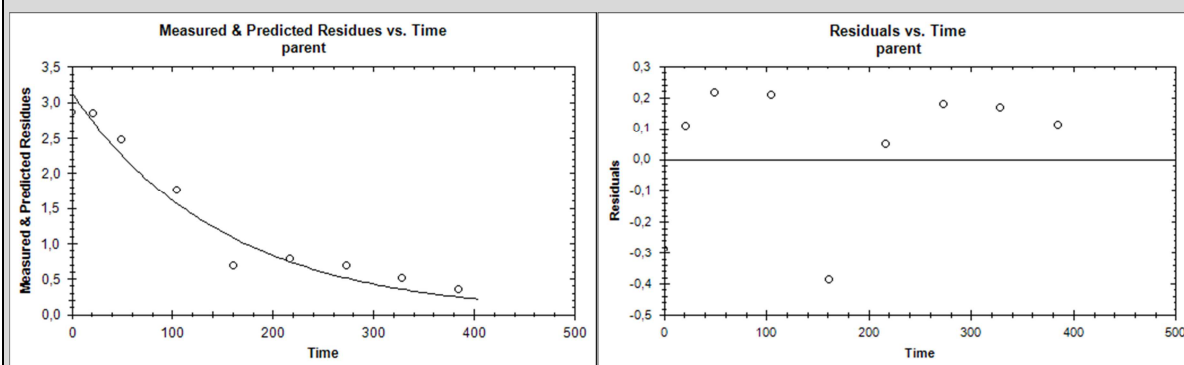
Chi2 error estimation
-----
          parent      All
Chi2Err% :      11.30    11.30
Kinetic model :      SFO

Parameter estimation
-----
Degrees of Freedom : 7
Parameter      Estimate      Lower CI      Upper CI      St.Dev      Prob > t
M(0) parent    :      3.0616523    2.7337615      3.390      0.1672943    1.80e-07
k parent       :      0.00460771    0.0046807      0.007      0.0007125    3.02e-25

DT50 and DT90 values
-----
          parent
DT50 :      114.06
DT90 :      378.90
Kinetic model :      SFO

```

Kinetic evaluation Mainz B, non normalized (FOMC)



```

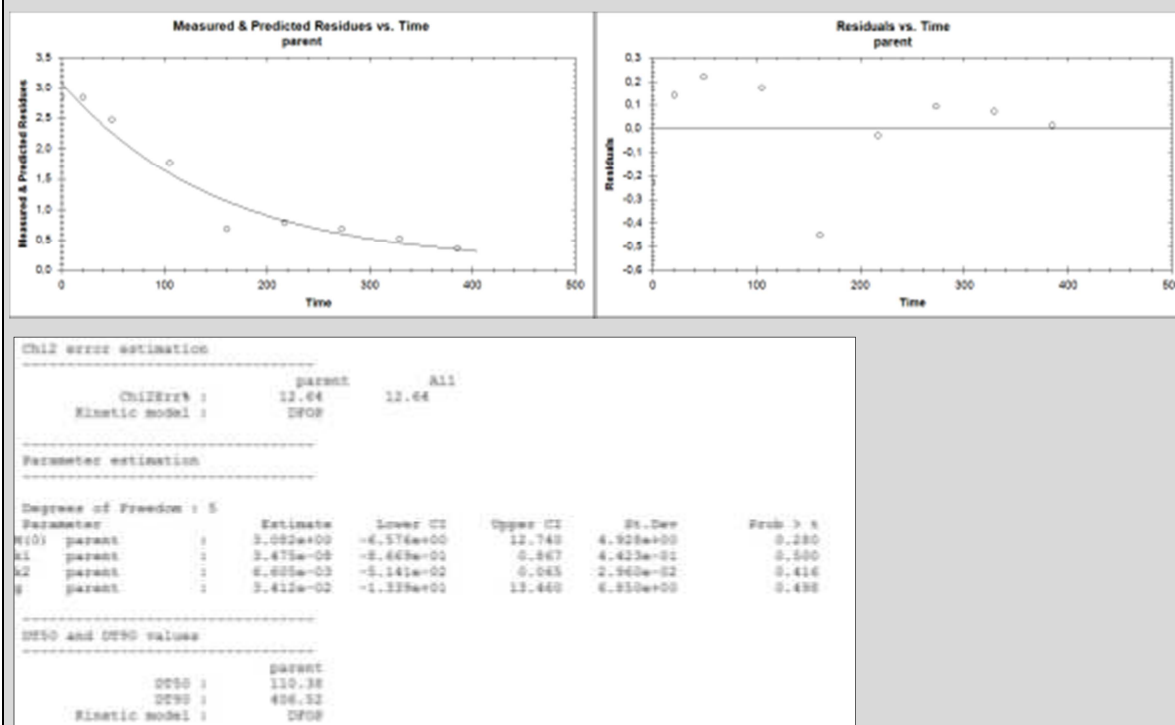
Chi2 error estimation
-----
          parent      All
Chi2Err% :      12.53    12.53
Kinetic model :      FOMC

Parameter estimation
-----
Degrees of Freedom : 6
Parameter      Estimate      Lower CI      Upper CI      St.Dev      Prob > t
M(0) parent    :      3.141e+00    2.210e+00    3.473e+00    1.692e-01    7.87e-07
alpha parent   :      6.769e+02    -1.236e+03    2.590e+03    9.759e+02    0.237
beta parent    :      1.011e+05    -1.950e+05    3.873e+05    1.460e+03    0.257

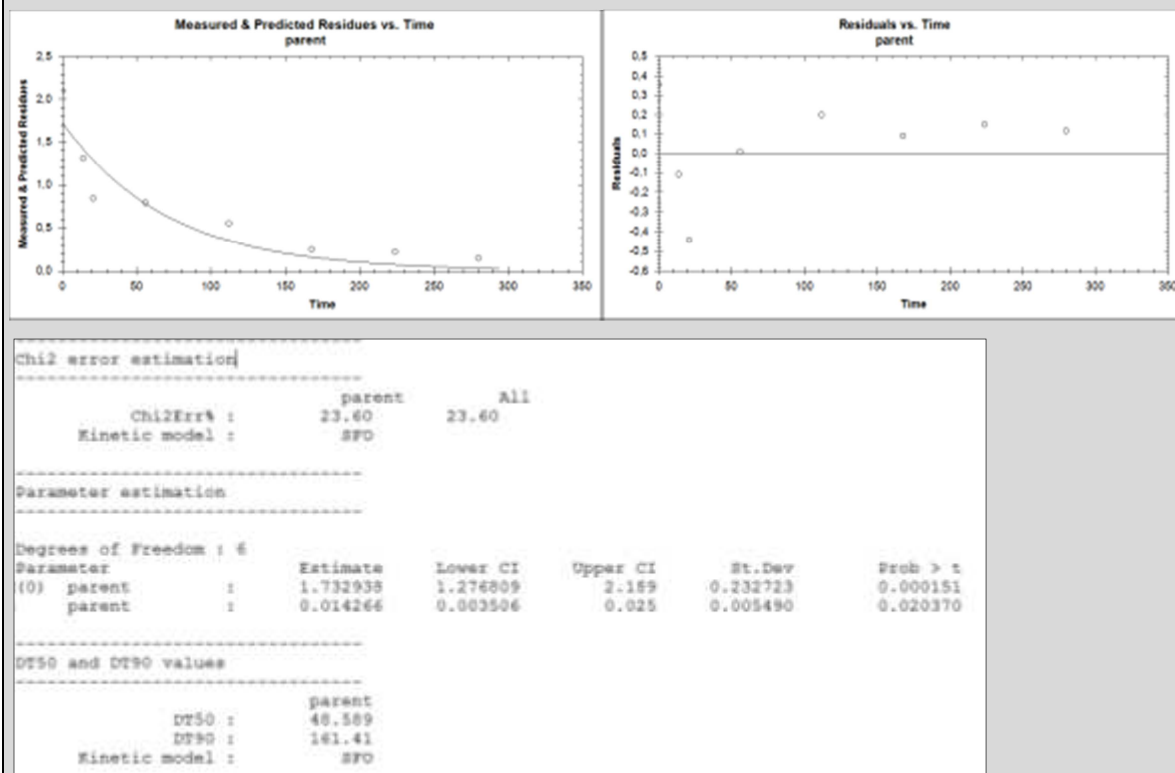
DT50 and DT90 values
-----
          parent
DT50 :      103.63
DT90 :      344.65
Kinetic model :      FOMC

```

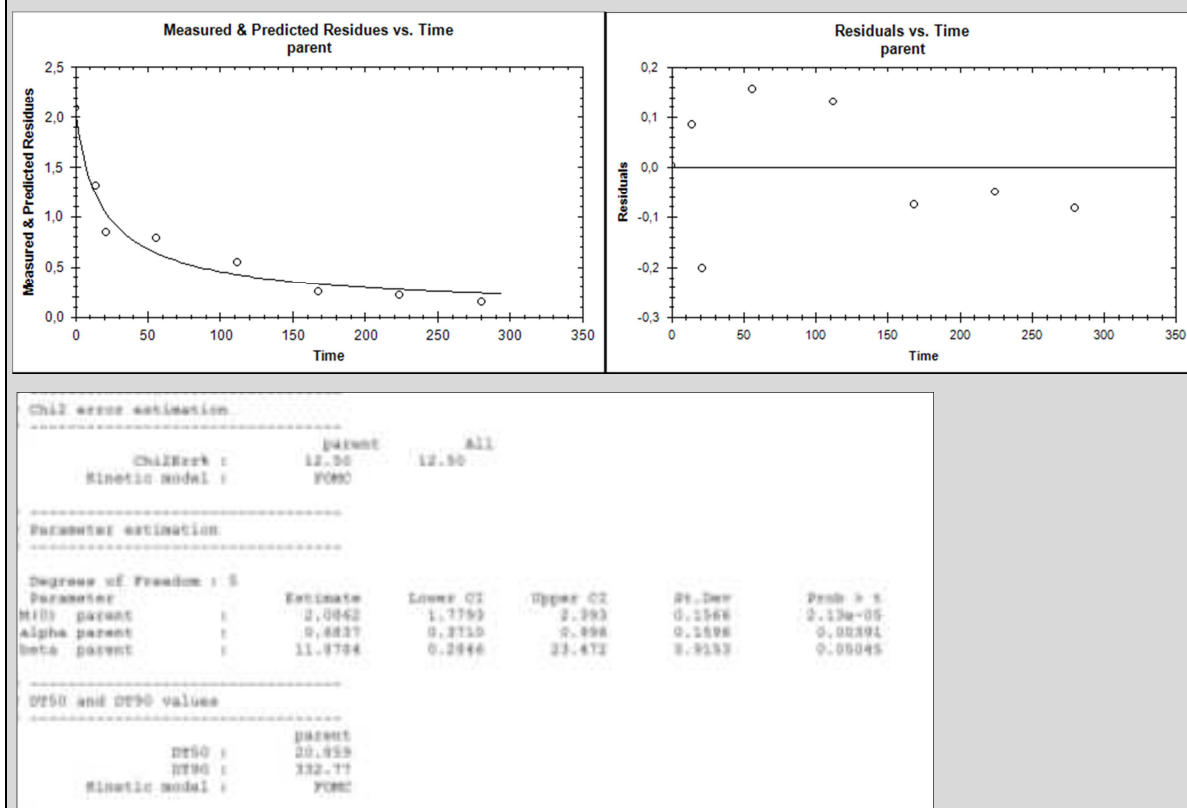
Kinetic evaluation Mainz B, non normalized (DFOP)



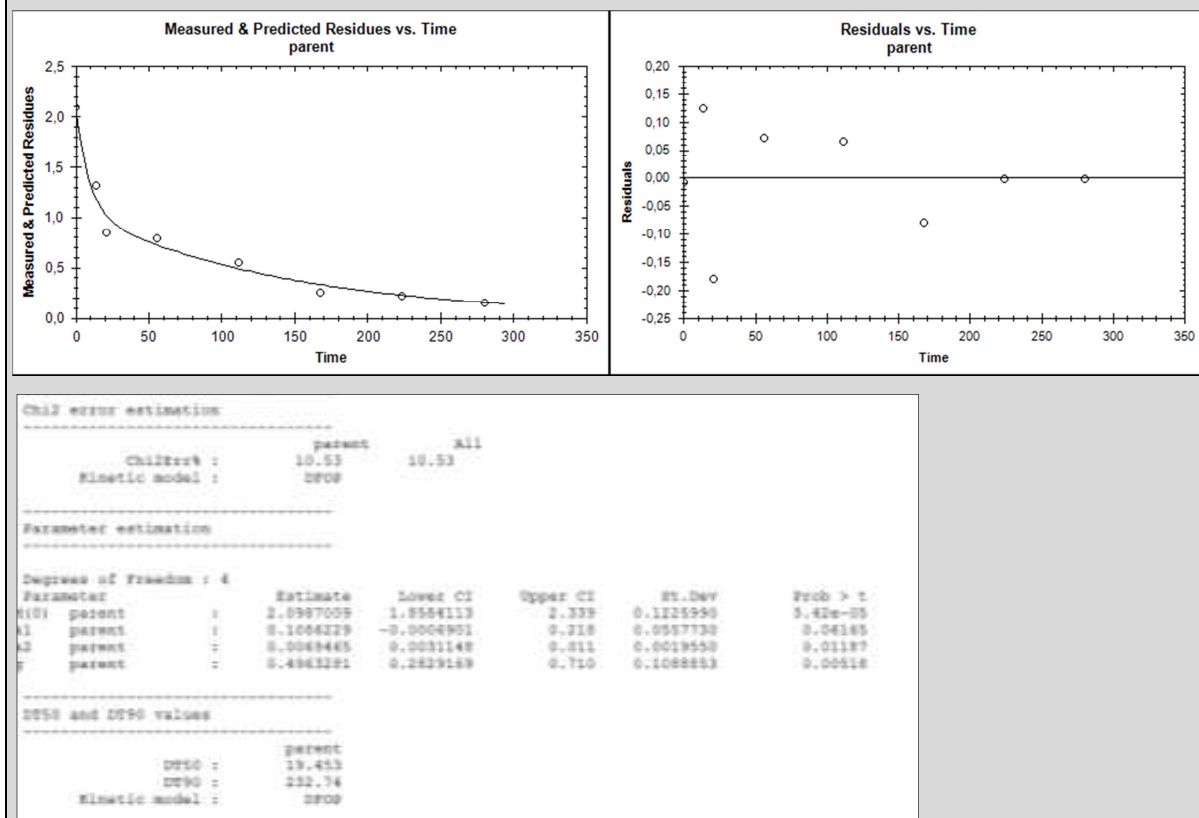
Kinetic evaluation Speyer A, non normalized (SFO)



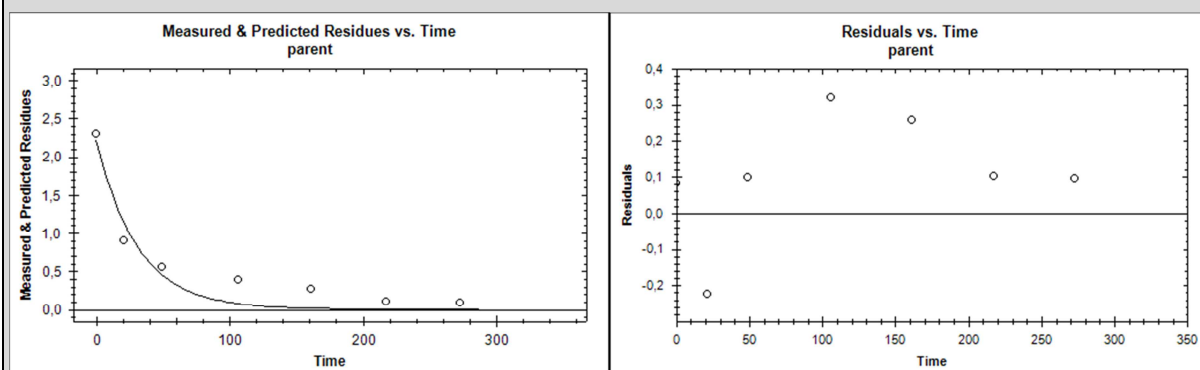
Kinetic evaluation Speyer A, non normalized (FOMC)



Kinetic evaluation Speyer A, non normalized (DFOP)



Kinetic evaluation Speyer B, non normalized (SFO)



```

      parent      All
Chi2Err% :      22.99      22.99
Kinetic model :      SFO

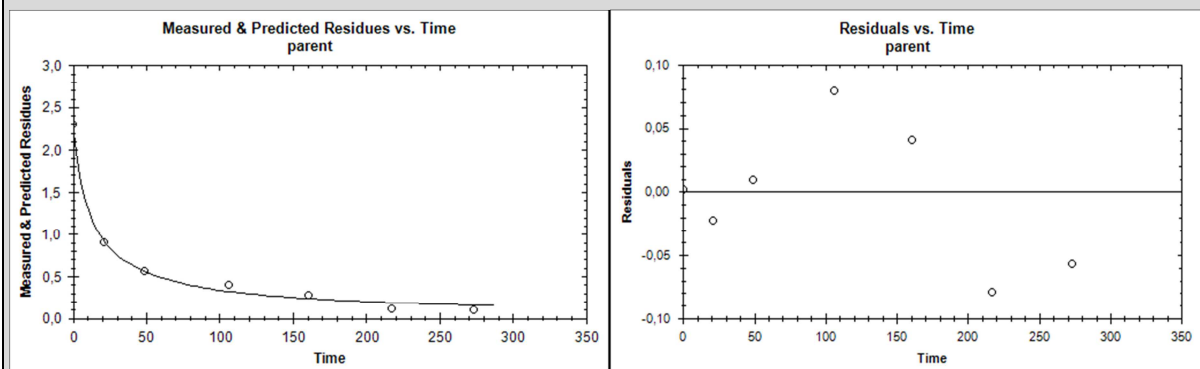
-----
Parameter estimation
-----

Degrees of Freedom : 5
Parameter      Estimate      Lower CI      Upper CI      St.Dev      Prob > t
M(0) parent :      2.21799      1.75621      2.676      0.23459      0.000112
k parent :      0.03200      0.01332      0.051      0.00953      0.010081

-----
DT50 and DT90 values
-----

      parent
DT50 :      21.662
DT90 :      71.961
Kinetic model :      SFO
  
```

Kinetic evaluation Speyer B, non normalized (FOMC)



```

      parent      All
Chi2Err% :      6.562      6.562
Kinetic model :      FOMC

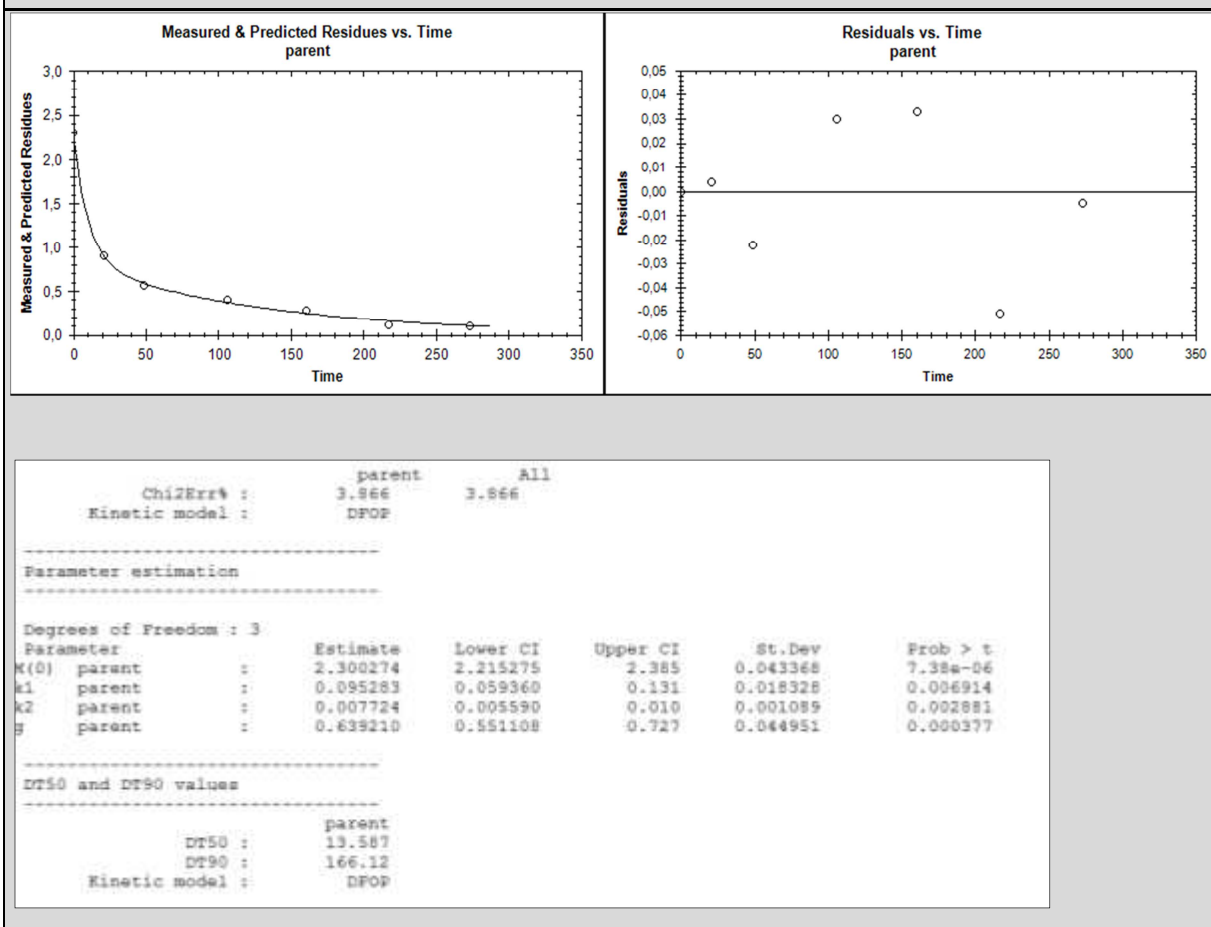
# -----
# Parameter estimation
# -----

Degrees of Freedom : 4
Parameter      Estimate      Lower CI      Upper CI      St.Dev      Prob > t
M(0) parent :      2.29822      2.17066      2.426      0.06508      1.52e-06
alpha parent :      0.82249      0.57828      1.067      0.12460      0.00136
beta parent :      10.46035      3.32243      17.638      3.65207      0.02274

# -----
# DT50 and DT90 values
# -----

      parent
DT50 :      13.863
DT90 :      161.78
Kinetic model :      FOMC
  
```

Kinetic evaluation Speyer B, non normalized (DFOP)



The following studies were evaluated and summarized in the course of the previous evaluation: Crofts, M.; Whiteoak, R. J.(1974); Crofts, M.; Whiteoak, R. J.(1977); Whiteoak, R. J.(1975); Crofts, M.; Whiteoak, R. J. (1974); Crofts, M.; Whiteoak, R. J.(1974); Whiteoak, R. J.; Crofts, M.(1973). They were all deemed not valid. For the current re-evaluation, the RMS did choose not to provide detailed study summaries but rather to better explain the reasons for their previous exclusion.

| | |
|---------------------|--|
| Reference: | DECLINE OF NC 8438 RESIDUES IN SOIL AND END-SEASON SOIL RESIDUES FROM FRENCH TRIALS (BY PRELIMINARY METHOD) |
| Notifier: | Taskforce |
| Author(s), year: | Whiteoak, R. J.; Crofts, M.;1973 |
| Report/Doc. number: | A83287 / W 31 / M-155556-01-1 |
| Guideline(s): | None |
| GLP: | no |
| Deviations: | |
| Validity: | Not valid |
| Status: | Previous evaluation in DAR for original approval / baseline dossier. |

Study summary based on previous draft assessment report

Materials and Methods

The dissipation of ethofumesate from soil was investigated under field conditions on four plots situated in France in 1972 and 1973. At three plots, 2 kg a.s./ha were applied pre-emergence, at one site 1 kg a.s./ha was applied post-emergence.

Samples were taken only once at study end (126 – 204 days after application) at depth of 0-15 cm. Samples were airdried and ground. Soils were extracted with diluted hydrochloric acid and a dichloromethane:methanol mixture and – after a reflux step – extracted again with the same extractants. Samples were analysed with GLC.

Comments RMS

The study was regarded as not valid in the previous evaluation.

Each experimental site was sampled only once (e.g. only day-zero plus one data point) at 0-15cm depth. Neither soil nor weather data are reported. Recovery and mass balance are not available. The data are not sufficient quality for kinetic analysis. Therefore, the study is excluded from further considerations

| | |
|---------------------|--|
| Reference: | DECLINE OF NORTON RESIDUES IN SOIL IN COLORADO AND MICHIGAN (USA) IN 1972 |
| Notifier: | Taskforce |
| Author(s), year: | Crofts, M.; Whiteoak, R. J.; 1974 |
| Report/Doc. number: | A83288 / W 32 / M-155557-01-1 |
| Guideline(s): | None |
| GLP: | no |
| Deviations: | |
| Validity: | Not valid |
| Status: | Previous evaluation in DAR for original approval / baseline dossier. |

Study summary based on previous draft assessment report

Materials and Methods.

Residue decline studies with Norton-treated sugarbeet were carried out in Colorado and Michigan in 1972. The sugarbeet plots were treated pre-emergence at 3.3 and 6.6 kg a.i./ha, at each site. Control and treated plots were replicated four times. In Colorado, ethofumesate was incorporated into the soil after spraying.

Soil samples were taken to a depth of ca. 15 cm soon after spraying. Later samples were taken at 0 - 15 and 15 - 30 cm. The analytical method refers to Whiteoak and Crofts (1973). The LOD was 0.1 mg/kg. Recoveries range between 98 and 104 % for the Colorado soil, and between 64 and 119% for the Michigan soil.

Comments RMS

The study was regarded as not valid in the previous evaluation.

The Michigan data covered just four time points, which are insufficient for a kinetic analysis. The limit of detection is five times higher than the LOD in other studies. The authors mention a so-called “minimal clean up routine”, for which no validation is available. For instance, in the Michigan samples recoveries range between 64% and 119% and apparent residues in unspiked samples reach up to 0.1 mg kg⁻¹. Overall, the uncertainties of the applied analytical method are considerable. Weather data are not completely reported. Only the Colorado soil was fully characterized. Therefore, the study is excluded from further considerations

| | |
|---------------------|--|
| Reference: | HARVEST RESIDUES IN SUGAR BEET AND SOIL FROM 1973 POST-EMERGENCE APPLICATIONS OF NORTON (TRAMAT) IN ITALY |
| Notifier: | Taskforce |
| Author(s), year: | Crofts, M.; Whiteoak, R. J.; 1974 |
| Report/Doc. number: | A83290/ W 34 / M-155559-01 |
| Guideline(s): | None |
| GLP: | no |
| Deviations: | |
| Validity: | Not valid |
| Status: | Previous evaluation in DAR for original approval / baseline dossier. |

Study summary based on previous draft assessment report

Materials and methods

The dissipation of ethofumesate, applied post-emergence as Norton at 0.8 kg a.s./ha, was studied at three Italian sites. The analytical method is cross referred to “R.J. WHITEOAK, M. CROFTS and R.J. HARRIS, Fisons Report RESID/73/1 8/1 (Dec. 1973)”. Soil cores were sampled at 0-15 cm and the cores were then split into 0-7.5cm and 7.5-15cm sections. Samples were taken at sugar beet harvest.

Comments RMS:

The study was regarded as not valid in the previous evaluation.

Soil samples were taken only at time of sugar-beet harvest. Soils are not characterized. No weather data are reported. The data do not lend themselves to kinetic analysis. Therefore, the study is excluded from further considerations

| | |
|---------------------|---|
| Reference: | DECLINE OF SOIL RESIDUES AFTER PRE- EMERGENCE APPLICATION OF NORTRON TO SUGAR BEET IN THREE REGIONS OF USA |
| Notifier: | Taskforce |
| Author(s), year: | Whiteoak, R. J.;1975 |
| Report/Doc. number: | A83298/ W 42 / M-155567-01-1 |
| Guideline(s): | None |
| GLP: | no |
| Deviations: | |
| Validity: | Not valid |
| Status: | Previous evaluation in DAR for original approval / baseline dossier. |

Study summary based on previous draft assessment report

Materials and Methods

NORTRON was applied pre-emergence and incorporated at sugar beet plots in Colorado, Nebraska and Montana in 1972, 1973 and 1974, respectively. Application rates were 3.3 and 6.6 kg a.s./ha in Colorado and 3.3 and 4.4 kg a.s./ha in Nebraska and Montana, respectively. Soil samples (0 - ca. 15 and ca. 15- 30 cm) were taken during the beet growing season: in Colorado up to 184 days after treatment, in Nebraska 78 days and in Montana 52 days. In the trials in Nebraska and Montana later samples were taken up to 12 and 18 months after the NORTRON application. There, a cereal crop (barley or wheat) was grown during the second year, with normal cultivation procedures.

The residue of NC 8438 was extracted by heating the soil under reflux with 9:1 v/v methanol + water. It was analysed by gas liquid chromatography with a flame photometric detector operated in the sulphur mode. Mean recoveries ranged between 83 and 99.3 %

Comments RMS

The study was regarded as not valid in the previous evaluation.

Except texture classification according to USDA, no soil data are available. Since no soil data is available for these three USA trials, a comparison to European soils is not possible. First application in the Nebraska trial was in April 1973, and analysis was done in April / May 1975, a long period for sample storage. Irrigation was applied at the Nebraska and Montana sites, but there are no records of the amounts of water irrigated. Moreover, no weather data are reported. In sum, the trials are not considered sufficiently well documented for reliable kinetic analysis. Therefore, the study is excluded from further considerations.

| | |
|---------------------|---|
| Reference: | DECLINE OF SOIL RESIDUES IN A UK FIELD AFTER APPLICATION OF NORTRON IN FOUR SUCCESSIVE YEARS |
| Notifier: | Taskforce |
| Author(s), year: | Crofts, M.; Whiteoak, R. J.;1977 |
| Report/Doc. number: | A83297 / W 41 / M-155566-01-1 |
| Guideline(s): | None |
| GLP: | no |
| Deviations: | |
| Validity: | Not valid |
| Status: | Previous evaluation in DAR for original approval / baseline dossier. |

Study summary based on previous draft assessment report

Materials and Methods

Plots of sugar beet at Shelford, Cambridgeshire were sprayed either pre-emergence (at 2 kg a.s./ha) or post-emergence (at 1.5 kg a.i./ha) with NORTRON in 1973. Soil was sampled to a depth of 15 cm at intervals up to sugar beet harvest. The plots were re-sprayed at the same application rates at the appropriate time of the year for pre- or post-emergence treatment in 1974, 1975 and 1976, in the absence of a crop and without cultivation. Samples were taken at various intervals up to 232 days after each application.

The samples were analysed using GLC with a flame photometric detector. Four recovery experiments were carried out with the 1973-75 series of samples, in which 2, 10, 10 and 20 µg ethofumesate were added to 20g control samples. The mean recovery was 31.4% (range 88-100%).

Comments RMS:

The study was regarded as not valid in the previous evaluation.

Weather data are well reported. Soils are not fully characterized, for instance the pH is not reported. The sampling depth (0-15 cm) is not appropriate as losses due to translocation into deeper soil layers cannot be ruled out. Therefore, the study is excluded from further considerations.

| | |
|---------------------|---|
| Reference: | SOIL RESIDUES AT HARVEST FOLLOWING PRE- EMERGENCE APPLICATION OF NORTRON (TRAMAT) IN 1973 TO SUGAR BEET IN ITALY |
| Notifier: | Taskforce |
| Author(s), year: | Crofts, M.; Whiteoak, R. J.;1974 |
| Report/Doc. number: | A82991 / R 26 / M-155268-01-1 |
| Guideline(s): | None |
| GLP: | no |
| Deviations: | |
| Validity: | Not valid |
| Status: | Previous evaluation in DAR for original approval / baseline dossier. |

Study summary based on previous draft assessment report

Nortron (Tramat) was applied both with and without pre-plant incorporation at three sites, with rates from 1.8 to 2.4 kg a.i./ha. Three experimental plots were sampled with sampling taking place on day-zero and two additional dates (after 139 and 145 days, after 154 and 171 days, and after 148 and 153 days, respectively. Samples consisted of a minimum of 20 cores from each trial, divided into 0 to 7.5 cm and 7.5 to 15 cm depths. The corresponding portions of each core were combined and mixed to provide the sample from each plot.

Comment RMS:

The study was regarded as not valid in the previous evaluation.

Since plots were sampled only once at sugar beet harvest, insufficient residue data are available for a kinetic analysis. Moreover, neither the analytical method nor soil or weather data are reported. Therefore, the study is excluded from further considerations.

| | |
|---------------------|--|
| Reference: | TESTS ON THE DEGRADATION OF ETHOFUMESATE IN THE TOPSOIL UNDER FIELD CONDITIONS AT 4 DIFFERENT LOCATIONS |
| Notifier: | Taskforce |
| Author(s), year: | Aldag, R.; Andre, W.;1993 |
| Report/Doc. number: | A87604 / W 504-1 / M-161533-01-1 |
| Guideline(s): | BBA: IV, 4-1 |
| GLP: | no |
| Deviations: | |
| Validity: | |
| Status: | Previous evaluation in DAR for original approval / baseline dossier. |

Comments RMS

This study was also submitted as Aldag (1992) and is not further considered.

| | |
|---------------------|--|
| Reference: | Kinetic evaluation of the soil dissipation of ethofumesate under field conditions |
| Notifier: | Taskforce |
| Author(s), year: | Schmitt, W.; 2008 |
| Report/Doc. number: | MEF-08/334 / M-305786-01-1 |
| Guideline(s): | None |
| GLP: | no |
| Deviations: | |
| Validity: | Valid |
| Status: | New study. |

Executive summary

Residue data from European and US field dissipation studies (Moede, 1992; Straszewski, 1990; Crofts & Whiteoak, 1977; Castro, 1991; Snowdon, 1991b; and Andre, 1992) were assessed for their suitability for deriving kinetic parameters suitable for modelling and environmental risk assessments. Of twenty-six trials from different studies, fourteen were deemed suitable. For twelve of these temperature and moisture normalised DT₅₀ values for ethofumesate could be derived for standard FOCUS reference conditions (20°C and 100% field capacity). This normalisation was accomplished by a timestep normalisation approach using the Arrhenius equation with standard activation energy and Walker equation with standard moisture exponent based on daily soil temperatures and moisture. The kinetic evaluation was performed according to the guidance in the FOCUS Kinetics report (FOCUS, 2006). The selection of the most appropriate kinetic model was based on a detailed statistical analysis including visual assessment, χ^2 statistic, randomness of residuals, and T-test significance.

Exclusion of Results from Field Dissipation Studies:

Seven other trial studies are also available that address ethofumesate residues in soil. However, these studies were considered unuseable in their entirety. These were:

1. Crofts and Whiteoak, 1974a (W34): this study is strictly a residue study, not a soil dissipation study, and although soil samples were taken, insufficient residue data is available for a kinetic analysis.
2. Whiteoak and Crofts, 1973 (W31): a French beet residue trial that, for methodology, cross references a 1973 UK trial (Crofts and Whiteoak, 1977). Samples were stored frozen for 12 months, and first sampling date was three months after application. Neither soil nor weather data are reported. The data are not considered to be of sufficient quality for kinetic analysis.
3. Crofts and Whiteoak 1974b (R26): soil samples were taken only at time of sugar-beet harvest. Soil data is very sparse. The data do not lend themselves to kinetic analysis.

4. Whiteoak, 1975 (W42) : no soil data is available for these three USA trials, so a comparison to European soils is not possible. First application in the Nebraska trial was April 1973, and analysis was done in April / May 1975, a long period for sample storage. The Colorado trial had just five measurements, which are too few for reliable kinetic analysis. Irrigation was applied at the Nebraska and Montana sites, but there are no records of how much was irrigated. In sum, the trials are not considered sufficiently well documented for reliable kinetic analysis.

5. Snowdon, 1986 (W58) : the trial design was for an accumulation study. Insufficient time points are available for a kinetic analysis of soil dissipation.

6. Crofts and Whiteoak, 1974c (W32): the Michigan data covered just four time points, which are insufficient for a kinetic analysis. The method of analysis was deemed suspect, as the LOD was 5 times higher than that of earlier studies. The analytical approach appeared to use a “minimal cleanup” routine. Although the Colorado data could be used and does demonstrate a reliable decline curve (reported DT_{50} , 19.5 days), the data is insufficiently reliable to be included in the kinetic analysis.

7. Snowdon, 1991a (W85): the trials were located in Germany at Thann, Niederkirchen, Nierswalde, and Langforden. A single large plot was used at each site, in typical agricultural land. The application (2000 g/ha) was made to bare soil (and kept bare) at all sites, on the 13th June, 1988 at Nieder-Kirchen; on 28th May, 1988 at Nierswalde; and on 31st May, 1988 at Langforden.

However, as the soil texture data was either non-existent, extremely sparse, or ambiguous, all data from these trials have been excluded from the analysis. Soil data consisted only of an abbreviation for soil classification system (probably the German classification), and the percentage of soil in size class < 20 μ m. The quality of soil information is insufficient to support the analysis performed here.

Geographical Data of the Evaluated Field Dissipation Trials

The behaviour of ethofumesate under field conditions was investigated in thirteen terrestrial field soil dissipation studies, encompassing 26 trial sites, designed to determine the dissipation after a representative field use. Six studies were used in the evaluation: Moede, 1992; Straszewski, 1990; Crofts & Whiteoak, 1977; Castro, 1991; Snowdon, 1991b; and Andre, 1992. The fourteen trial sites drawn from the six studies were deemed of acceptable quality. Relevant geographical data identifying the fourteen trials are summarised in Schmitt (2013). In the original study reports, first-order dissipation half-lives were estimated, but without any normalisation to reference conditions.

Agro-climatic Conditions

The field dissipation studies used in the kinetic analysis were carried out at eleven sites in the UK, Germany, and the USA, in order to cover different representative agro-climatic regions: the UK (3 trial sites), Germany (7 trial sites) and the USA (1 trial site). There was duplication of trials at sites in the UK and Germany, but these were sufficiently different to be considered separate trials, rather than replicates. A more detailed overview of the

climatic conditions as reported in the trial documents are given in Schmitt (2013), for the trials used in the analysis. In general, the climatic conditions at all field trial sites used in the analysis are representative for agroclimatic conditions in Europe and lay within the range of the FOCUS groundwater scenarios (FOCUS, 2000); for details see Schmitt (2013).

Characterisation of the Field Soils

The field soils of the fourteen evaluated trials cover a wide textural range representative for the foliar treatment uses of ethofumesate. The relevant physicochemical properties of the six field soils are summarised in Schmitt (2013) for the top soil. The soil textures clearly indicate that the field soils of the fourteen trials assessed are representative for European growing conditions and lie within the range of the FOCUS groundwater scenarios.

Data Pre-processing of Soil Residue Values

For the calculation of the total residue employed for the kinetic evaluation in the soil profile covering all soil layers, the following general procedure was followed:

- values between LOD and LOQ were set to $0.5 \times (\text{LOQ} + \text{LOD})$
- all samples $< \text{LOD}$ were set to $1/2 \text{ LOD}$ or after the first non-detect (time and depth), to zero in case no detects appeared later on.

The following residue data were summarized in this report (DAA...days after application):

| Moede, 1992 | | | | | |
|-------------|--------------|---------------------------|------------|--------------|---------------------------|
| Keeken | | | Weeze | | |
| Date | Original DAA | Residues $\mu\text{g/kg}$ | Date | Original DAA | Residues $\mu\text{g/kg}$ |
| 25. Jun 90 | 0 | 0.08 | 27. Jun 90 | 0 | 0.39 |
| 26. Jun 90 | 1 | 0.41 | 28. Jun 90 | 1 | 0.32 |
| 02. Jul 90 | 7 | 0.41 | 04. Jul 90 | 7 | 0.36 |
| 09. Jul 90 | 14 | 0.39 | 11. Jul 90 | 14 | 0.36 |
| 23. Jul 90 | 28 | 0.39 | 25. Jul 90 | 28 | 0.19 |
| 25. Aug 90 | 61 | 0.05 | 27. Aug 90 | 61 | 0.24 |
| 25. Okt 90 | 122 | 0.07 | 27. Okt 90 | 122 | 0.17 |
| 25. Jan 91 | 214 | 0.05 | 27. Jan 91 | 214 | 0.17 |
| 21. Jun 91 | 361 | 0.02 | 21. Jun 91 | 359 | 0.09 |
| Nierswalde | | | | | |
| Date | Original DAA | Residues $\mu\text{g/kg}$ | | | |
| 20. Jun 90 | 0 | 0.22 | | | |
| 21. Jun 90 | 1 | 0.28 | | | |
| 27. Jun 90 | 7 | 0.19 | | | |
| 04. Jul 90 | 14 | 0.25 | | | |
| 18. Jul 90 | 28 | 0.2 | | | |
| 20. Aug 90 | 61 | 0.34 | | | |

| | | |
|------------|-----|------|
| 20. Okt 90 | 122 | 0.23 |
| 20. Jan 91 | 214 | 0.18 |
| 21. Jun 91 | 366 | 0.07 |

| Straszewski, 1990 | | | | | |
|-------------------|--------------|----------------|------------|--------------|----------------|
| Thann | | | Langforden | | |
| Date | Original DAA | Residues µg/kg | Date | Original DAA | Residues µg/kg |
| 09. Jun 89 | 0 | 0.595 | 05. Jun 89 | 0 | 0.63 |
| 10. Jun 89 | 1 | 0.575 | 06. Jun 89 | 1 | 0.19 |
| 12. Jun 89 | 3 | 0.545 | 08. Jun 89 | 3 | 0.74 |
| 16. Jun 89 | 7 | 0.565 | 12. Jun 89 | 7 | 0.53 |
| 23. Jun 89 | 14 | 0.615 | 19. Jun 89 | 14 | 0.36 |
| 08. Jul 89 | 29 | 0.365 | 03. Jul 89 | 28 | 0.38 |
| 08. Aug 89 | 60 | 0.235 | 04. Aug 89 | 60 | 0.42 |
| 28. Dec 89 | 202 | 0.025 | 08. Dec 89 | 186 | 0.24 |
| 11. Jun 90 | 367 | | 06. Jun 90 | 366 | 0.4 |

| Crofts and Whiteoak, 1977 | | | | | |
|---------------------------|--------------|----------------|--------------------|--------------|----------------|
| Great Shelford (A) | | | Great Shelford (B) | | |
| Date | Original DAA | Residues µg/kg | Date | Original DAA | Residues µg/kg |
| 01. Mai 73 | 0 | | 30. Mai 73 | 0 | |
| 08. Mai 73 | 7 | 1.63 | 01. Jun 73 | 2 | 1.75 |
| 25. Mai 73 | 24 | 1.03 | 06. Jun 73 | 7 | 0.8 |
| 06. Jun 73 | 36 | 0.68 | 19. Jun 73 | 20 | 0.9 |
| 19. Jun 73 | 49 | 0.7 | 31. Jul 73 | 62 | 0.31 |
| 26. Jul 73 | 86 | 0.26 | 13. Sep 73 | 106 | 0.13 |
| 31. Jul 73 | 91 | NA | 19. Dec 73 | 203 | 0.13 |
| 13. Sep 73 | 135 | 0.1 | | | |
| 19. Dec 73 | 232 | 0.08 | | | |

| Castro, 1991 | | |
|-----------------|--------------|----------------|
| Fresno, CA. USA | | |
| Date | Original DAA | Residues µg/kg |
| 13. Apr 89 | 0 | 1.328 |
| 14. Apr 89 | 1 | 1.092 |
| 27. Apr 89 | 14 | 0.678 |
| 11. Mai 89 | 28 | 0.965 |
| 13. Jun 89 | 61 | 0.878 |
| 11. Aug 89 | 120 | 0.328 |
| 16. Okt 89 | 186 | 0.238 |
| 19. Jan 90 | 281 | 0.145 |
| 12. Apr 90 | 364 | 0.133 |
| 13. Jul 90 | 456 | 0.042 |
| 11. Okt 90 | 546 | 0.032 |

Comments RMS

The study does not correspond to the current EFSA Guidance Document for evaluating laboratory and field dissipation studies (EFSA, 2014). Therefore, regarding the normalization procedure it is superseded by Schmitt (2013). However, it provides the raw residue data for the study by Schmidt (2013).

For details on the individual trials, please refer to the respective study in this section.

| | |
|---------------------|--|
| Reference: | Kinetic evaluation of the soil dissipation of ethofumesate under field conditions (re-evaluation according to EFSA guidance 2010) |
| Notifier: | Taskforce |
| Author(s), year: | Schmitt, W.; 2013 |
| Report/Doc. number: | EnSa-13-0274/ M-455136-01-1 |
| Guideline(s): | None |
| GLP: | no |
| Deviations: | |
| Validity: | Valid |
| Status: | New study. |

EXECUTIVE SUMMARY

Terrestrial field dissipation studies with ethofumesate were evaluated in order to derive dissipation times (DT_{50}) for use in model simulations of environmental exposures. The dissipation of ethofumesate under field conditions was investigated in various European and US studies (Moede, 1992; Straszewski, 1990; Crofts & Whiteoak, 1977; Castro, 1991; Snowdon, 1991; and Andre, 1992). The suitability of the data from these studies for kinetic evaluation has been assessed already (Schmitt, 2008) and fourteen of the twenty-six trials performed in total, were deemed suitable.

The present report comprises the re-evaluation of the data previously selected for evaluation but according to the EFSA guidance for evaluating field dissipation studies (EFSA, 2010). The kinetic evaluation was also performed according to the guidance given by the FOCUS Kinetics report (FOCUS, 2006).

Normalized DT_{50} values for ethofumesate ranged from 15 to 112 d, with a geometric mean of 37.5 d. The normalized kinetic parameters determined for the dissipation under realistic field conditions are considered appropriate as input for modeling purposes.

Table 8-81: Geodata of the eleven field trial sites

| Trial No. | Location | Weather station | Distance* (km) |
|-----------|----------------|-------------------------|----------------|
| W121 | Keeken | Bocholt | 35 |
| W121 | Weeze | Geldern | 14 |
| W121 | Nierswalde | Geldern | 25 |
| W106 | Thann | Nürnberg | 45 |
| W106 | Langforden | Diepholz | 25 |
| W41 | Great Shelford | Cambridge (Bot. Garden) | 5 |
| W110 | Fresno CA | Fresno (Airport) | 20 |

| | | | |
|---|------------------------|------------|----|
| W97 | Willingham | Wyton | 12 |
| W97 | Isleham | Honington | 26 |
| R500-1 | Mainz-Bretzenheim | Geisenheim | 20 |
| R500-1 | Speyer-Rinkenbergerhof | Mannheim | 15 |
| *best estimates since exact position of field trials is unknown | | | |

Estimation of Soil Temperature

Soil temperature and soil moisture during the field trials were not measured at any of the sites except for the Speyer-Rinkenbergerhof site (Andre, 1992). Therefore, the daily values of both parameters were simulated with the FOCUS PEARL model (Leistra et al., 2000) based on the daily weather data (surrogate or from reports) and applied to all sites.

The PEARL model was chosen because it is a widely used, physically based, state-of-the-art model to simulate water and heat flow, and solute transport in soils including plants. By the use of a model, it is assured that the mass balance is correct and that meaningful soil hydraulic values are obtained. The main driving forces for soil water flow are rainfall and potential evapotranspiration which can be measured or calculated with sufficient precision, respectively. Moreover, PEARL is used as regulatory model to calculate predicted concentrations in groundwater (FOCUS, 2000).

Simulation Domain, Discretisation and Boundary Conditions

A soil profile of 1.5 m depth was implemented to minimise the influence of the lower boundary of the simulation domain on the region of interest, the 0-10 cm layer. The profile was discretised at 2.5 cm intervals for the first 60 cm, at 5 cm intervals to 100 cm, and at 10 cm intervals for the remainder. The lower boundary condition was set to ‘free drainage’ to represent well drained soils not affected by shallow groundwater.

Soil

Appropriate soil layers for the PEARL simulations were defined for each field trial based on the available textural information from the study reports. The final subsoil horizon was defined as reaching down to the bottom of the soil profile. Hydraulic parameters were derived using the software ROSETTA (Schaap et al, 1999). ROSETTA is a hierarchical pedotransfer function model to predict soil hydraulic properties from soil texture and related data employing a neural network and bootstrap approach.

Table 8-82: Soil characteristics

| Location | Textural Class ¹ [USDA] | Sand [%] | Silt [%] | Clay [%] | OC [%] | pH |
|--|---------------------------------------|-------------|-------------|-------------|-----------|------|
| W121 Moede 1992 | Silty clay loam | 10.6 | 57.1 | 32.3 | 4.4 | 6.1 |
| W121 Moede 1992 | Loamy sand | 85.7 | 7.8 | 6.5 | 3.8 | 5.8 |
| W121 Moede 1992 | Silty loam | 17.7 | 70.4 | 11.9 | 3.5 | 6.2 |
| W106 Straszewski 1990 | Silty loam | 24.1 | 54.6 | 21.3 | 1.5 | 7.1 |
| W106 Straszewski 1990 | Sandy loam | 63.1 | 20.4 | 16.5 | 6.4 | 5.15 |
| W41 Crofts & Whiteoak 1977 (trials A&B) | Sandy loam | 61.4 | 21.7 | 16.9 | 1.8 | NA |
| W110 Castro 1991 | Sandy loam | 66.8 | 26 | 7.2 | 0.29 | 6.5 |
| W97 Snowdon 1991b | Sandy clay loam | 44 | 29 | 27 | 2 | 7.5 |
| W97 Snowdon 1991b | Loamy sand | 83 | 8 | 9 | 11.5 | 7.5 |
| R500-1 Andre 1992 Mainz (trials A&B) | Loamy silt | 13.9 | 73.8 | 12.3 | 1.92 | 7.5 |
| R500-1 Andre 1992 Speyer (trials A&B) | Silty sand | 61 | 31.2 | 7.8 | 0.84 | 6.7 |

¹ according to USDA classification

Vegetation

At the trial sites at time of application, the soil was either bare soil or some days post-emergence, then kept bare or used for sugar beet production followed by alfalfa or bare soil. This information together with planting dates is given in the field dissipation study reports and was implemented in the corresponding crop calendars used by PEARL. The crop development related parameters such as the relative development stage and leaf area index were taken from the FOCUS crop scenarios (FOCUS, 2000).

Output

The daily soil temperature and water content at depths of 1.25, 3.75, 6.25 and 8.75 cm as calculated by PEARL were averaged to obtain representative values for the 0 - 10 cm soil layer.

Results

Graphs of the simulated soil water content for the 0-10 cm soil layer were generated. Inspection of the graphs shows that due to the shallow depth of the soil considered, soil temperature closely follows that of air temperature. For the same reason, water content reacts rapidly to rainfall (or irrigation).

In the following tables the calculated time step values are listed.

Table 8-83: Timestep values for the Moede (1992) trials.

| Keeken, DE | | Weeze, DE | | Nierswalde, DE | |
|-------------------|--------------|-------------------|--------------|-------------------|--------------|
| Sampling Time (d) | Timestep (d) | Sampling Time (d) | Timestep (d) | Sampling Time (d) | Timestep (d) |
| 0 | 0 | 0 | 0 | 0 | 0 |
| 1 | 1.1 | 1 | 0.8 | 1 | 0.5 |
| 7 | 5 | 7 | 4.3 | 7 | 5.1 |
| 14 | 8.9 | 14 | 8.8 | 14 | 9.4 |
| 28 | 17.4 | 28 | 17.7 | 28 | 18.7 |
| 61 | 42.6 | 61 | 41 | 61 | 44.2 |
| 122 | 71.4 | 122 | 71.1 | 122 | 77.9 |
| 214 | 92.6 | 214 | 97.6 | 214 | 105.2 |
| 361 | 132.6 | 359 | 142.6 | 366 | 154 |

Table 8-84: Timestep values for the Straszewski (1990) trials

| Thann, DE | | Langforden, DE | |
|-------------------|--------------|-------------------|--------------|
| Sampling Time (d) | Timestep (d) | Sampling Time (d) | Timestep (d) |
| 0 | 0 | 0 | 0 |
| 1 | 0.6 | 1 | 0.4 |
| 3 | 1.7 | 3 | 1.4 |
| 7 | 3.6 | 7 | 3.7 |
| 14 | 8 | 14 | 8.3 |
| 29 | 19.7 | 29 | 18.7 |
| 60 | 40.9 | 60 | 42.1 |
| 202 | 96.3 | 186 | 105 |
| 367 | 151.3 | 366 | 173.1 |

Table 8-85: Timestep values for the Crofts and Whiteoak (1977) trials

| Great Shelford UK a | | Great Shelford UK b | |
|---------------------|--------------|---------------------|--------------|
| Sampling Time (d) | Timestep (d) | Sampling Time (d) | Timestep (d) |
| 0 | 0 | 0 | 0 |
| 7 | 2.7 | 2 | 0.8 |
| 24 | 10.5 | 7 | 2.7 |
| 36 | 16.3 | 20 | 9.9 |
| 49 | 23.5 | 62 | 39.1 |
| 86 | 49.6 | 106 | 66.8 |
| 91 | 52.4 | 203 | 100.6 |
| 135 | 80.2 | | |
| 232 | 113.9 | | |

Table 8-86: Timestep values for the Snowdon (1991) trials

| Willingham, UK | | Isleham, UK | |
|-------------------|--------------|-------------------|--------------|
| Sampling Time (d) | Timestep (d) | Sampling Time (d) | Timestep (d) |

| | | | |
|-----|-------|-----|-------|
| 0 | 0 | 0 | 0 |
| 1 | 0.3 | 1 | 0.4 |
| 3 | 1 | 3 | 1.3 |
| 7 | 2.8 | 7 | 2.5 |
| 14 | 5.5 | 14 | 5.4 |
| 28 | 12.2 | 28 | 10.2 |
| 56 | 27.4 | 56 | 23.7 |
| 91 | 51.4 | 91 | 40.9 |
| 197 | 104.7 | 190 | 88.8 |
| 289 | 124.9 | 282 | 112.2 |
| 366 | 151.8 | | |

Table 8-87: Timestep values for the Andre (1992) trials

| Mainz-Bretzenheim | | | |
|------------------------|--------------|-------------------|--------------|
| Sampling Time (d) | Timestep (d) | Sampling Time (d) | Timestep (d) |
| 0 | 0 | 0 | 0 |
| 14 | 4.3 | 21 | 5.5 |
| 28 | 8.2 | 49 | 16.9 |
| 56 | 19.6 | 105 | 51.4 |
| 112 | 54.1 | 161 | 85.2 |
| 168 | 87.9 | 217 | 100.5 |
| 224 | 103.1 | 273 | 108.4 |
| 280 | 111.1 | 329 | 116.8 |
| 336 | 119.5 | 385 | 131.1 |
| 392 | 133.7 | | |
| Speyer-Rinkenbergerhof | | | |
| Sampling Time (d) | Timestep (d) | Sampling Time (d) | Timestep (d) |
| 0 | 0 | 0 | 0 |
| 14 | 3.3 | 21 | 6.4 |
| 21 | 5.1 | 49 | 17.5 |
| 56 | 18.4 | 106 | 58.3 |
| 113 | 55.8 | 161 | 84.4 |
| 168 | 80.3 | 217 | 98.4 |
| 224 | 94 | 273 | 106.8 |
| 280 | 102.1 | | |

Table 8-88: Normalized field DT₅₀ values of ethofumesate (normalized to 20 °C and FC)

| Study | Model used | DT ₅₀ | DT ₉₀ |
|----------------------------|------------|-------------------|------------------|
| | | [d] | [d] |
| R500-1 Mainz-Bretzenheim A | SFO | 69.5 | 231 |
| R500-1 Mainz-Bretzenheim B | SFO | 47.4 | 157 |
| R500-1 Speyer A | DFOP | 47.2 | 157 |
| R500-1 Speyer B | DFOP | 46.5 | 155 |
| W 41 Great Shelford A | SFO | 15.0 | 49.9 |
| W 41 Great Shelford B | SFO | 21.7 | 72.0 |
| W97 Isleham | SFO | 25.7 | 85.2 |
| W97 Willingham | SFO | 18.0 | 60.0 |
| W 106 Langforden | SFO | 434 ¹ | - |
| W 106 Thann | SFO | 26.4 ¹ | - |
| W110 Fresno | SFO | 112 | 372 |
| W 121 Nierswalde | SFO | 184 ¹ | - |
| W121 Keeken | SFO | 22.1 | 73.5 |
| W121 Weeze | SFO | 75.7 | 252 |
| Geometric mean | | 37.5 | 124.5 |

¹ Dissipation rate not significantly different from zero and DT₅₀ not considered in calculation of geometric mean.

RESULT AND DISCUSSION

Normalized DT₅₀ values for ethofumesate ranged from 15 to 112 d, with a geometric mean of 37.5 d.

Comments RMS

The normalization study is acceptable. However, the studies by Straszewski (1990) and Crofts and Whiteoak (1977) were found not valid. Therefore, the results for studies W 41 (Crofts and Whiteoak) and W 106 (Straszewski, 1990) are excluded.

Relevant endpoints:

| Study | Kinetic model | DT ₅₀ [d] | DT ₉₀ [d] |
|----------------------------|---------------|-------------------------|-------------------------|
| R500-1 Mainz-Bretzenheim A | SFO | 69.5 | 231 |
| R500-1 Mainz-Bretzenheim B | SFO | 47.4 | 157 |
| R500-1 Speyer A | DFOP | 47.2 ¹ | 157 ¹ |
| R500-1 Speyer B | DFOP | 46.5 ¹ | 155 ¹ |
| W97 Isleham | SFO | 25.7 | 85.2 |
| W97 Willingham | SFO | 18.0 | 60.0 |
| W110 Fresno | SFO | 112 | 372 |

| | | | |
|-------------|-----|------|------|
| W121 Keeken | SFO | 22.1 | 73.5 |
| W121 Weeze | SFO | 75.7 | 252 |

Reference: Ethofumesate: Field Dissipation Studies in Northern and Southern Europe

Notifier: UPL

Author(s), year: Andrews, G. (2014)

Report/Doc. number: NZ/11/007

Guideline(s): None

GLP: Yes

Deviations:

Validity: Valid

Status: New study

Executive summary

The dissipation behaviour of ethofumesate under field conditions, was determined in four soil trials at sites in northern Europe (UK and Germany) and southern Europe (France and Spain), conducted between May 2012 and June 2013. The soil was characterised as listed below.

Table 8-89: Soil characteristics

| Test Site Location | Soil Type | pH (CaCl ₂) | % Organic Carbon Content |
|-----------------------------|-----------------|-------------------------|--------------------------|
| NZ11007/1 (United Kingdom) | Clay loam | 7.13 | 2.25 |
| NZ11007/2 (Germany) | Silty Clay Loam | 7.57 | 1.50 |
| NZ11007/3 (Southern France) | Silty clay loam | 7.72 | 0.89 |
| NZ11007/4 (Spain) | Loam | 7.70 | 1.07 |

A single application of Ethofol 500 SC was applied to bare soil at a nominal application rate of 1000 g a.i./ha. The actual amount applied was based on actual spray volume and measured concentration of ethofumesate in the test product and is shown in the table below. Immediately after application, the soil surface was covered with a layer of soil 0.5 to 1 cm deep. A control plot was also established adjacent to the treated plot.

Soil samples from treated plots were collected on the day of application and at further intervals of 3, 7, 14 (± 1), 21 (± 1), 28, 56 (± 1), 90 (± 1) and 180 (± 1) or 186 days after application (DAA). In the case of the Spanish trial additional samples were collected at 274 and 300 days after application (DAA) and in Southern France an additional sample was collected at 379 days after application (DAA). Additionally, control soil was sampled at Day 0 and at 14 (± 1), 56 (± 1), 90(± 1) and 180 (± 1) days after application (DAA), except in the UK where control soils were sampled at Day 0 and at 14, 56 and 186 DAA. In Spain a further control soil sampling was conducted at 274 days after application (DAA). Soil sampling was conducted using apparatus that collected

cores measuring 5 x 30 cm. Soil was initially sampled from treated plots to a depth of 0-30 cm. The untreated plot was sampled to a depth of 30 cm. A total of 20 cores were sampled at each interval for the treated plot and 10 cores for untreated. Soil samples were frozen at the test site. Soil cores were shipped frozen to the test facility for analysis. For each sampling interval, soil cores were sub-sampled with respect to depth (0-10 cm, 10-20 cm and 20-30 cm) and the sub-samples combined and homogenised with dry-ice to provide a composite sample for each of the three depths.

The determination of ethofumesate residues in soil samples was conducted using a previously validated method (Jooss, 2011). Residues were extracted with acetonitrile and then diluted before final determination by LC-MS/MS monitoring two transitions for each analyte. To overcome the observed LC-MS/MS ion suppression due to the sample matrix in the Spanish and British samples, calibration solutions were prepared with the addition of control extract. Method performance was verified by conducting recovery efficiency tests on the day of analysis. The limits of detection for ethofumesate were 0.002, 0.0005, 0.0005, and 0.0002 mg/kg for trials 1, 2, 3 and 4 respectively. The limit of quantification for ethofumesate, based on lowest level of fortification, was 0.01 mg/kg, corresponding to approximately 1% of the initial applied amount.

The mean recovery efficiency was 95%, with relative standard deviations of less than 20%. No residue was detected above the 30% of the LOQ (0.01 mg/kg) at the retention time of ethofumesate in any control samples. With the exception of the Spanish day zero sample which had a residue of 0.0156 mg/kg. Samples were analysed up to 186 DAA in the UK, 91 DAA in Germany, 379 DAA in France and 300 DAA in Spain when it became apparent that residues had declined to level below the DT90.

Residue levels of ethofumesate in treated samples are summarised below:

Table 8-90: Residue levels in soil samples from UK (NZ11007/1)

Ethofumesate residues in soil samples from United Kingdom (NZ11007/1)

| Sampling Interval (DAA) | Residue Level (mg/kg)* | | |
|----------------------------|------------------------|--------------------|--------------------|
| | 0-10 cm | 10-20cm | 20-30 cm |
| 0 + 2 hours | 0.892 ¹ | 0.026 ² | 0.022 ³ |
| 3 | 1.08 | 0.203 | 0.011 |
| 7 | 0.814 | 0.134 | 0.027 |
| 14 | 0.642 | 0.035 | < LOQ |
| 20 | 0.567 | 0.026 | < LOQ |
| 28 | 0.402 | < LOQ | < LOQ |
| 56 | 0.181 | 0.013 | < LOQ |
| 90 | 0.081 | 0.031 | < LOQ |
| 186 | 0.041 | 0.015 | < LOQ |

* soil concentrations were corrected for soil moisture content

1. Average of three extractions (1.038 mg/kg, 0.744 mg/kg and 0.893 mg/kg)

2. Average of two extractions (0.0270 mg/kg and 0.0245 mg/kg)

3. Average of two extractions (0.0206 mg/kg and 0.0237 mg/kg)

Where multiple extractions reported, extractions are from same homogenised mixture of all cores from sampling horizon.

Table 8-91: Residue levels in soil samples from Germany (NZ11007/2)

| Sampling Interval (DAA) | Residue Level (mg/kg)* | | |
|----------------------------|------------------------|---------|----------|
| | 0-10 cm | 10-20cm | 20-30 cm |
| 0 + 2 hours | 0.917 | NA | NA |
| 3 | 0.549 | <LOQ | NA |
| 7 | 0.509 | <LOQ | NA |
| 14 | 0.390 | <LOQ | NA |
| 21 | 0.334 | <LOQ | NA |
| 28 | 0.323 | <LOQ | NA |
| 55 | 0.129 | <LOQ | NA |
| 91 | 0.074 | <LOQ | NA |

* soil concentrations were corrected for soil moisture content
NA = not analysed

Table 8-92: Residue levels in soil samples from South France (NZ11007/3)

| Sampling Interval (DAA) | Residue Level (mg/kg)* | | |
|----------------------------|------------------------|---------|----------|
| | 0-10 cm | 10-20cm | 20-30 cm |
| 0 + 2 hours | 0.943 | NA | NA |
| 3 | 0.787 | <LOQ | NA |
| 7 | 0.765 | <LOQ | NA |
| 14 | 0.693 | <LOQ | NA |
| 21 | 0.620 | <LOQ | NA |
| 28 | 0.498 | <LOQ | NA |
| 55 | 0.298 | <LOQ | NA |
| 90 | 0.310 ¹ | <LOQ | NA |
| 181 | 0.204 | <LOQ | NA |
| 379 | 0.068 | <LOQ | NA |

* soil concentrations were corrected for soil moisture content

1. Average of three extractions (0.335 mg/kg, 0.287 mg/kg and 0.308 mg/kg)

Where multiple extractions reported, extractions are from same homogenised mixture of all cores from sampling horizon.

NA = not analysed

Table 8-93: Residue levels in soil samples from Spain (NZ11007/4)

| Sampling Interval (DAA) | Residue Level (mg/kg)* | | |
|----------------------------|------------------------|---------|----------|
| | 0-10 cm | 10-20cm | 20-30 cm |
| 0 + 2 hours | 0.934 | NA | NA |
| 3 | 0.698 | <LOQ | NA |
| 7 | 0.554 | <LOQ | NA |
| 14 | 0.525 | <LOQ | NA |
| 21 | 0.282 | <LOQ | NA |
| 28 | 0.415 | <LOQ | NA |
| 57 | 0.368 | <LOQ | NA |
| 90 | 0.184 | <LOQ | NA |
| 179 | 0.112 | <LOQ | NA |
| 274 | 0.078 | <LOQ | NA |
| 300 | 0.065 | 0.022 | NA |

*soil concentrations were corrected for soil moisture content

NA = not analysed

Using the residue data obtained from the field trials, DT_{50} and DT_{90} values were estimated using first order (SFO), double first order in parallel (DFOP) and first order multi compartment (FOMC) kinetics. The results are summarised in the table below.

The following figures and tables show the results of the kinetic evaluations carried out by the notifier.

Figure 8-67: Kinetic evaluation field trial UK (SFO)

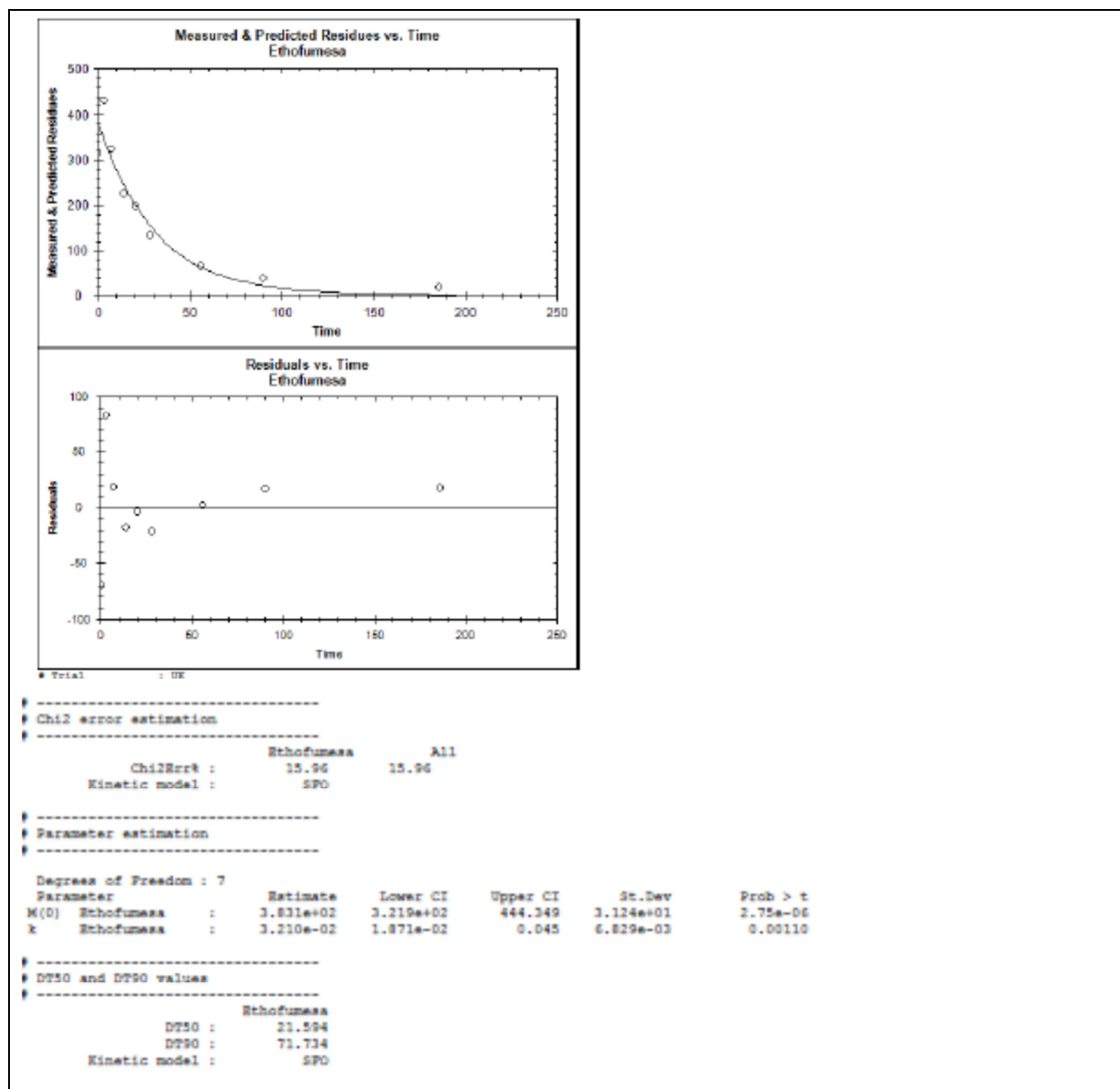


Figure 8-68: Kinetic evaluation field trial UK (FOMC)

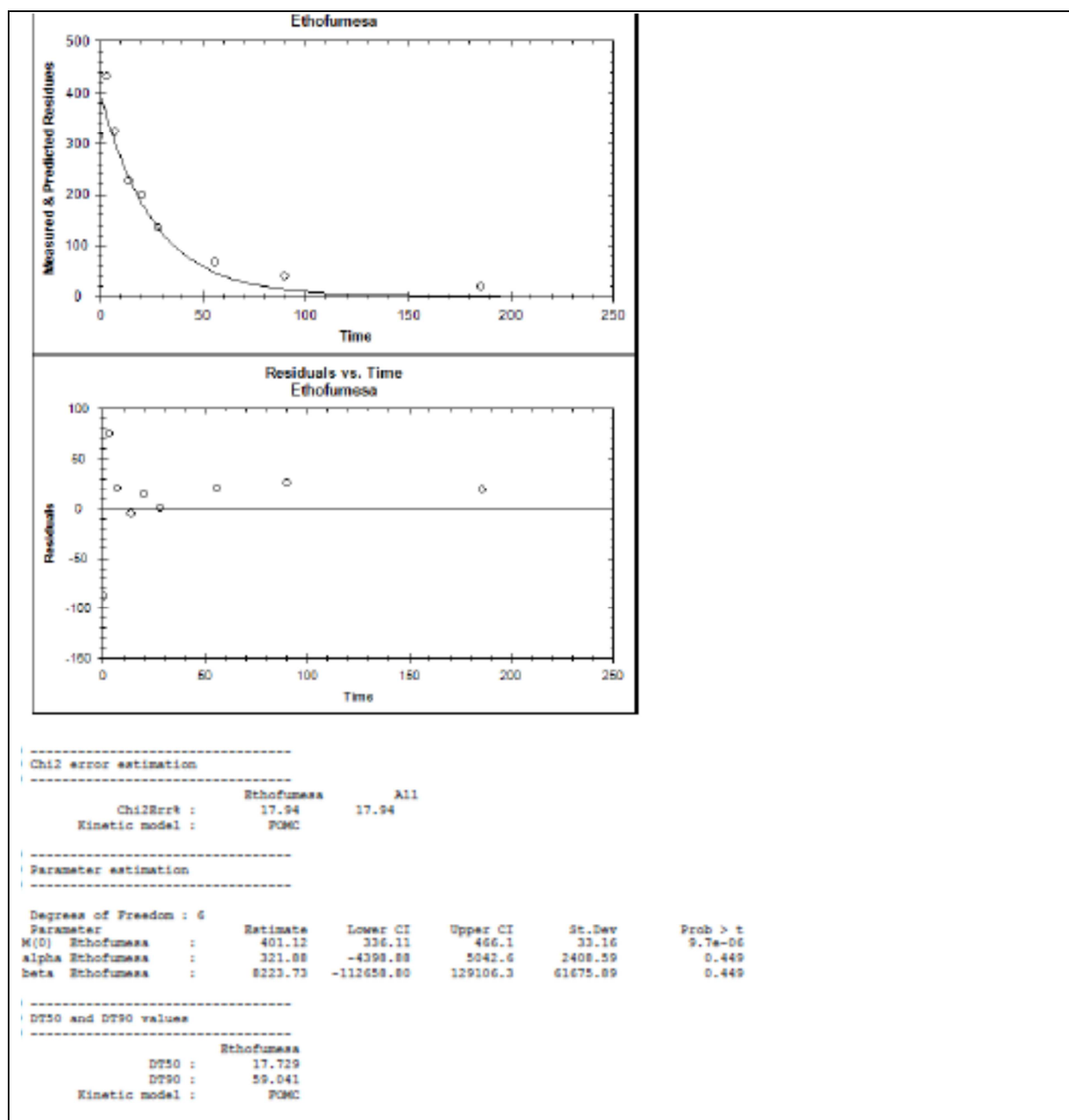


Figure 8-69: Kinetic evaluation field trial UK (SFO), with day zero as outlier

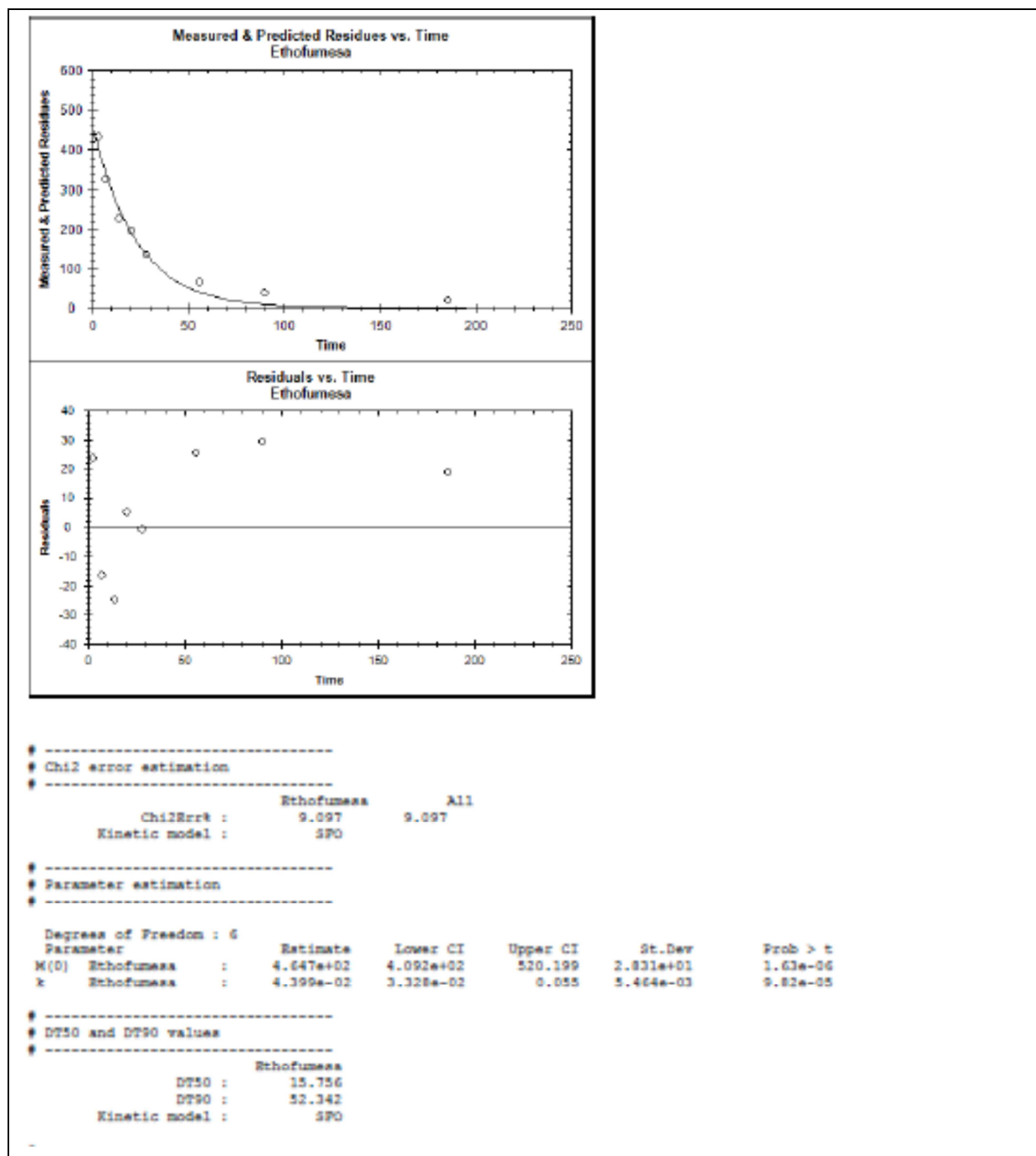


Figure 8-70: Kinetic evaluation field trial UK (FOMC), with day zero as outlier

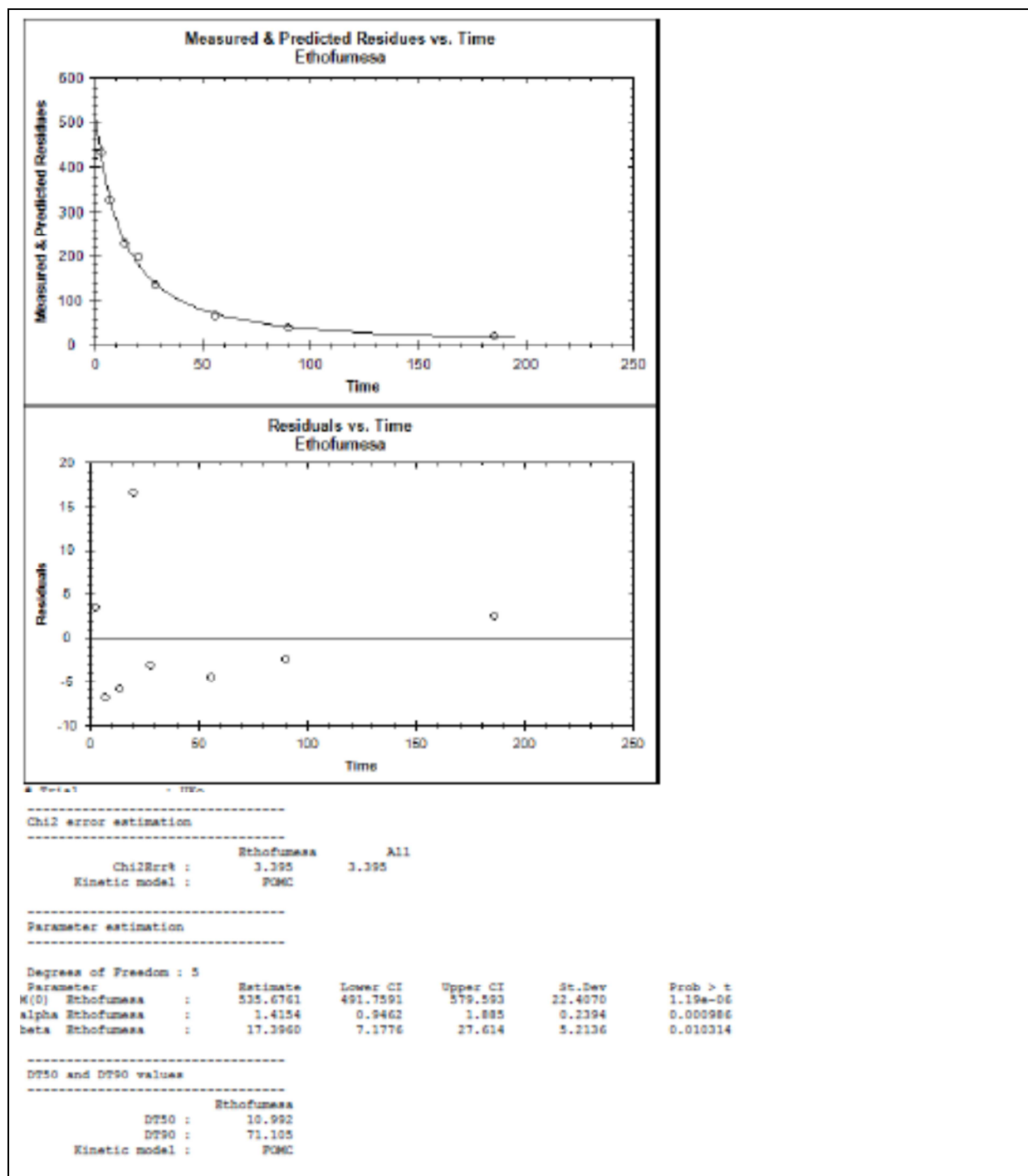


Figure 8-71: Kinetic evaluation field trial UK (DFOP)

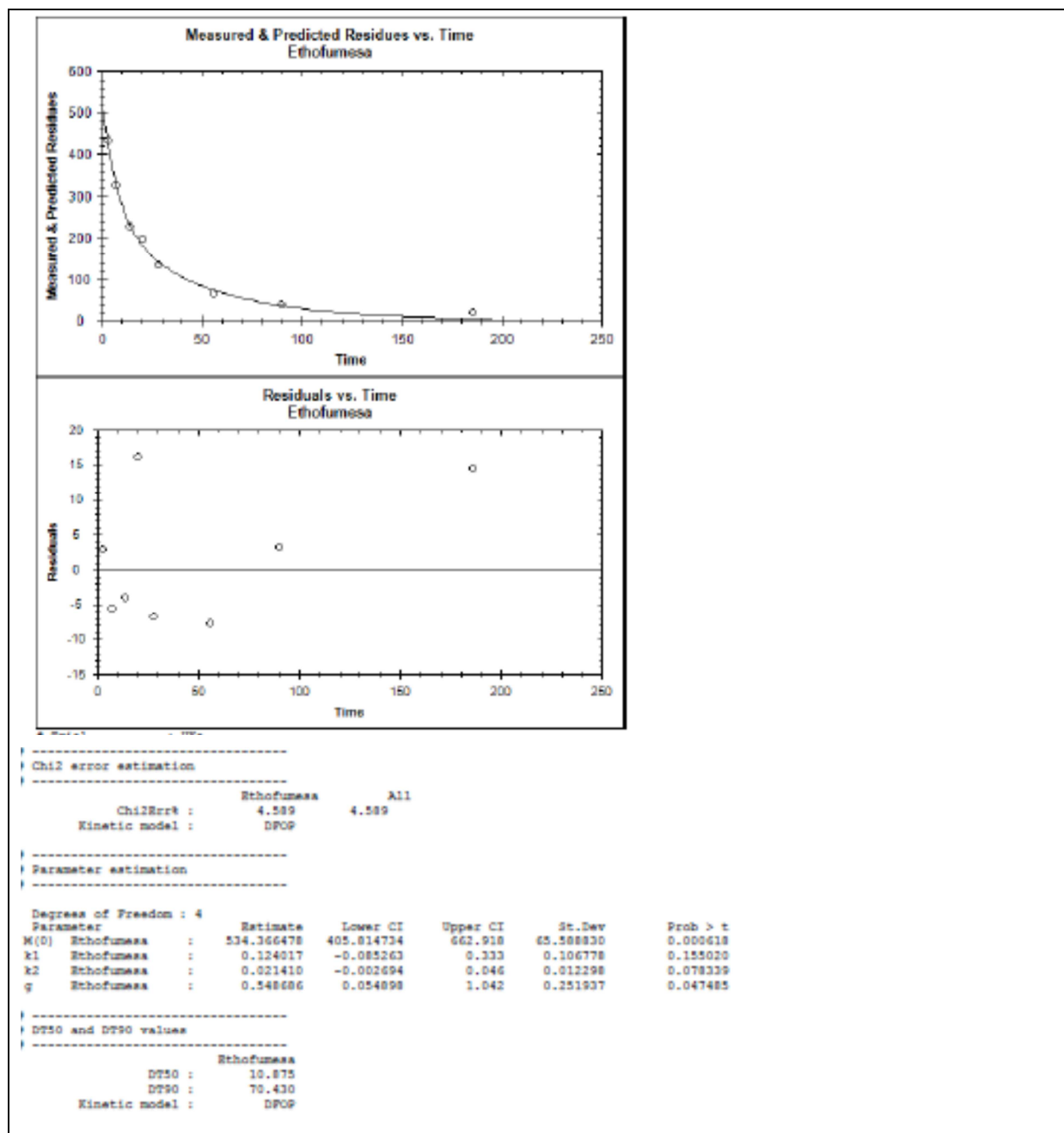


Figure 8-72: Kinetic evaluation field trial Germany (SFO)

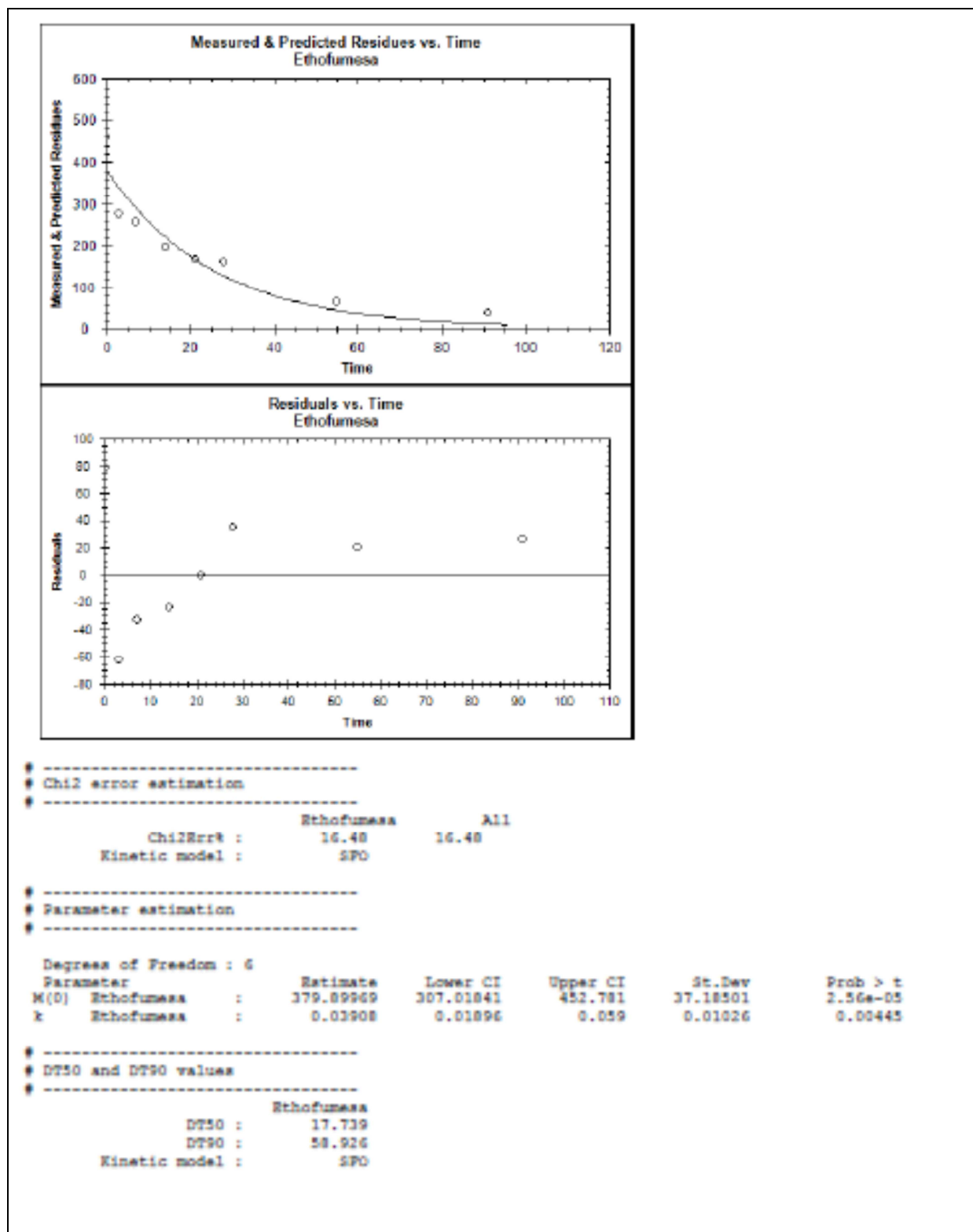


Figure 8-73: Kinetic evaluation field trial Germany (FOMC)

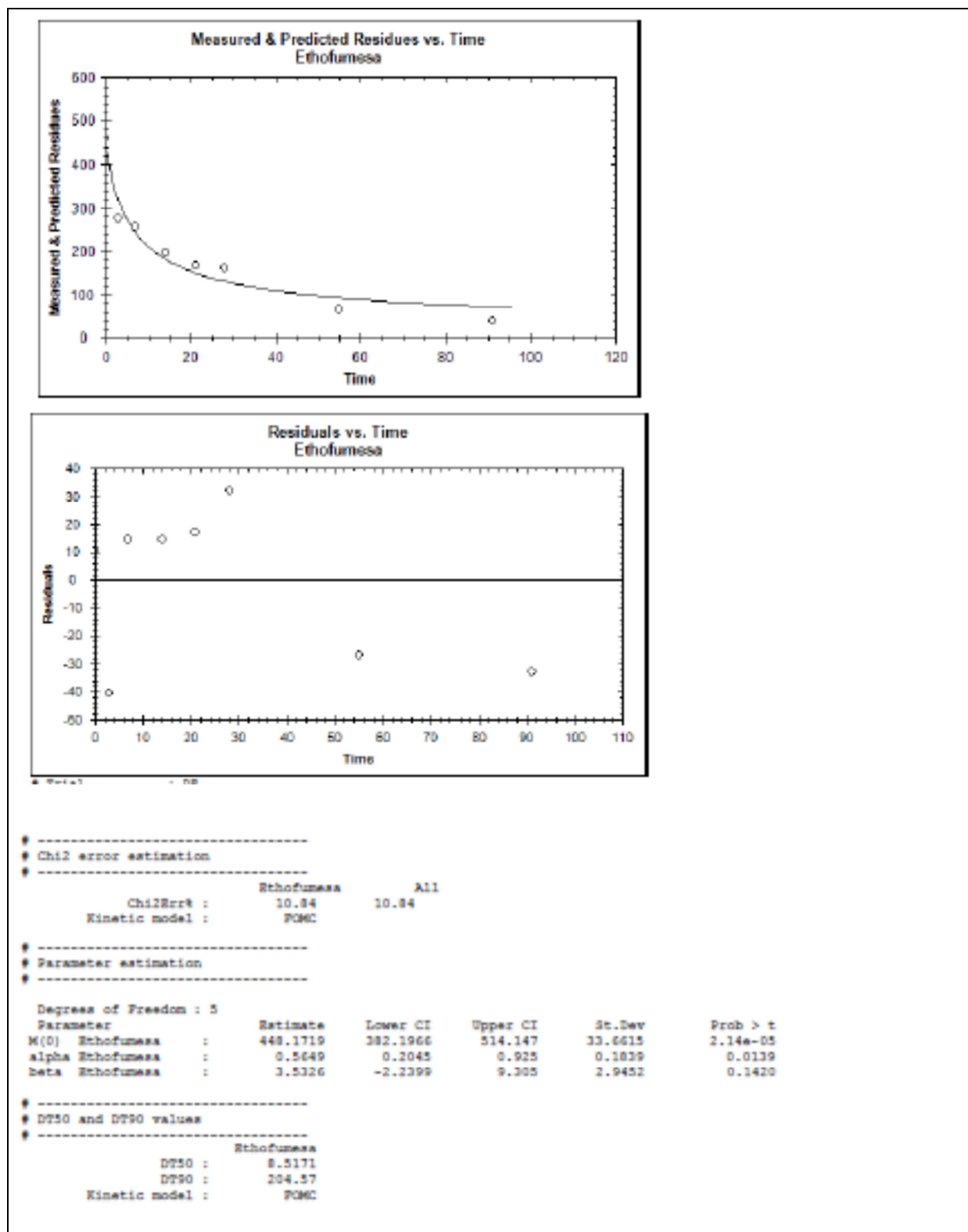


Figure 8-74: Kinetic evaluation field trial Germany (DFOP)

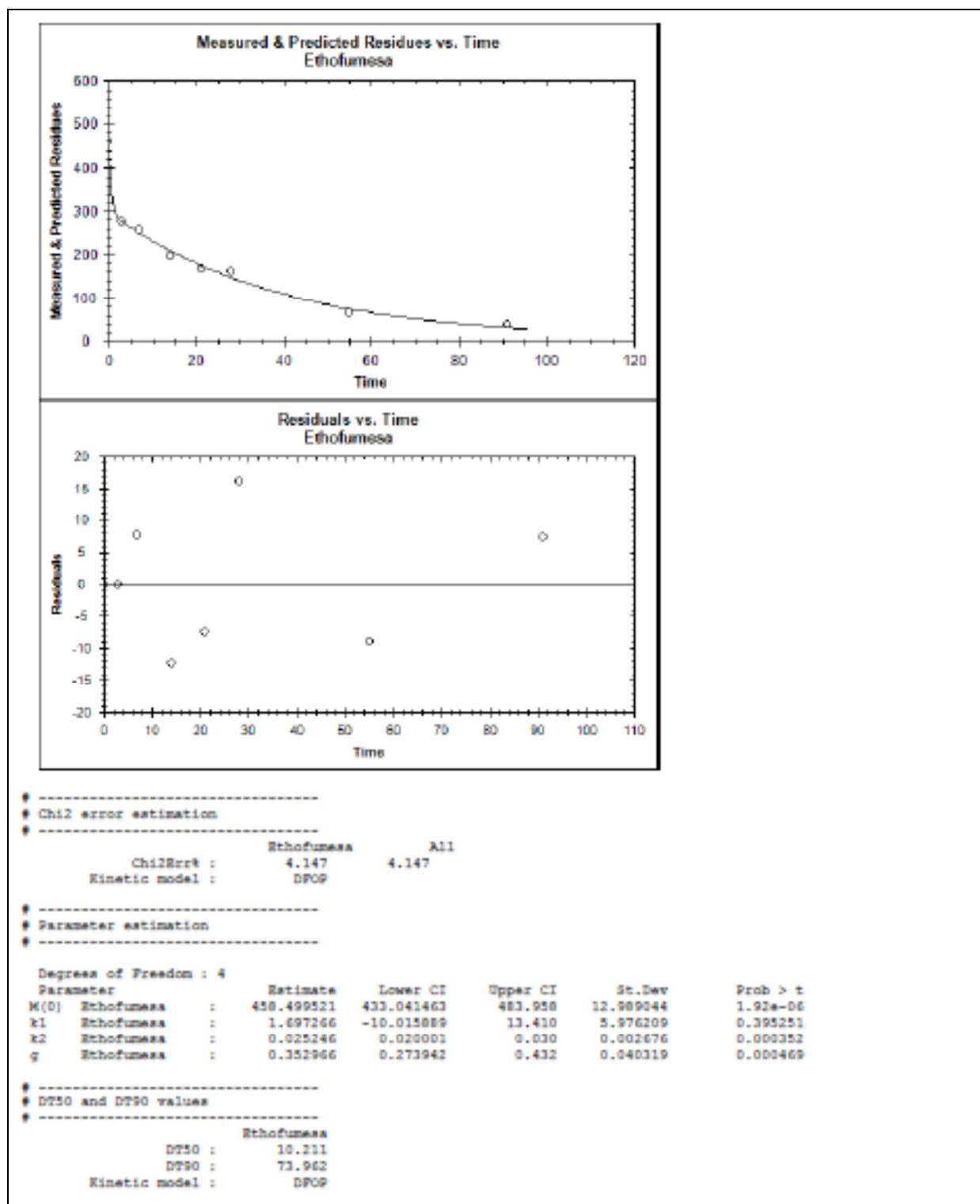


Figure 8-75: Kinetic evaluation field trial France (SFO)

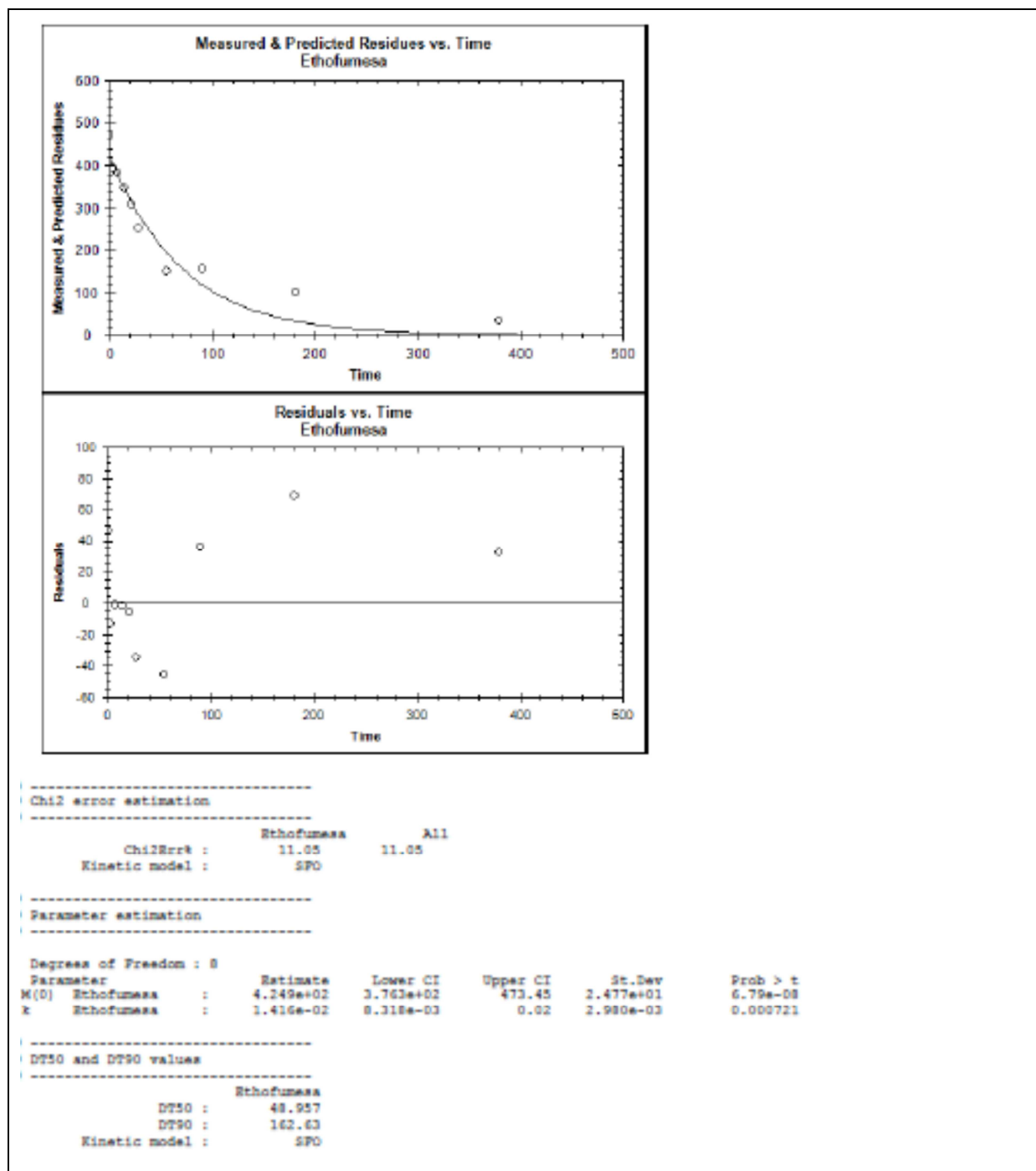


Figure 8-76: Kinetic evaluation field trial Germany (FOMC)

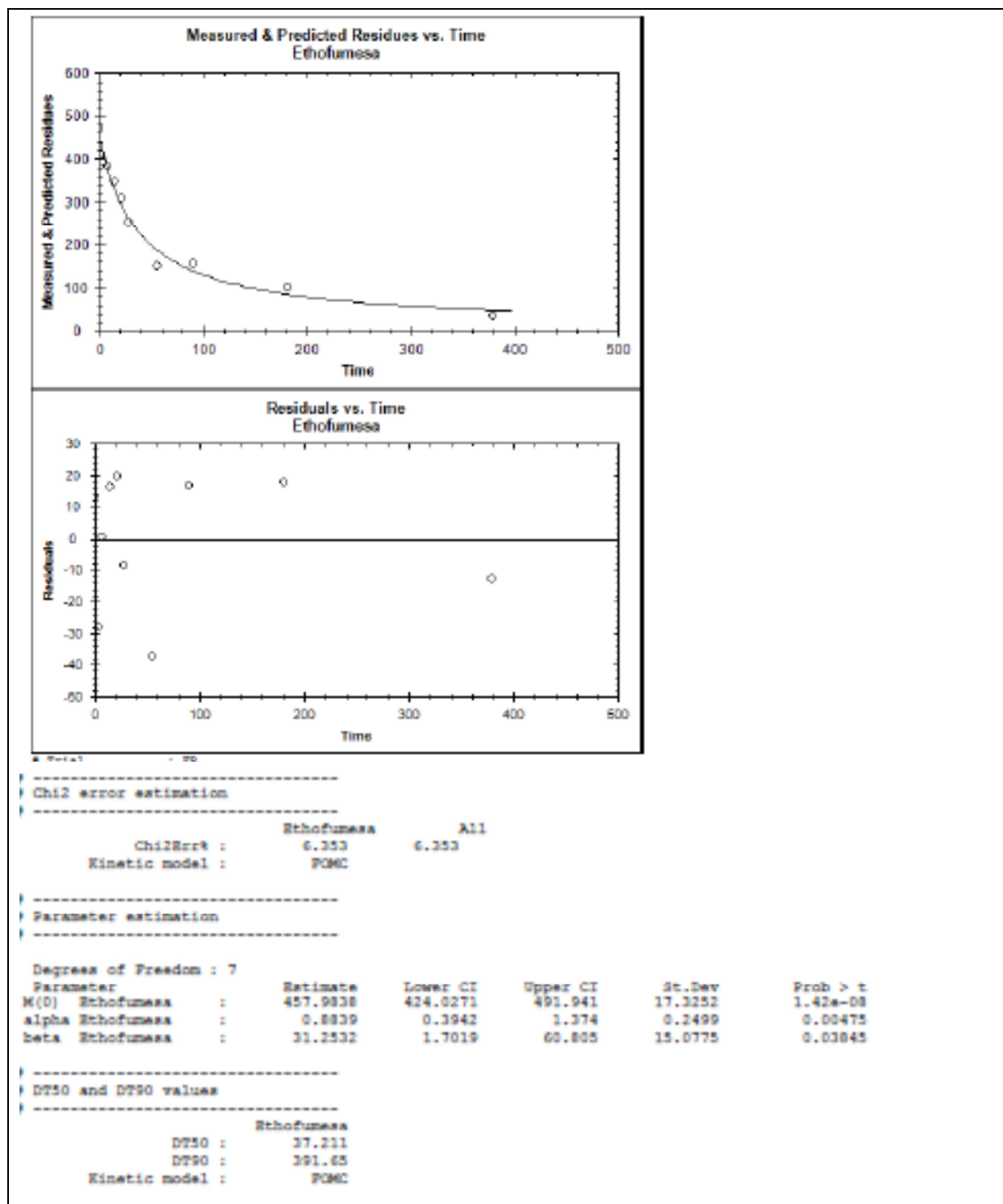


Figure 8-77: Kinetic evaluation field trial Germany (DFOP)

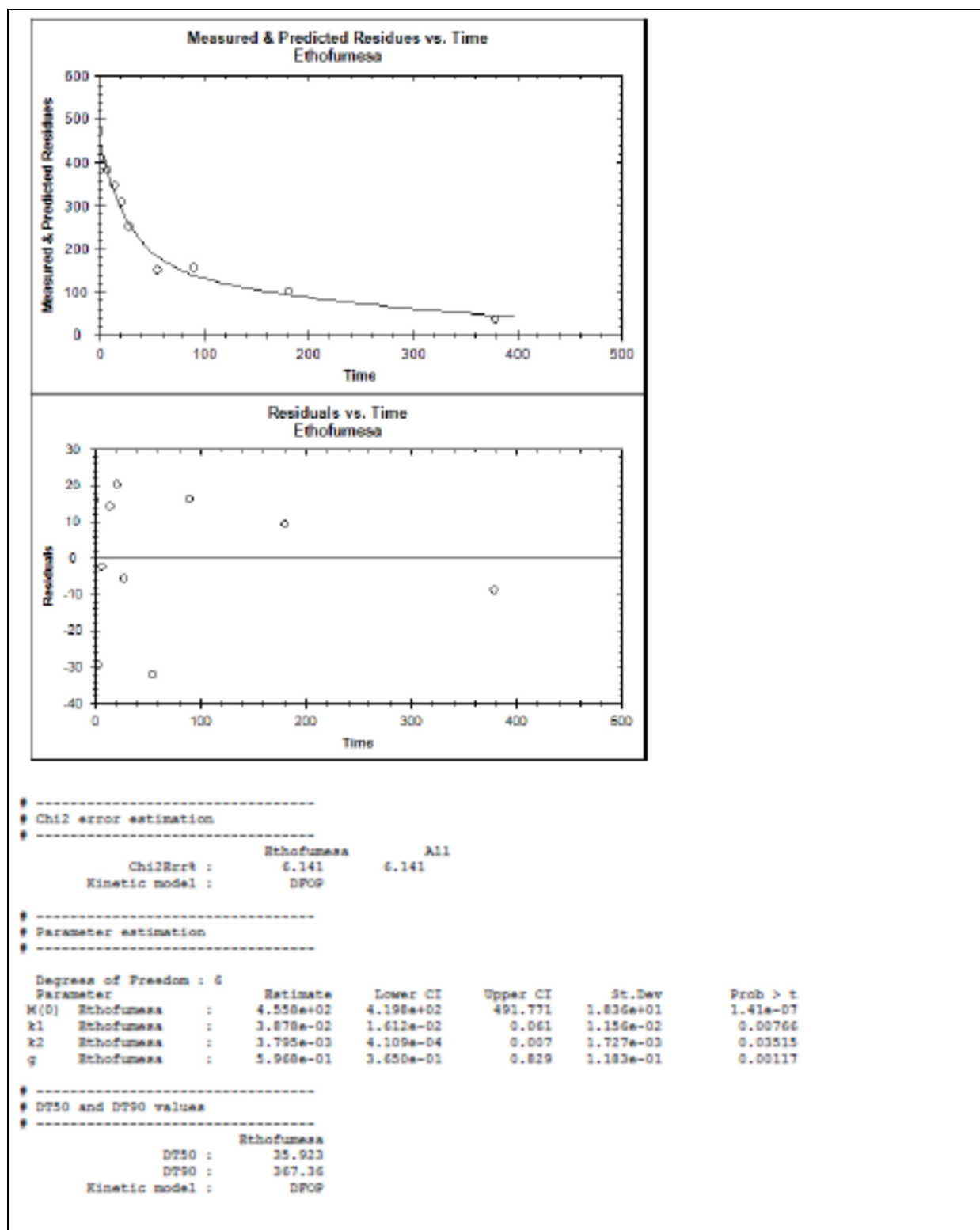


Figure 8-78: Kinetic evaluation field trial Spain (SFO)

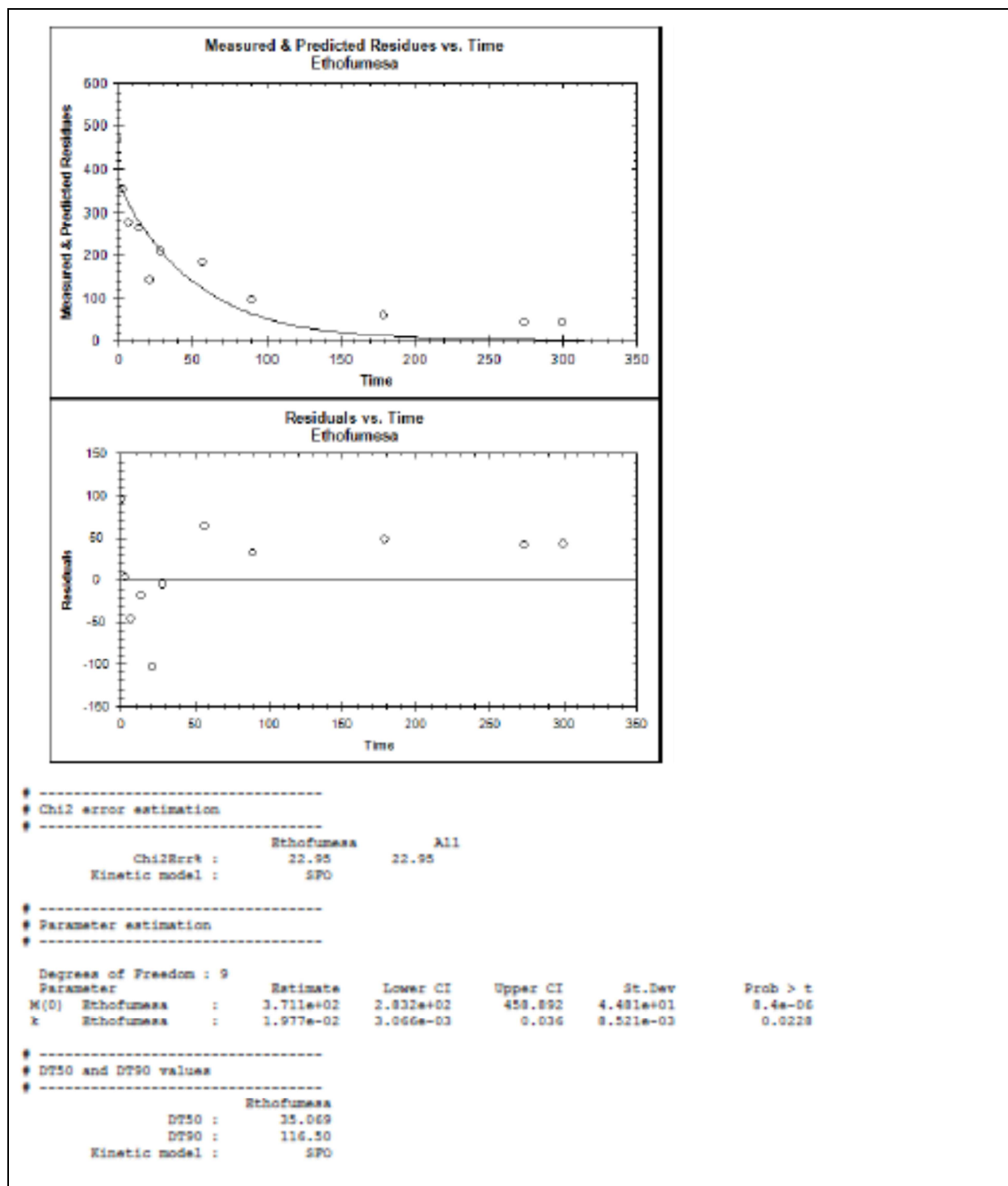


Figure 8-79: Kinetic evaluation field trial Spain (FOMC)

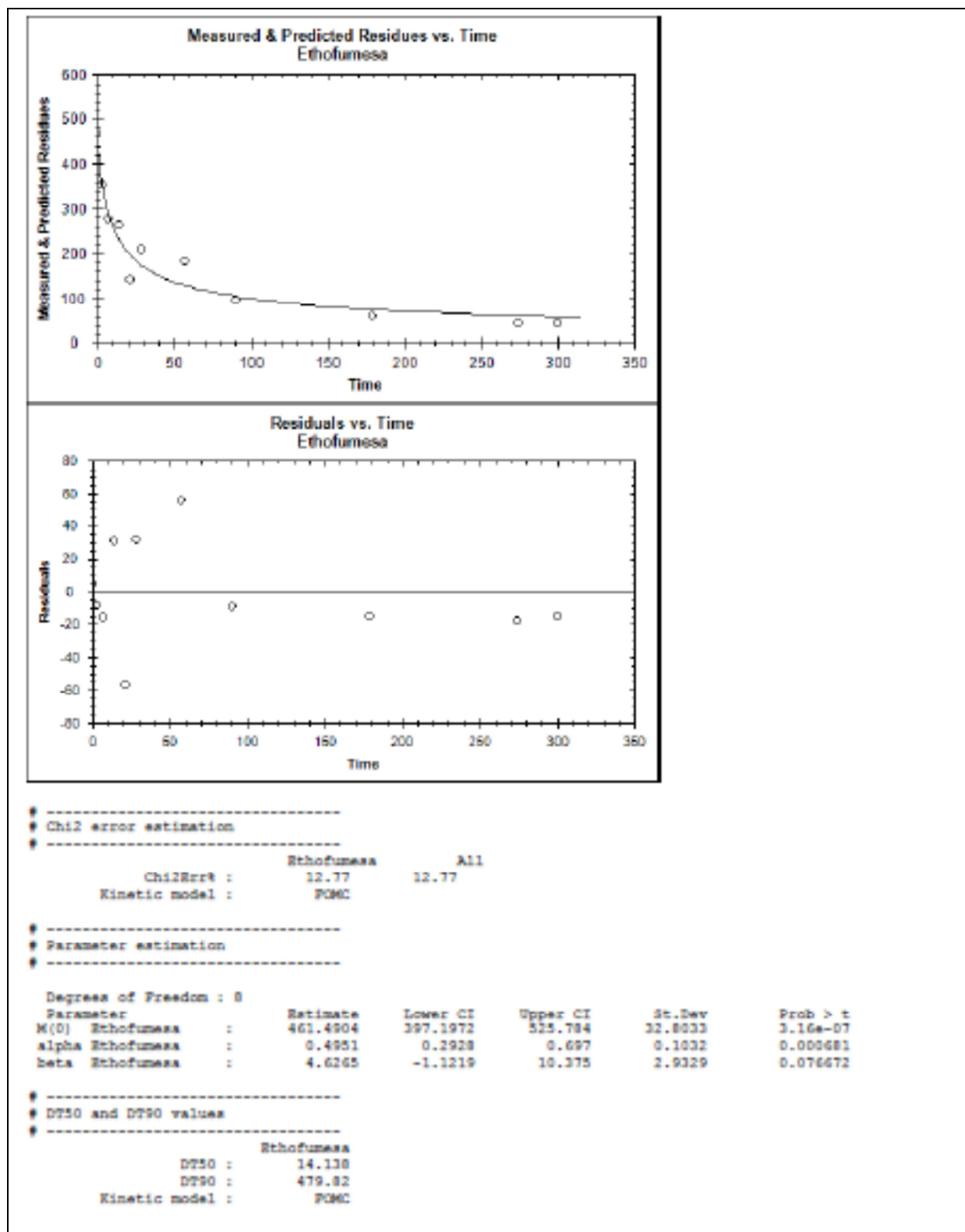


Figure 8-80: Kinetic evaluation field trial Spain (DFOP)

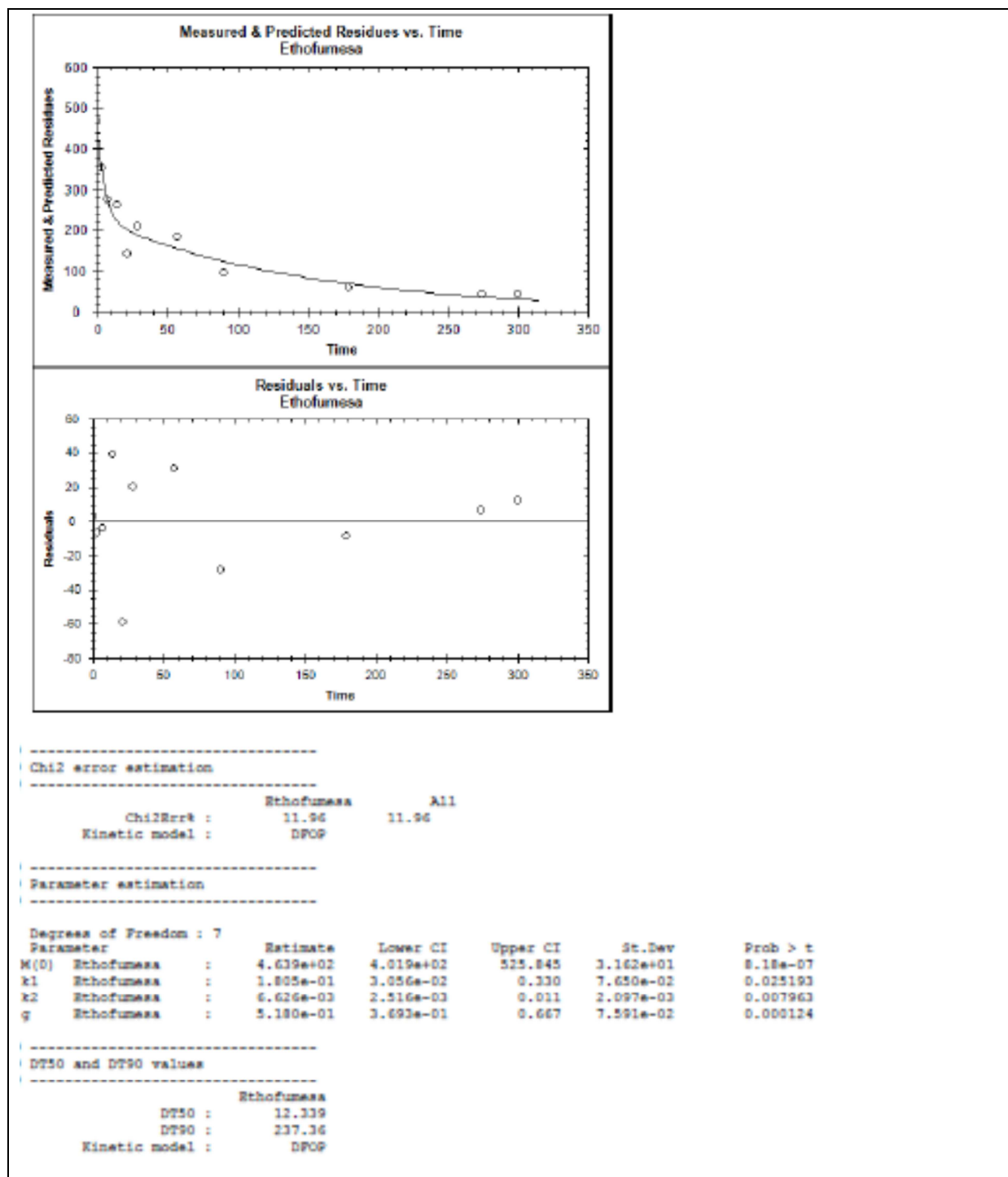


Table 8-94: Non-normalized endpoints for the field trial site

| Test Site Location | Soil type | Ethofumesate | | | | | | Visual fit |
|--------------------------------|-----------------|--------------|--------|----------|-------------------------|-------------------------|--------------------------|------------|
| | | pH | OC (%) | kinetics | DT ₅₀ (days) | DT ₉₀ (days) | χ ² error (%) | |
| NZ11007/1 (United Kingdom) | Clay Loam | 7.57 | 1.50 | SFO | 21.6 | 71.7 | 16.0 | acceptable |
| | | | | FOMC | 17.7 | 59.0 | 17.9 | acceptable |
| | | | | SFO* | 15.8 | 52.3 | 9.1 | good |
| | | | | FOMC* | 11.0 | 71.1 | 3.4 | very good |
| | | | | DFOP* | 10.9 | 70.4 | 4.6 | very good |
| NZ11007/2 (Germany) | Silty Clay Loam | 7.70 | 1.07 | SFO | 17.7 | 58.9 | 16.5 | acceptable |
| | | | | FOMC | 8.5 | 204.6 | 10.8 | acceptable |
| | | | | DFOP | 10.2 | 74.0 | 4.1 | very good |
| NZ11007/3 (Southern France) | Silty Clay Loam | 7.72 | 0.89 | SFO | 49.0 | 162.6 | 11.1 | acceptable |
| | | | | FOMC | 37.2 | 392.0 | 6.4 | very good |
| | | | | DFOP | 35.9 | 367.4 | 6.1 | very good |
| NZ11007/4 (Spain) | Loam | 7.13 | 2.25 | SFO | 35.1 | 116.5 | 23.0 | acceptable |
| | | | | FOMC | 14.1 | 479.8 | 12.8 | good |
| | | | | DFOP | 12.3 | 237.4 | 12.0 | good |

*day 0 value was considered as outlier for these kinetics calculations

Note: The kinetics given in bold are considered appropriate to be used for the persistence endpoints.

Comments RMS

The study is generally acceptable. However, the RMS does not agree with the exclusion of the day zero sample of the UK trial. The exclusion of the day 0 data point in the UK soil data series does not seem to be justified. It should be justified by statistical analysis or by arguments regarding any error in the handling of this sample during the experiment. Or else the data point should not be excluded.

The relevant endpoints are

| Site | | DT50 | DT90 | Chi ² Error |
|---------|---------------|------|------|------------------------|
| | Kinetic Model | [d] | [d] | [%] |
| UK | SFO | 21.6 | 71.7 | 16 |
| Germany | DFOP | 10.2 | 74 | 4.1 |
| France | DFOP | 35.9 | 367 | 6.1 |
| Spain | DFOP | 12.3 | 237 | 12 |

| | |
|---------------------|--|
| Reference: | Determination of Soil Characteristics |
| Notifier: | UPL |
| Author(s), year: | Seibert, K.; 2012 |
| Report/Doc. number: | BP/10/12 |
| Guideline(s): | None |
| GLP: | Yes |
| Deviations: | |
| Validity: | Valid |
| Status: | New study |

Comments RMS

In this study, the soils of the study sites in Andrews (2014) were characterized. The study is acceptable.

| | |
|---------------------|---|
| Reference: | Kinetic evaluation of soil dissipation studies with Ethofumesate according to recommendations of the work group on degradation kinetics of FOCUS |
| Notifier: | UPL |
| Author(s), year: | Stangelj, A.; 2014 |
| Report/Doc. number: | 118608-CA-0701020201-01 |
| Guideline(s): | None |
| GLP: | No |
| Deviations: | |
| Validity: | Valid |
| Status: | New study |

Executive summary

Degradation DT50 and DT90 values (DegT50, DegT90) of Ethofumesate were calculated from experimental values obtained at four field trials (Andrews, 2014) according to recommendations of the FOCUS workgroup on degradation kinetics (2006) and according to EFSA guidance (2010) for use as modelling endpoints. For these calculations the model software KinGUI3 version 2.0 was used.

In order to calculate modelling endpoints the field data were normalised to a reference temperature of 20°C and soil moisture of pF2 as proposed by the FOCUS workgroup on degradation kinetics. EFSA guidance (2010) was followed when selecting acceptable DegT50 values. The study endpoints were estimated with a two compartment model: parent and sink. The data was optimized and integrated according to standard recommendations. The calculated output data (consisting of daily concentrations) and residuals (differences between calculated concentrations and actual measured concentrations) were graphically fitted and visually assessed. Following an acceptable visual assessment, the deviations between observed and calculated values relative to the uncertainty of the measurements was assessed using the chi-square (χ^2) statistical test where the FOCUS trigger level of < 15% was applied. A final test of the confidence of the calculated data returned after optimisation was performed using a t-test and employing the FOCUS trigger value for probability of < 0.05.

At first the first-order kinetics was fitted to all unmodified data without constraints in the initial concentration. The goodness of fit was assessed using visual evaluation and a χ^2 -test. No further action was required and half-life can be used for modelling if the fit was visually acceptable and passed the χ^2 -test at an error level of 15% or less. In case the concentrations decreased to 10% of the initial value within the study period, FOMC model could be tested. If the FOMC fit was visually significantly better than the SFO fit and the χ^2 -test did not significantly exceed 15% then the half-life from this model can be used. The half-life for modelling was then calculated based on the DT90 divided by 3.32.

It has to be considered that the error term required to pass χ^2 -test may be larger in case of field studies. In such case, a decision was made based on visual assessment. If the overall pattern of decline in pesticide concentration of the residuals is random the half-life from the SFO model was used for modelling.

For the NZ11007/1 trial (UK) the decline curve could be sufficiently described with SFO. The χ^2 value was slightly above the threshold of 15%, but could be accepted because field data is often characterised by large scatter of data. However, the FOMC model was tested as well but does not present any improvement in the fitting. Furthermore, even when considering the day 0 sample as an outlier the curve fitting does not show any improvement in case of SFO, but present improvement in the fitting with FOMC. However, due to only minor improvements, it is recommended to use the DegT50 of 15.22 days, obtained with the SFO.

For the NZ11007/2 trial (Germany) the decline was tested with SFO and FOMC fitting. Since the fit is adequately presented by SFO and the FOMC model did not present significant improvement the DegT50 of 13.46 days (SFO) was chosen for modelling.

For the NZ11007/3 trial (Southern France) the decline curve could be sufficiently described with SFO. However, the FOMC model was tested as well but did not present any significant improvement in the fitting and therefore the DegT50 of 55.20 days (SFO) was chosen for modelling.

For the NZ11007/4 trial (Spain) the decline curve could not be described satisfactorily with SFO. Hence, FOMC was used. FOMC resulted in an acceptable curve fitting compared to SFO. Because of that the modelling endpoint was derived from DegT90 FOMC / 3.32. The resulting DegT50 is 94.12 days.

The outcome of the evaluation of the soil dissipation study with Ethofumesate after normalisation to FOCUS reference conditions is summarised below:

Table 8-95: Field soil dissipation of ethofumesate – Kinetic parameters for modelling endpoints

| Kinetic model | DegT ₅₀ [d] | DegT ₉₀ [d] | Visual fit | Chi ² ^a | t-test ^b | r ² |
|------------------------------------|------------------------------|---------------------------|------------|-------------------------------|---------------------------------------|----------------|
| United Kingdom (NZ11007/1) | | | | | | |
| SFO | 15.22 | 50.55 | Good | 15.77 | < 0.05 | 0.9191 |
| SFO ^c | 11.45 | 38.04 | Acceptable | 9.04 | < 0.05 | 0.9815 |
| FOMC | 15.21 (15.24 ^c) | 50.61 | Good | 16.67 | α : 0.489 β : 0.489 | 0.9191 |
| FOMC ^c | 8.07 (14.05 ^c) | 46.65 | Good | 5.09 | α : < 0.05 β : < 0.05 | 0.9938 |
| Germany (NZ11007/2) | | | | | | |
| SFO | 13.46 | 44.71 | Acceptable | 14.40 | < 0.05 | 0.9200 |
| FOMC | 8.17 (33.98 ^c) | 112.80 | Acceptable | 9.45 | α : < 0.05 β : 0.128 | 0.9675 |
| Southern France (NZ11007/3) | | | | | | |
| SFO | 55.20 | 183.36 | Acceptable | 10.23 | < 0.05 | 0.9459 |
| FOMC | 38.50 (101.98 ^c) | 338.58 | Acceptable | 6.67 | α : < 0.05 β : 0.0576 | 0.9774 |
| Spain (NZ11007/4) | | | | | | |
| SFO | 25.17 | 83.62 | Acceptable | 22.63 | < 0.05 | 0.8474 |
| FOMC | 9.83 (94.12 ^c) | 312.49 | Acceptable | 14.24 | α : < 0.05 β : 0.1242 | 0.9373 |

a Error value at which the χ^2 -test is passed should be below 15%. The χ^2 -test considers the deviations between observed and calculated values relative to the uncertainty of the measurements.

b A model parameter is considered significantly different from zero if the probability corresponding to the calculated t-value is smaller than 0.05, i.e. considering a 5 percent significance level. Probabilities between 0.05 and 0.1 can be considered to be acceptable due to the large scatter of data typical for field studies.

c Day 0 sample treated as an outlier

* SFO Half-life calculated from DT50/3.32

Modelling endpoints are marked in bold

Comments RMS

In this study, the normalization of the field data by Andrews (2014) was carried out. The study is acceptable. However, for the sites in Southern France and Spain, the DFOP model gave better and more reliable fits (i.e. better p-values). Moreover, the exclusion of the day 0 data point in the UK soil data series does not seem to be justified. It should be justified by statistical analysis or by arguments regarding any error in the handling of this sample during the experiment. Or else the data point should not be excluded. Evaluation of kinetics based on the DFOP model was carried out by the RMS.

The results are shown in the figures and tables below.

The endpoints are:

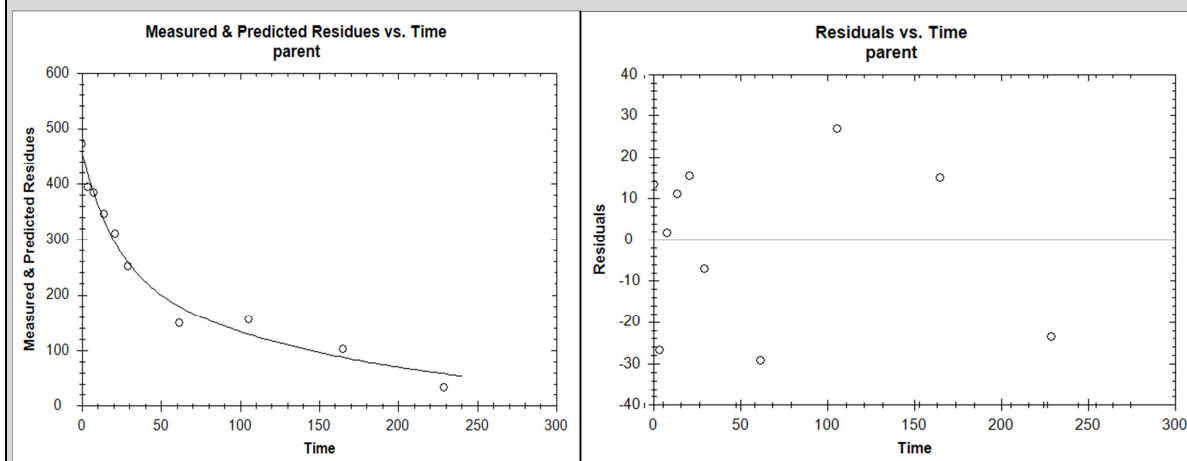
| Site | Kinetic Model | DegT ₅₀ [d] | DegT ₉₀ [d] | Chi ² Error [%] |
|------|---------------|---------------------------|---------------------------|-------------------------------|
| UK | SFO | 15.2 | 50.6 | 15.8 |

| | | | | |
|---------|------|------------|-------|------|
| Germany | SFO | 13.5 | 44.7 | 14.4 |
| France | DFOP | 38 (110*) | 266.6 | 6.6 |
| Spain | DFOP | 8.4 (60**) | 140.9 | 13.2 |

* calculated from slow phase $DT_{50}(k_2 = 6.321 \times 10^{-3})$

** calculated from slow phase $DT_{50}(k_2 = 1.158 \times 10^{-2})$

Kinetic evaluation field trial South France (DFOP)



```

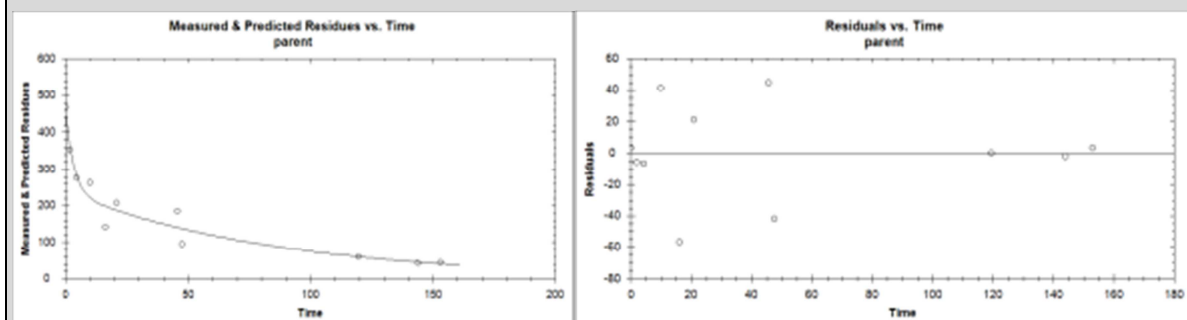
# Chi2 error estimation
-----
                parent      All
Chi2Err%      :      6.553    6.553
Kinetic model  :      DFOP

# Parameter estimation
-----
Degrees of Freedom : 6
Parameter          Estimate      Lower CI      Upper CI      St.Dev      Prob > t
M(0) parent       : 4.582e+02    4.203e+02    495.982    1.930e+01    1.83e-07
k1 parent         : 4.778e-02    5.059e-03    0.090    2.179e-02    0.0354
k2 parent         : 6.321e-03    1.578e-03    0.011    2.420e-03    0.0200
q parent          : 4.608e-01    1.354e-01    0.786    1.660e-01    0.0161

# DT50 and DT90 values
-----
                parent
DT50           :      37.854
DT90           :     266.57
Kinetic model   :      DFOP

```

Kinetic evaluation field trial Spain (DFOP)



| | | | | | | |
|------------------------|--------|------------|------------|----------|-----------|----------|
| Chi2Err% | 13.20 | 13.20 | | | | |
| Kinetic model | DFOP | | | | | |
| # ----- | | | | | | |
| # Parameter estimation | | | | | | |
| # ----- | | | | | | |
| Degrees of Freedom | 7 | | | | | |
| Parameter | | Estimate | Lower CI | Upper CI | St.Dev | Prob > t |
| M(0) parent | : | 463.710751 | 391.478418 | 535.943 | 36.853908 | 2.31e-06 |
| k1 parent | : | 0.308567 | -0.034599 | 0.652 | 0.175088 | 0.060692 |
| k2 parent | : | 0.011578 | 0.004133 | 0.019 | 0.003798 | 0.009315 |
| q parent | : | 0.488944 | 0.316501 | 0.661 | 0.087982 | 0.000427 |
| # ----- | | | | | | |
| # DT50 and DT90 values | | | | | | |
| # ----- | | | | | | |
| | parent | | | | | |
| DT50 | : | 8.4182 | | | | |
| DT90 | : | 140.90 | | | | |
| Kinetic model | DFOP | | | | | |

| | |
|---------------------|--|
| Reference | Comparison of the behaviour of three herbicides in a field experiment under bare soil conditions. |
| Notifier: | Taskforce |
| Author(s), year: | Siimes, K.; Nikunen, U.; Laitinen, P.; Ramo, S.; Welling, L.;2006; |
| Report/Doc. number: | M-458582-01-1 |
| Guideline(s): | None |
| GLP: | No |
| Deviations: | |
| Validity: | Not valid |
| Status: | Scientific peer-reviewed literature |

Study summary

A case-study was designed in order to rank three alternative herbicides according to their exposure to surface waters. Herbicide persistence and losses to surface waters were studied in an uncultivated Finnish field (ca. 3500 m², slope <1%). Glyphosate, glufosinate-ammonium and ethofumesate were sprayed onto bare soil in July. Surface runoff and subsurface drainage volumes were automatically recorded and sampled for herbicide analysis on volumetric basis until the following May. Soil was cored six times (0–131 days after the spray) for herbicide residue analyses. Herbicides were detected mainly in the topsoil (0–3 cm). The field dissipation half-life time of ethofumesate was about 10 weeks (normalized 41 days). The herbicide was detected in surface runoff in summer and in spring. Moreover, ethofumesate was found in subsurface drainage water in April. Although herbicide concentrations in runoff water were at their highest in summer, the main part of herbicide losses was generated by surface runoff during snow melt and soil thaw. Ethofumesate loss was 1.0% of the applied amounts within 302 days after application. These figures, obtained without a crop, may be higher than those in cultivated fields. However, the leaching potential of ethofumesate appears to be the highest of the three herbicides on sandy silt loam under boreal climate conditions.

Comments RMS

The full text paper was not available for evaluation. The study was excluded.

B.8.1.1.2.2.2. Soil accumulation studies

| | |
|---------------------|---|
| Reference | DECLINE OF SOIL RESIDUES IN A UK FIELD AFTER APPLICATION OF NORTRON IN FOUR SUCCESSIVE YEARS |
| Notifier: | Taskforce |
| Author(s), year: | Crofts, M.; Whiteoak, R. J.;1977 |
| Report/Doc. number: | A83297 / W 41 / M-155566-01-1 |
| Guideline(s): | None |
| GLP: | No |
| Deviations: | |
| Validity: | Not valid |
| Status: | Previous evaluation in DAR for original approval / baseline dossier. |

Materials and Methods

Plots of sugar beet at Shelford, Cambridgeshire were sprayed either pre-emergence (at 2 kg a.s./ha) or post-emergence (at 1.5 kg a.i./ha) with NORTRON in 1973. Soil was sampled to a depth of 15 cm at intervals up to sugar beet harvest. The plots were re-sprayed at the same application rates at the appropriate time of the year for pre- or post-emergence treatment in 1974, 1975 and 1976, in the absence of a crop and without cultivation. Samples were taken at various intervals up to 232 days after each application.

The samples were analysed using GLC with a flame photometric detector. Four recovery experiments were carried out with the 1973-75 series of samples, in which 2, 10, 10 and 20 µg ethofumesate were added to 20g control samples. The mean recovery was 31.4% (range 88-100%).

Comments RMS:

The study was regarded as not valid in the previous evaluation.

Weather data are well reported. However, soils are not fully characterized, for instance the pH is not reported.

The sampling depth (0-15 cm) is not appropriate as losses due to translocation into deeper soil layers cannot be ruled out. The study is not valid.

| | |
|---------------------|---|
| Reference: | THE ACCUMULATION OF RESIDUES IN SOIL FOLLOWING ANNUAL APPLICATIONS OF ETHOFUMESATE (20 EC) AT SHELFORD AND CHESTERFORD PARK, UK, BETWEEN 1980 AND 1983 |
| Notifier: | Taskforce |
| Author(s), year: | Snowdon, P. J.;1986 |
| Report/Doc. number: | A83315/ W 58 / M-155584-01-1 |
| Guideline(s): | None |
| GLP: | No |
| Deviations: | |
| Validity: | Not valid |
| Status: | Previous evaluation in DAR for original approval / baseline dossier. |

Study summary based on previous draft assessment report

Materials and methods

The soil accumulation of NC8438 was investigated in a field study on two sites in the UK, between 1980 and 1983. Duplicate plots, consisting of series of 2 x 15 m bare soil (sandy loam and clay, respectively, for soil properties, see table below) were sprayed with 1 or 2 kg NC8438/ha in a 20% EC formulation yearly in May or June.

Table 8-96: Soil characteristics

| Soil | O C (%) | pH | sand (%) | silt (%) | clay (%) | MHC (%) | CEC meq/100 g |
|-----------------------|---------|-----|----------|----------|----------|---------|---------------|
| Shelford sandy loam | 1.3-2.3 | 7.8 | 50-59 | 20-24 | 18-26 | n.r. | n.r. |
| Chesterford Park clay | 3.0 | 7.6 | 30 | 15 | 53 | n.r. | n.r. |

n.r. = not reported

During the 2 - 3 weeks period after the applications, the mean soil temperature at 5 cm depth were 13 - 16°C, and the precipitation 11 - 34 mm. The plots were kept weed-free during the study by treatment with paraquat. At the end of each season (65 - 246 days after application), 15 soil cores (3.8 x 22.5 cm) were taken from each plot (treated and control). The cores were divided into sections of 7.5 cm, and all segments from each depth were combined before deep freeze storage. Prior to analysis, duplicate soil samples were extracted with methanol and NC8438 was partitioned into dichloromethane. The extracts were analysed by GLC.

Results

Residue levels in soil samples at the end of the test periods are summarised in the table below.

Table 8-97: Study duration and residues of NC8438 found in the top 7.5 cm soil layer at the end of the studies. The figures represent the mean of duplicate samples, and are corrected for the mean recovery efficiency (97%) of the method of analysis.

| Year of treatment | Appl. rate (kg as/ha) | Sampling (days after appl.) | | NC8438 (mg/kg) | |
|-------------------|--------------------------|-----------------------------|---------|----------------|---------|
| | | Shelford | C. Park | Shelford | C. Park |
| 1980 | 1.0 | 183 | 189 | 0.26 | 0.26 |
| | 2.0 | | | 0.13 | 0.44 |
| 1981 | 1.0 | 153 | 154 | 0.08 | - |
| | 2.0 | | | 0.20 | - |
| 1982 | 1.0 | 246 | 239 | - | - |
| | 2.0 | | | 0.19 | - |
| 1983 | 1.0 | 168 | 65 | 0.07 | 0.22 |
| | 2.0 | | | 0.15 | 0.30 |

The residue levels in most of the samples from deeper soil layers were below the limit of detection (0.05 mg/kg). The highest value in the 7.5 - 15.0 cm section was 0.12 mg/kg, and in the 15.0 - 22.5 cm section 0.06 mg/kg (ca. 10% of applied).

Comments RMS

No samples were taken immediately after applications of the test compound. The weather data reported cover only 2 - 3 weeks following treatments. The recovery efficiency of the method of analysis ranged between 69 and 127%. The corrections of the residue levels were based on the average value (97%). Besides, the limit of detection and residue levels in the control samples (up to 0.073 mg/kg, mean 0.013 mg/kg) were unacceptably high. The results are not further considered in the assessment of ethofumesate.

B.8.1.1.3. Summary: soil studies

In the aerobic metabolism studies evaluated in the course of the first approval, ethofumesate was slowly degraded (lab DT50 up to 211 days). The main degradation products were carbon dioxide and non-extractable residues. Ethofumesate was degraded in soil through the action of soil micro flora via either dealkylation (NC 8493, ethofumesate- 2- hydroxy) followed by oxidation (NC 9607, ethofumesate-lactone) and ring opening (NC 20645, ethofumesate-carboxylic acid). These studies, however, were often characterized by inappropriate handling of the experimental soils (storage of the soils outdoors or under ambient conditions for up to three months, low microbial biomass levels, no pre-incubation prior application of the spiking solutions). The newly submitted aerobic soil degradation studies confirmed the previously established degradation route, but degradation was faster due to the use of freshly sampled soils. Considering the valid studies from the previous evaluation and the new studies, ethofumesate was generally moderately fast degraded (Dt50 lab: 9.4 – 137 d; geomean = 18.7 d; n =17). The main degradation products were carbon dioxide and unextractable residues. Ethofumesate is degraded to NC 8493 (ethofumesate- 2- hydroxy) followed by NC 9607 (ethofumesate-lactone) and NC 20645 (ethofumesate-carboxylic acid) or the loss of the methanesulfonate moiety to transient degradates which are converted to non-extractable residues (21 - 64% AR; n = 17) and mineralized to CO₂ (4 - 60% AR; n = 17) at 100 days. Metabolites were detected in minor amounts only (< 5% AR).

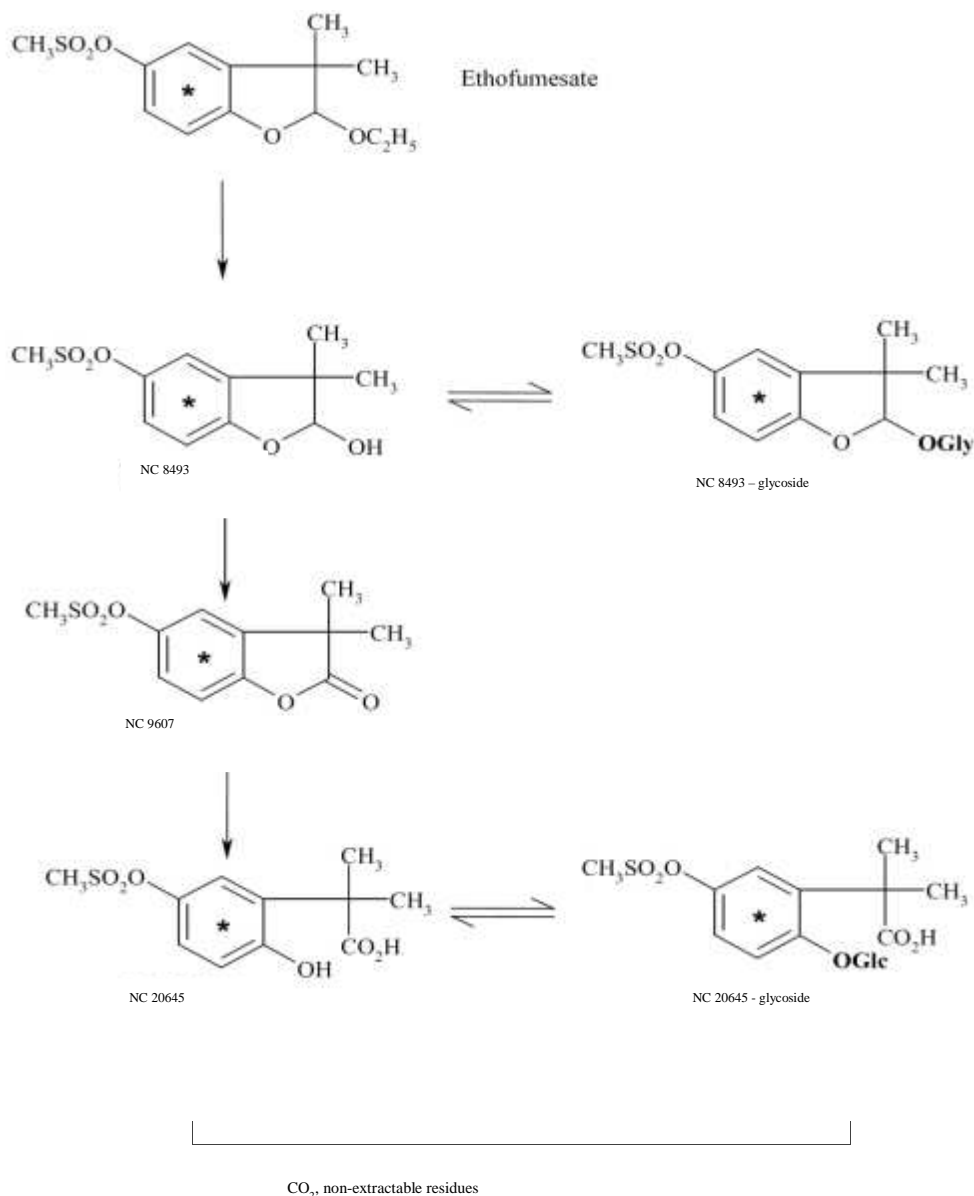
In anaerobic conditions, ethofumesate was not mineralized (CO₂-evolvment during anaerobiosis 2.5% AR after 152 days). It was regarded as stable under anerobic soil conditions and therefeore the anaerobic degradation is not considered to contribute significantly to the degradation route of ethofumesate.

In the studies submitted for the first approval, photolysis on soil surface showed inconsistent results. The DT50 of the degradation of ethofumesate in soil under environmental conditions was 65 days and 13.8 days. In the first study one main phototransformation product was identified (NC 8493 with maximum amounts of about 30%). This metabolite was also observed as transient metabolite in the soil metabolism study. One minor product < 5% was formed. In the second study three radioactive fractions were detected but not identified (D2, D3 < 5%, D4 at 7.1% AR at day 30). The previous photolysis in soil studies were repeated due to experimental insufficiencies and the occurrence of considerable levels of unidentified radioactivity. In the new studies, the main transformation product was NC 8493 (max. 24.2 %). A second minor transformation product was identified as NC 20645 (max. 4.8%). All other metabolites did not exceed 1%.

Metabolites NC 20645 and NC8493 and/or their respective glycoside conjugate were considered to represent the Peak A detected in Lysimeter studies carried out for the first approval of ethofumesate. The theoretically possible back reaction of NC 20645 to NC 9607 was investigated and was shown not to contribute significantly to the degradation of NC20645. Degradation rates of the soil metabolites NC 8493, NC 9607 and NC 20645 were determined in three separate studies. The DT50 were less than 1,5 hours for NC 8493, NC 9607 and 1-3 hours for NC 20645. This fast degradation is in line with the observed very low occurrence in the aerobic soil metabolism studies. The groundwater risk assessment was carried out for both NC20645 and NC8493 as aglycon.

For the first approval of ethofumesate, several field studies were submitted. In the previous list of end-points, values for 13 sites were included with DT50 values (not normalized) of 15 to 250 days with a mean of 77 days and a median of 56 days. Several of these studies were not considered acceptable after the current re-evaluation due to insufficient sampling depth. In addition to the existing field studies, the notifier UPL submitted new field studies. These field dissipation studies were evaluated to determine DT50 values, normalized to standard conditions of 20°C and field capacity for use in modeling (DT50 13.5 – 112 days; geomean 40.7 days). Since DT50 from field studies were shown, not to be statistically different from the lab degradation studies' population, the combined geomean of lab and field studies (26.2 d) was used in the further groundwater and surface water assessment.

The following metabolic pathway including formation of conjugates observed in outdoor studies is proposed (all metabolites < 5%):



The behaviour of both enantiomers of ethofumesate was exemplarily investigated under laboratory conditions in soil and water/sediment. The degradation was not enantioselective. In one scientific paper, the potentially enantioselective degradation of ethofumesate was investigated in four Chinese soils under laboratory conditions. No significant difference was observed in three out of four soils. In one of the four soils, a minor difference (max. enantiomeric ratio: 1.65) was observed. In this soil, the half-life of the (+) enantiomer was in the typical range of the other soils, whereas the half-life of the (-) enantiomer was faster. The reliability of this study for regulatory purposes is not given. Therefore, it is considered adequate that all studies on the active substance where performed using the racemic mixture.

B.8.1.2. Adsorption and desorption in soil

B.8.1.2.1. Adsorption and desorption

B.8.1.2.1.1. Adsorption and desorption of the active substance

| | |
|---------------------|--|
| Reference: | Determination of adsorption/desorption for ethofumesate |
| Notifier: | Taskforce |
| Author(s), year: | Mueller, J.;1990 |
| Report/Doc. number: | OFC00004873 / M-352102-01-1 |
| Guideline(s): | OECD 106 |
| GLP: | yes |
| Deviations: | |
| Validity: | Valid |
| Status: | Previous evaluation in DAR for original approval / baseline dossier. |

Study summary based on previous draft assessment report

Materials and Methods

The adsorption/desorption of ethofumesate (purity 99.9%) was investigated in three soils (for soil properties, see table below) in accordance with OECD Guidelines 106.

Table 8-98: Soil characteristics.

| Soil | O C (%) | pH | sand (%) | silt (%) | clay (%) | MHC (%) | CEC meq/100 g |
|---------------|------------|-----|-------------|-------------|-------------|---------|------------------|
| Podsol | 1.5 | 6.1 | 94 | 2.7 | 3.0 | n.r. | n.r. |
| Parabraunerde | 1.1 | 7.6 | 4.9 | 81 | 14 | n.r. | n.r. |
| Light sand | 1.5 | 6.7 | 74 | 23 | 3.8 | n.r. | n.r. |

n.r = not reported

The test samples consisted of 10 g dw soil and 50 mL sterile test solution (0.01 M CaCl₂). For determination of the adsorption kinetics, the concentration of ethofumesate was 5.0 mg/l, and the samples were mechanically shaken for 2, 6, 16, 24, 48 and 72 hours prior to analysis with HPLC. In adsorption/desorption experiments, the test concentration was 5.4 mg as/L and samples shaken for 16 hours in the adsorption step, 2x16 hours in two desorption steps. The adsorption isotherms were determined using concentrations of 2.2, 0.56 and 0.11 mg as/l. The tests were performed at 20±1°C.

Results

Table 8-99: Adsorption data from three soils.

| Soil | K _f [L/kg] | K _{oc} [L/kg] | 1/n [-] | R [-] | total recovery [%] |
|---------------|--------------------------|---------------------------|------------|----------|-----------------------|
| Podsol | 3.7 | 245 | 0.96 | 1.0 | 97 |
| Parabraunerde | 1.1 | 99 | 0.91 | 1.0 | 102 |
| Light sand | 3.0 | 204 | 0.94 | 1.0 | 98 |

Comments RMS

The adsorption/desorption of ethofumesate (purity 99.9%) was investigated in three soils in accordance with OECD Guidelines 106. However, only three concentrations (2.2, 0.56 and 0.11 mg as/l) were tested. Nevertheless, the study is acceptable.

When calculating the K_{foc} from the K_f-values and the respective organic carbon content (OC), minor rounding errors occurred in the original study. The RMS has recalculated these K_{foc} values.

The correct endpoints are:

| Soil | K _f | K _{foc} | 1/n |
|---------------|----------------|------------------|------|
| Podsol | 3.7 | 247 | 0.96 |
| Parabraunerde | 1.1 | 100 | 0.91 |
| Light sand | 3.0 | 200 | 0.94 |

| | |
|---------------------|--|
| Reference: | THE ADSORPTION AND DESORPTION OF ETHOFUMESATE IN SOIL |
| Notifier: | Taskforce |
| Author(s), year: | Bruhl, R.; 1984 |
| Report/Doc. number: | A83285/ M-155554-01-1 / W29 |
| Guideline(s): | OECD 106 |
| GLP: | yes |
| Deviations: | |
| Validity: | Valid |
| Status: | Previous evaluation in DAR for original approval / baseline dossier. |

Study summary based on previous draft assessment report

Materials and Methods

Adsorption and desorption of [benzene ring-U-¹⁴C] ethofumesate with a radiochemical purity >95%, were determined in a sandy loam (German standard soil 2.3, Hatzenbühl) according to OECD Guidelines 106. For soil characteristics see Table 7.2a.

Table 8-100: Soil characteristics.

| OC | pH | Sand | Silt | Clay | CEC |
|------|-----|-------------------|----------------|--------------|-----------|
| (%) | | 20 µm-2 mm (%) | 2-20 µm (%) | <2 µm (%) | meq/100 g |
| 1.16 | 6.0 | 76.9 | 14.8 | 8.3 | 5.5 |

The following test concentrations were used: 0.041, 0.20, 1.0 and 4.7 mg ethofumesate/L 0.01M CaCl₂, duplicate samples. The soil was dried and sieved (2 mm). For each test 20 g of the test soil was re-equilibrated with 30 mL of 0.01 M CaCl₂ prior to the addition of the test solutions. The test substance was added and 0.01 M CaCl₂ solution was added to a final volume of ca. 100 ml. The test slurry was equilibrated on a head shaker over night (14 hours) at 25°C. After centrifugation and withdrawal of supernatant, four desorption steps were carried out. Radioactivity in the solutions was determined by LSC. To determine the mass balance, the total amount of solution was removed after the last step, measured and analysed. The soil was thereafter extracted with acetone and the remaining radioactivity in the soil was determined by combustion to ¹⁴CO₂. The radioactive purity and stability was determined at the start and the end of the study.

Results

The adsorption coefficient was calculated according to Freundlich equation over the concentration range 0.041 to 4.7 mg as/l.

$$x/m = K \cdot C_e^{1/n}$$

$$K_{\text{ads}} (K_f) = 1.13; \quad (r^2 = 0.99); \quad 1/n = 0.84$$

$$K_{\text{oc}} = 97$$

After three desorption steps, approximately 47 to 64% of the initially adsorbed ethofumesate was desorbed at the three highest concentrations and about 94% was desorbed at the lowest concentration. Between 97 and 131% of the applied radioactivity had been recovered at the end of the study.

Comments RMS

The study followed OECD Guidelines and was well performed and reported. However, only four concentrations were tested. Nevertheless, the study is acceptable.

| | |
|---------------------|--|
| Reference: | [14C]-ETHOFUMESATE: ADSORPTION/DESORPTION IN SOIL |
| Notifier: | Taskforce |
| Author(s), year: | Allen, R.;1988 |
| Report/Doc. number: | A83336 / M-155605-01 / W78 |
| Guideline(s): | Not specified |
| GLP: | yes |
| Deviations: | |
| Validity: | Valid |
| Status: | Previous evaluation in DAR for original approval / baseline dossier. |

Study summary based on previous draft assessment report

Materials and Methods

Adsorption and desorption of [¹⁴C] ethofumesate, radiochemical purity >96.7%, were determined in four soils, according to HUK (Hazleton UK) Standard Operating Procedures. For soil characteristics see Table 7.2.1.b.

Table 8-101: Soil Characteristics.

| Soil type | Organic C (%) | pH | Sand 63 µm-2 mm (%) | Silt 2-63 µm (%) | Clay <2 µm (%) | CEC meq/100 g |
|-----------------------------|------------------|-----|---------------------------|------------------------|----------------------|------------------|
| Icklingham, Sand * | 0.35 | 6.8 | 87 | 6 | 6 | 1.9 |
| Abington, Sandy loam * | 1.9 | 7.4 | 71 | 22 | 16 | 9.2 |
| Terling, Silt (clay) loam * | 3.2 | 6.6 | 14 | 58 | 28 | 25 |
| Shelford, Clay * | 4.9 | 6.6 | 39 | 18 | 43 | 39 |

* USDA classification

The soils were air dried at 21°C and were sieved before use. Duplicate samples were prepared for each of the four soil types. For the adsorption test 25 mL of the test solutions, 0.016, 0.19, 1.06 and 10.5 mg ethofumesate/L 0.01 M CaCl₂ solutions, were added to 5 g of each soil. The samples were shaken continuously for 4 hours. Desorption was carried out in four sequential steps. Radioactivity in the solutions was determined by LSC.

Results

The adsorption coefficient was calculated for each soil according to Freundlich equation.

Table 8-102: Adsorption and desorption of ethofumesate in soil.

| Adsorption | Desorption After 4th desorption |
|------------|------------------------------------|
|------------|------------------------------------|

| Soil | K _f | 1/n | r ² | K _{oc} | K _f |
|--------------------------|----------------|------|----------------|-----------------|----------------|
| Icklingham, Sand | 0.73 | 0.87 | 0.94 | 208 | 2.9 |
| Abington, Sandy loam | 2.3 | 0.93 | 0.88 | 124 | 6.4 |
| Terling, Silt (clay)loam | 5.3 | 0.89 | 0.99 | 166 | 7.9 |
| Shelford, Clay | 6.2 | 0.82 | 0.99 | 126 | 8.8 |

Comments RMS

The study did not follow any specific guideline, but seems to have followed OECD Guideline 106. However, test solutions were added directly to the dry soils without a previous equilibrium period with calcium chloride solution (or water). This may have influenced the results. However, results are in the range of the other experiments and appear plausible.

K_{foc} values were re-calculated, since in the previous evaluation minor rounding errors occurred.

The correct endpoints are:

| Soil | K _f | K _{foc} | 1/n |
|------------|----------------|------------------|------|
| Icklingham | 0.73 | 209 | 0.87 |
| Abington | 2.3 | 121 | 0.93 |
| Terling | 5.3 | 166 | 0.89 |
| Shelford | 6.2 | 127 | 0.82 |

| | |
|---------------------|--|
| Reference: | ADSORPTION/DESORPTION IN SOIL 14C-Ethofumesate |
| Notifier: | Taskforce |
| Author(s), year: | Cameron, B. D.; Mackie, J. A.; Hall, B. E.;1991 |
| Report/Doc. number: | A87601/ M-161528-01-1/ W501 |
| Guideline(s): | OECD 106 |
| GLP: | yes |
| Deviations: | |
| Validity: | Valid |
| Status: | Previous evaluation in DAR for original approval / baseline dossier. |

Study summary based on previous draft assessment report

Materials and Methods

Adsorption and desorption of [¹⁴C] ethofumesate, radiochemical purity of the test substance was 98.5%. were determined in three soils according to OECD Guidelins 106. For soil characteristics see table below.

Table 8-103: Soil characteristics of the test soils

| Soil | Organic C (%) | pH | Sand (%) | Silt (%) | Clay (%) | CEC meq/100 g |
|---------------------|------------------|-----|-------------|-------------|-------------|------------------|
| Sand | 1.12 * | 4.6 | 89.5 | 6.9 | 3.6 | 4.64 |
| Acidic Sandy Loam | 1.45 | 5.7 | 74.2 | 10.2 | 15.6 | 10.1 |
| Alkaline Sandy Loam | 1.66 | 7.3 | 66.4 | 15.6 | 17.9 | 10.5 |

* % organic carbon was calculated using the multiplying % organic matter by 1.7

The soils were sieved and air dried. In a preliminary test the following conclusions regarding ethofumesate were made: solubility in water was 49 µg/ml, there was no adsorption to glass walls and there was no degradation during the test period (16 h). The study was performed all through the test according to OECD Guideline 106 and therefore no details are reported here. The Freundlich coefficient was determined using the following test solutions: 0.04, 0.2, 1 and 5 µg ethofumesate/g solution (0.01 M CaCl₂).

Results

Adsorption of ethofumesate was fairly low, 26, 26 and 30% in the alkaline sandy loam, acidic sandy loam and the sand. After two desorption steps, 81, 86 and 70% of the adsorbed substance was desorbed in the three respective soils.

Table 8-104: Adsorption and desorption in a sand, an acidic sandy loam and an alkaline sandy loam

| Soil | Adsorption | | | |
|---------------------|----------------|------|----------------|-----------------|
| | K _f | 1/n | r ² | K _{oc} |
| Sand | 2.3 | 0.88 | 1.0 | 205 |
| Acidic Sandy Loam | 1.9 | 0.89 | 0.99 | 132 |
| Alkaline Sandy Loam | 1.9 | 0.87 | 1.0 | 116 |

Comments RMS

The study was carried out according to OECD 106 Guideline. However, only three concentrations were tested. The study is acceptable.

It appears that in the course of the previous evaluation the wrong values were extracted from the study. The original study report gives the values below:

| Soil Type | K _f | 1/n |
|---------------------|----------------|--------|
| Alkaline Sandy Loam | 0.677 | 0.9164 |
| Acidic Sandy Loam | 0.677 | 0.9232 |
| Sand | 0.797 | 0.9282 |

The correct endpoints are:

| Soil Type | OC | pH | K _f | K _{foc} | 1/n |
|---------------------|------|-----|----------------|------------------|------|
| | [%] | | [L/kg] | [L/kg] | |
| Sand | 1.12 | 4.6 | 0.7 | 63 | 0.92 |
| Acidic sandy loam | 1.45 | 5.7 | 0.7 | 48 | 0.92 |
| Alkaline Sandy loam | 1.66 | 7.3 | 0.8 | 48 | 0.93 |

Reference: ADSORPTION OF ETHOFUMESATE TO DITCH-BOTTOM SEDIMENT

| | |
|---------------------|--|
| Notifier: | Taskforce |
| Author(s), year: | Hoven, A.; Vonk, J. W.; 1988 |
| Report/Doc. number: | A87606/ M-161536-01 |
| Guideline(s): | Not specified |
| GLP: | yes |
| Deviations: | |
| Validity: | Not valid |
| Status: | Previous evaluation in DAR for original approval / baseline dossier. |

Study summary based on previous draft assessment report

Materials and Method

An adsorption study was carried out with non-labelled ethofumesate, with a chemical purity of 98 - 99%, in two Dutch ditch-bottom sediments. The sediments were sieved (2 mm) prior to the test. Samples of ethofumesate, dissolved in methanol, were added to 1 g (dry weight) sediment samples in 25 mL screw-cap flasks and 0.01 M CaCl₂ was added to a final volume of 10 mL. The test concentrations of ethofumesate were: 5, 10, 20 and 40 µg as/l. Duplicate samples were shaken for 24 hours at 20°C. After centrifugation, aliquots of the supernatant were analysed by reversed phase HPLC/UV.

Comments RMS

The relevance of the studied sediment for European agricultural soils is unclear. Therefore, the study is considered as supplementary information and not considered for endpoints.

| | |
|---------------------|--|
| Reference: | Aged soil leaching ¹⁴C Ethofumesate |
| Notifier: | Taskforce |
| Author(s), year: | Cameron, B. D.; Mackie, J. A.; Hall, B. E.; 1991 |
| Report/Doc. number: | A87602/ M-161529-01 / W502 |
| Guideline(s): | BBA: IV, Section 4.2 (1986) |
| GLP: | yes |
| Deviations: | |
| Validity: | Not valid |
| Status: | Previous evaluation in DAR for original approval / baseline dossier. |

Study summary based on previous draft assessment report

Materials and Methods

The mobility of the aged residues of ¹⁴C-ethofumesate (radiochemical purity >98.8%) was investigated in a sandy loam soil (for soil properties, see table below) in a column leaching study according to BBA Guidelines IV 4-2 and Dutch Regulatory Guidelines G.1.2.

Table 8-105: Soil characteristics

| Soil | Org. C (%) | pH | sand (%) | silt (%) | clay (%) | MHC (%) | CEC meq/100 g |
|------------|---------------|-----|-------------|-------------|-------------|------------|------------------|
| Speyer 2.1 | 0.64 | 6.0 | 69 | 28 | 3.1 | n.r. | 5 |
| Speyer 2.2 | 2.2 | 5.6 | 61 | 33 | 6.1 | n.r. | 10 |
| Speyer 2.3 | 1.1 | 6.4 | 37 | 55 | 8.3 | n.r. | 8 |

n.r. = not reported

¹⁴C-ethofumesate was applied to the soil at a rate corresponding to 3.08 mg as/kg dry soil and aged aerobically at 21±2°C and 40% MWHC in the soil for 60 days. After ageing, 100 g of the soils (corresponding to 1.6 kg ethofumesate equivalents/ha) were introduced to each of duplicate water saturated leaching columns (ca. 35 cm high, 5 cm i.d.). During incubation, evolved ¹⁴CO₂ was collected in ethanolamine.

The soil columns were leached with 392 mL of de-ionised water over 2 days, corresponding to ca. 200 mm of rain. Leachate was collected daily and analysed by LSC. After leaching, the columns were divided into 5 cm segments and the distribution and characterisation of radioactivity determined by acetonitrile extraction, LSC, TLC and HPLC.

Results

Total recovery for Speyer 2.1, 2.2, 2.3 after the ageing period was 92, 99 and 97%, respectively, of which extractable radioactivity accounted for 44, 46 and 52%, evolved $^{14}\text{CO}_2$ for 8.1, 3.7 and 7.4%, and unextractables for 40, 49 and 37% of applied radioactivity.

After leaching, total recovery was 90, 91 and 96% of applied radioactivity, including evolved $^{14}\text{CO}_2$. The distribution of the recovered residues are summarised in the table below.

Table 8-106: Distribution of ^{14}C -radioactivity (% of applied) in soil columns following 60 days of incubation and 2 days of leaching after application of ^{14}C -ethofumesate. Mean of duplicate columns.

| Segment | Speyer 2.1 | | Speyer 2.2 | | Speyer 2.3 | |
|--------------|-------------|---------------|-------------|---------------|-------------|---------------|
| | extractable | unextractable | extractable | unextractable | extractable | unextractable |
| 0-5 cm | 9.3 | 14 | 15 | 6.1 | 13 | 19 |
| 5-10 cm | 12 | 11 | 30 | 10 | 20 | 11 |
| 10-15 cm | 8.1 | 5.4 | 18 | 4.5 | 15 | 2.3 |
| 15-20 cm | 9.0 | 2.1 | 0.23 | 0.61 | 3.4 | 2.0 |
| 20-25 cm | 3.2 | 3.5 | 0.26 | 0.26 | 0.17 | 0.36 |
| 25-30 cm | 0.42 | 0.48 | 0.17 | 0.20 | 0.14 | 0.13 |
| 30-35 cm | 0.14 | 0.29 | 0.16 | 0.15 | 0.15 | 0.26 |
| Total column | 78 | | 86 | | 87 | |
| Leachate | 4.2 | | 0.9 | | 1.7 | |

Comments RMS

The study was performed generally in accordance with the referred guidelines. The radioactivity was not characterised. No relevant adsorption endpoints were derived.

| | |
|---------------------|--|
| Reference: | Adsorption/desorption of ^{14}C-ethofumesate on soil – advanced test, |
| Notifier: | UPL |
| Author(s), year: | Hellstern, J.; 2007 |
| Report/Doc. number: | RCC Study No. B01912 |
| Guideline(s): | OECD 106 |
| GLP: | yes |
| Deviations: | |
| Validity: | Valid |
| Status: | New study |

Executive Summary

The adsorption/desorption of Ethofumesate was studied in one additional study because the compliance of the Monograph studies with the most recent OECD guidelines cannot be clearly evaluated.

The adsorption/desorption behaviour of ^{14}C -Ethofumesate was determined in one soil.

Determined K_{FOC} value was 187 indicating moderate mobility of the substance in soil. The Freundlich isotherm coefficient was higher for desorption than adsorption, indicating a partially irreversible sorption process.

No degradation of the substance in the aqueous phases was observed during the adsorption. The mass balance was 98%.

I. MATERIALS AND METHODS

A: MATERIALS

| | |
|--------------------------------|--|
| 1. Test material: | ^{14}C-Ethofumesate |
| Batch No.: | CFQ12729 |
| Radiochemical Purity: | 98.6% |
| Specific radioactivity: | 1.04 GBq/mmol; 28 mCi/mmol; 3.607 MBq/mg |
| 2. Test Material: | Ethofumesate technical |
| Purity: | 98.5% |
| CAS No.: | 26225-79-6 |
| Batch No.: | 50811 |

3. Soils:

The soil used in the study was Borstel soil (loamy sand). For this study the top 20 cm layer was taken and air dried soil was sieved through a 2-mm sieve and the soil moisture was determined.

Table 8-107: Soil physiochemical properties

| | |
|--|-------------------------------|
| Soil name/origin | Borstel/Lower Saxony, Germany |
| Soil type | Loamy sand |
| Clay [%] | 7.06 |
| Silt [%] | 16.17 |
| Sand [%] | 76.77 |
| pH (CaCl ₂) | 6.67 |
| % OC | 1.41 |
| Cation exchange capacity [mmol/z/100 g soil] | 8.62 |
| % CaCO ₃ | 0.80 |
| MWHC [g/100 g dry soil] | 43.22 |

B. STUDY DESIGN

1. Experimental condition

The pH of the aqueous phase after contact with soil was 6.82. Soils were pre-equilibrated with 0.01 M CaCl₂ solution and centrifuged before aliquot of 1.5 mL of the corresponding application solution was added on the surface of the supernatant and the aqueous solution was adjusted with 0.01 M CaCl₂ solution to the final volume of 15 mL. The test tubes were then shaken by hand and mechanically in a temperature-controlled room. The control samples (without soil) and blank samples (without test item) were prepared with the same steps.

In the advanced test, five concentrations (1.507, 0.441, 0.150, 0.044 and 0.018 mg/L) together with a soil solution ratio 1/3 and an agitation time of 24 hours were used. After 24 hours of adsorption, the samples were centrifuged for 10 minutes and samples were taken for analysis. The desorption step was carried out immediately after adsorption.

2. Description of analytical procedures

The aqueous and organic (extracts) samples were analysed by LCS and HPLC was used to analyse 14C-Ethofumesate. One-dimensional TLC was performed in order to check the stability of the test item in the treated samples.

The limit of quantification in water (LOQ_w) and soil (LOQ_s) was 0.004 mg/L and 0.008 mg/L, respectively.

II. RESULTS AND DISCUSSION

A. MASS BALANCE

The mass balance was 98.4% AR. About half of applied amount was detected in the supernatant (52.4%) and in the soil extracts (44.8%). The non-extracted residues presented about 1% AR.

B. FINDINGS

The K_{FOC} for adsorption and Freundlich isotherm of ^{14}C -Ethofumesate were calculated to be 187 mL/g and 0.93, respectively. The $K_{des, FOC}$ and Freundlich isotherm were determined to be 248 mL/g and 1.96, respectively.

Table 8-108: Adsorption/desorption constants and correlation coefficients for Ethofumesate in one soil

| Borstel soil (loamy sand) | | | |
|---------------------------|-------|----------------|-------|
| Adsorption | | Desorption | |
| K_F | 2.634 | $K_{des, F}$ | 3.491 |
| K_{FOC} | 187 | $K_{des, FOC}$ | 248 |
| K_{FOM} | 108 | $K_{des, FOM}$ | 144 |
| 1/n | 0.93 | 1/n | 0.96 |
| r^2 | 1.00 | r^2 | 1.00 |

III. CONCLUSIONS

The Freundlich isotherm coefficient for desorption was higher than that obtained for adsorption, indicating a partially irreversible sorption process.

The 1/n values obtained indicated that adsorption and desorption was independent of the test item concentration.

Comments RMS

The study is acceptable.

B.8.1.2.1.2. Adsorption and desorption of metabolites, breakdown and reaction products

| | |
|---------------------|--|
| Reference: | [phenyl-UL-14C] AE C508493: Adsorption/desorption in five different soils |
| Notifier: | Taskforce |
| Author(s), year: | Hein, W.; Moendel, M.; D'Ambrosio, A.;2011 |
| Report/Doc. number: | AS201 / M-431772-01-1 |
| Guideline(s): | OECD 106 US EPA OPPTS 835.1220 |
| GLP: | yes |
| Deviations: | |
| Validity: | Valid |
| Status: | New study |

MATERIALS AND METHODS:

Materials :

Test Material : [Phenyl-UL-¹⁴C] NC 8493 (AE C508493)

Specific activity: 4.34 MBq/mg (117.30 µCi/mg)

Soils :

Five test soils (European origin) were used within this study, chosen to cover a representative range in soil physico-chemical properties.

Table 8-109: Soil characteristics

| Number | I | II | III | IV | V |
|--------------------------|------------------|-------------------------------|----------------------|-------------------------|------------------------|
| Soil Designation | Wurmwiese | Höfchen am Hohensch 4a | Dollendorf II | Laacher Hof AXXa | Hanscheider Hof |
| Abbreviation | WuW | HaH | Doll | AXXa | HH |
| Textural class [USDA] | Sandy loam | Silt loam | Loam | Loamy sand | Silt loam |
| Textural analysis [USDA] | | | | | |
| Sand [2000-50 µm] | 57 | 27 | 37 | 77 | 31 |
| Silt [phenyl-UL0-2 µm] | 30 | 60 | 40 | 16 | 54 |
| Clay [<2µm] | 13 | 13 | 23 | 7 | 15 |
| pH value: | | | | | |
| Water | 5.4 | 6.5 | 7.5 | 6.2 | 5.5 |
| CaCl ₂ | 5.1 | 6.3 | 7.3 | 5.9 | 5.2 |

| | | | | | |
|----------------------|-------|-------|-------|-------|-------|
| Organic carbon (%) | 2.0 | 2.9 | 4.4 | 2.0 | 2.9 |
| Organic matter (%) | 3.44* | 4.99* | 7.57* | 3.44* | 4.99* |
| CEC (meq/100 g soil) | 10.3 | 12.9 | 19.2 | 9.3 | 10.0 |

* Calculated: Organic Matter = Organic Carbon \times 1.724

Methods :

Study design

The study was designed as batch equilibrium test with soil and aqueous 10 mM CaCl₂ using ¹⁴C labeled test substance and five soils. Pre-tests were performed with all soils in order to determine the conditions for the main test.

Experimental Conditions

Pre-test were performed with a nominal test concentration of 1 mg/L in aqueous 10 mM CaCl₂ solution in the dark at 20 °C.

In Preliminary Test I the soil to solution ratios were defined to be 1:1 for the soils Wurmwiess, Hoefchen am Hohenseh 4a, Dollendorf II and Laacher Hof AXXa and 1:2 for the soil Hanscheider Hof. 24 h after application a purity check of the supernatant was carried out by means of Radio-HPLC. No test item was detectable in the supernatant after 24 h indicating a very fast degradation under test conditions. The radioactivity balance was in a range from 91.2 -98.5%.

The instability observed in Preliminary Test I was confirmed by the results of the Preliminary Test II (Determination of Equilibration Time for Adsorption and Parental Mass Balance). Independent on the soil type already 4 h after application no test item was detectable in the supernatant. Also the radioactivity in soil extracts represented < 2% of the unchanged test item and the parental mass balances were always < 1% Test Item recovery determined 4, 6 and 24 h after application. The radioactivity mass balance (4, 6 and 24 h after application) was in a range from 95.2 -98.8%. Due to the degradation of the test item after 24 h it was decided to terminate Preliminary Test II after 24 h.

Due to the observed instability of the test item under test conditions and the insufficient parental mass balance (< 1% Test Item recovery after 24 h) in the Preliminary Test II a third Preliminary Test (Preliminary Test III) was carried out. In this experiment the stability of the test item was investigated using gamma-sterilized and non-sterilized soil and two different biocides (HgCl₂ and NaN₃) with one soil (Höfchen am Hohenseh 4a).

Using gamma sterilized soil together with the biocide NaN₃ no sufficient stability of the test item was determined. Already 24 h after application only 30% of the radioactivity in the supernatant represented the unchanged test item. At all other treatments the purity after 24 h shaking period was < 13%.

Test Concentrations :

1 mg/L in aqueous 10 mM CaCl₂ solution

Analytical Procedures :

The test substance was determined in the supernatant by LSC and HPLC with radiodetection.

RESULT AND DISCUSSION

The test substance was not stable in the water / soil test system even under short equilibrium conditions and using sterile soil.

Conclusion:

It was not possible to determine a batch Koc for adsorption and desorption using the batch equilibrium test.

With regard to the instability and the short half-life in soil the Koc of NC 8493 can be calculated by EPI WIN (Version 2.00 ; 2010) as 24.82 mL/g (Kow method) 20.82 mL/g (MCI method) (no report available).

(Estimation Programs Interface (EPI) Suite™ was developed by the US Environmental Protection Agency's Office of Pollution Prevention and Toxics and Syracuse Research Corporation (SRC). It is a screening-level tool, intended for use in applications such as to quickly screen chemicals for release potential and "bin" chemicals by priority for future work. Estimated values should not be used when experimental (measured) values are available.)

Comments RMS

The test substance was not stable in the water / soil test system even under short equilibrium conditions and using sterile soil. It was not possible to determine a batch Koc for adsorption and desorption using the batch equilibrium test.

The more conservative Koc (20.82 L/kg) calculated by EPI WIN with the MCI method was used for the risk assessment.

| | |
|---------------------|--|
| Reference: | [phenyl-UL-14C] AE C509607: Adsorption/desorption in five different soils |
| Notifier: | Taskforce |
| Author(s), year: | Moendel, M.; D'Ambrosio, A.;2012 |
| Report/Doc. number: | AS202 / M-446351-01-1 |
| Guideline(s): | OECD 106 US EPA OPPTS 835.1220 |
| GLP: | yes |
| Deviations: | |
| Validity: | Valid |
| Status: | New study |

MATERIALS AND METHODS

Materials :

Test Material : [Phenyl-UL-¹⁴C] NC 9607 (AE C509607)

Specific activity: 4.01 MBq/mg (138.38 µCi/mg)

Soils :

Five test soils representative for agricultural soils (European origin) were used within this study, chosen to cover a representative range in soil physico-chemical properties. For Preliminary Test III one gamma sterilized soil (Höfchen am Hohenseh 4a) was used. An aliquot of the soil was gamma sterilized with 25 Kgray.

Table 8-110: Soil characteristics

| Number | I | II | III | IV | V |
|--------------------------|------------------|-------------------------------|-----------------------|-------------------------|------------------------|
| Soil Designation | Wurmwiese | Höfchen am Hohenseh 4a | Dollen-dorf II | Laacher Hof AXXa | Hanscheider Hof |
| Abbreviation | WuW | HaH | Doll | AXXa | HH |
| Textural class [USDA] | Sandy loam | Silt loam | Loam | Loamy sand | Slit loam |
| Textural analysis [USDA] | | | | | |
| Sand [2000-50 µm] | 57 | 27 | 37 | 77 | 31 |
| Silt [phenyl-UL0-2 µm] | 30 | 60 | 40 | 16 | 54 |
| Clay [<2µm] | 13 | 13 | 23 | 7 | 15 |
| pH value: | | | | | |
| Water | 5.4 | 6.5 | 7.5 | 6.2 | 5.5 |
| CaCl ₂ | 5.1 | 6.3 | 7.3 | 5.9 | 5.2 |
| Organic carbon (%) | 2.0 | 2.9 | 4.4 | 2.0 | 2.9 |
| Organic matter (%) | 3.44* | 4.99* | 7.57* | 3.44* | 4.99* |
| CEC (meq/100 g soil) | 10.3 | 12.9 | 19.2 | 9.3 | 10.0 |

* Calculated: Organic Matter = Organic Carbon × 1.724

Methods :

Study design

The study was designed as batch equilibrium test with soil and aqueous 10 mM CaCl_2 using ^{14}C labeled test substance and five soils. Pre-tests were performed with all soils in order to determine the conditions for the main test.

Experimental Conditions

Pre-test were performed with a nominal test concentration of 1 mg/L in aqueous 10 mM CaCl_2 solution in the dark at 20 °C.

In Preliminary Test I the soil to solution ratios were defined to be 1:1 for the soils Höfchen am Hohenseh 4a, Dollendorf II and Laacher Hof AXXa and 1:2 for the soils Wurmwielse and Hanscheider Hof. In order to evaluate the stability of the Test Item under test conditions in Preliminary Test I a supplemental purity check of the supernatant was carried out by means of Radio-HPLC. After equilibration for 24 h less than < 8% of the radioactivity in the supernatant represented the unchanged Test Item, indicating a very fast degradation under test conditions.

Due to the observed instability of the Test Item in Preliminary Test I the Preliminary Test II was omitted and replaced by a further Preliminary Test. In this experiment the stability of the Test Item was investigated without soil, using gamma-sterilized soil and non-sterilized soil (Höfchen am Hohenseh 4a) and two different biocides (HgCl_2 and NaN_3). Samples were taken 4, 6 and 24 h after application. Neither using gamma sterilized soil nor the addition of HgCl_2 and NaN_3 could prevent the decomposition of the Test Item in the shaking solution. Independent on the sterilization technique and at all sampling dates < 1% of the radioactivity represented the unchanged Test Item. Control samples without soil were also tested. After a shaking period of 24 h the samples without biocide contained < 5% Test Item. The corresponding values using HgCl_2 as biocide were < 40% and < 30% for NaN_3 , respectively.

Exemplary for all soils a supplementary test was conducted to determine the ^{14}C -balance and a parental mass balance after a shaking period of 4 h. Soil/water ratios defined in Preliminary Test I and HgCl_2 as biocide were used. Already 4 h after application the parental mass balance was only in a range from 3.6% to 15.8% of the amount applied confirming the fast degradation of the Test Item under test conditions. ^{14}C -balance was in a range from 94.4% to 97.3% of the radioactivity applied, indicating the validity of this supplementary test.

Test Concentrations :

1 mg/L in aqueous 10 mM CaCl_2 solution.

Analytical Procedures :

The test substance was determined in the supernatant by LSC and HPLC with radiodetection.

RESULT AND DISCUSSION

Mass balance :

The test substance was not stable in the water / soil test system even under short equilibrium conditions and using sterile soil.

Conclusion: :

It was not possible to determine a batch Koc for adsorption and desorption using the batch equilibrium test.

With regard to the instability and the short half-life in soil (transient metabolite) the Koc of NC 9607 can be calculated by EPI WIN (Version 2.00 ; 2010) as 25.59 mL/g (Kow method) 104.3 mL/g (MCI method) (no report available).

(Estimation Programs Interface (EPI) Suite™ was developed by the US Environmental Protection Agency's Office of Pollution Prevention and Toxics and Syracuse Research Corporation (SRC). It is a screening-level tool, intended for use in applications such as to quickly screen chemicals for release potential and "bin" chemicals by priority for future work. Estimated values should not be used when experimental (measured) values are available.)

Comments RMS

The test substance was not stable in the water / soil test system even under short equilibrium conditions and using sterile soil. It was not possible to determine a batch Koc for adsorption and desorption using the batch equilibrium test.

The more conservative Koc (25.59 L/kg) calculated by EPI WIN with the Kow method was used for the risk assessment.

| | |
|---------------------|--|
| Reference: | [phenyl-UL-14C] AE C639175: Adsorption/desorption in five different soils |
| Notifier: | Taskforce |
| Author(s), year: | Moendel, M.; D'Ambrosio, A.; 2012 |
| Report/Doc. number: | AS204 / M-446350-01-1 |
| Guideline(s): | OECD 106 US EPA OPPTS 835.1220 |
| GLP: | yes |
| Deviations: | |
| Validity: | Valid |
| Status: | New study |

MATERIALS AND METHODS

Materials :

Test Material :

[Phenyl-UL- 14C] NC 20645 (AE C639175)

Specific activity: 2.94 MBq/mg (79.40 μ Ci/mg)

Soils :

Three test soils from Europe and two test soils from USA were used in the study. The soils were representative for agricultural used soils and cover a representative range of physico-chemical properties.

Table 8-111: Soil characteristics

| Number | I | II | III | IV | V |
|--------------------------|------------------|-------------------------------|-----------------------|---------------------|-----------------------|
| Soil Designation | Wurmwiese | Höfchen am Hohenseh 4a | Dollen-dorf II | Guadalupe CA | Springfield NE |
| Abbreviation | WuW | HaH | Doll | | |
| Textural class [USDA] | Sandy loam | Silt loam | Loam | Sandy loam | Silt loam |
| Textural analysis [USDA] | | | | | |
| Sand [2000-50 μ m] | 57 | 27 | 37 | 56.0 | 12.7 |
| Silt [50-2 μ m] | 30 | 60 | 40 | 32.6 | 60.8 |
| Clay [<2 μ m] | 13 | 13 | 23 | 11.4 | 26.5 |
| pH value: | | | | | |
| Water | 5.4 | 6.5 | 7.5 | 6.8 | 7.2 |
| CaCl ₂ | 5.1 | 6.3 | 7.3 | 6.7 | 6.6 |
| Organic carbon (%) | 2.0 | 2.9 | 4.4 | 0.7 | 1.7 |
| Organic matter (%) | 3.44* | 4.99* | 7.57* | 1.1 | 2.9 |
| CEC (meq/100 g soil) | 10.3 | 12.9 | 19.2 | 16.1 | 16.1 |

* Calculated: Organic Matter = Organic Carbon \times 1.724

Methods :

Study design

The study was designed as batch equilibrium test with soil and aqueous 10 mM CaCl₂ using ¹⁴C labeled test substance and five soils. Pre-tests were performed with all soils in order to determine the conditions for the main test.

Experimental Conditions

The adsorption test was performed in the dark at 20 °C with 5 test concentrations. The following soil to solution ratios were defined to the soils: Wurmwiese, Höfchen am Hohenseh 4a, Dollendorf II and Springfield NE 1:2 and Guadalupe CA 1:1.

The test substance was not stable in soil Wurmwiese. With biocide the equilibration time was 4 hours for the soil Höfchen am Hohenseh, 6 hours for the soil Dollendorf II, 24 hours for the soil Guadalupe CA and 6 hours for the soil Springfield NE.

A desorption step was not performed due to instability.

Test Concentrations :

The adsorption phase of the study (Definitive Test) was carried out using pre-equilibrated air-dried soil with [phenyl-UL-¹⁴C] NC 20645 at concentrations of nominal 1, 0.3, 0.1, 0.03, and 0.01 mg/L

Analytical Procedures :

RESULT AND DISCUSSION

Mass balance :

The mass balance of the soils was determined by LSC of the supernatants after adsorption and by combustion of the remaining soils. The overall material balance for all concentrations for individual specimens was in the range of 99.1-102.8%, 96.7-104.2%, 95.7-104.4%, and 97.1-105.5% of the applied radioactivity in soils Höfchen am Hohenseh 4a, Dollendorf II, Guadalupe CA and Springfield NE, respectively.

Stability :

The test was performed with 0.01 M aqueous CaCl₂ solution with 50 ppm HgCl₂ as biocide due to instability and short equilibration times.

With biocide the Parental Mass Balance was 92.9% after 4 hours for the soil Höfchen am Hohenseh, 91.7% after 6 hours for the soil Dollendorf II, 90.3% after 24 hours for the soil Guadalupe CA and 90.3% after 6 hours for the soil Springfield NE. The Parental Mass Balance with biocide of soil Wurmwiese was already <90% after 4 hours.

Adsorption

The following table summarizes the key soil properties and results from the study:

Table 7.1.3.1.2- 1: Sorption behavior of NC 20645 (AE C639175, ethofumesate-carboxylic acid) in soil

| Soil origin | Wurmwiese | Höfchen am Hohenseh 4a | Dollendorf II | Guadalupe CA | Springfield NE |
|--|------------|------------------------|---------------|--------------|----------------|
| | Germany | Germany | Germany | USA | USA |
| Soil type (USDA) | Sandy loam | Silt loam | Loam | Sandy loam | Silt loam |
| pH (0.01M CaCl ₂) | 5.1 | 6.3 | 7.3 | 6.7 | 6.6 |
| Organic carbon [%] | 2.0 | 2.9 | 4.4 | 0.7 | 1.7 |
| K _F ^(ads) [mL/g] | No | 0.12 | 0.16 | 0.03 | 0.17 |

| | | | | | |
|---|-----------------|--------|--------|--------|--------|
| 1/n | definitive test | 0.9333 | 0.9135 | 0.8716 | 0.9921 |
| K _{F,OC} ^(ads) [mL/g] | | 4.3 | 3.7 | 4.3 | 10.0 |

(Arithmetic mean K_{F,OC}^(ads): 5.6 mL/g)

Desorption :

A desorption step was not performed due to instability of the test substance in soil water test system.

Comments RMS

The study is acceptable.

Ethofumesate-carboxylic acid NC20645 was tested as potassium salt [phenyl-UL-14C] AE C639175 due to the instability of the acid. The geometric mean K_{foc} was determined to be 5.1 mL/g.

B.8.1.2.2. Aged sorption

| | |
|---------------------|---|
| Reference: | [Phenyl-UL-14C]ethofumesate (AE B049913): Time - dependent sorption in soils |
| Notifier: | Taskforce |
| Author(s), year: | Menke, U.; Telscher, M.; 2008 |
| Report/Doc. number: | MEF-08/514 / M-313317-01 |
| Guideline(s): | OECD 106 and 307 |
| GLP: | yes |
| Deviations: | Not specified |
| Validity: | Valid |
| Status: | New study |

Comments RMS

The study was evaluated with regard to aerobic degradation in 8.1.1.1.1.

Degradation kinetics of ethofumesate in aerobic soils was evaluated according to FOCUS (2006). The increase of sorption was calculated as ratio of concentration of [Phenyl-UL-¹⁴C]Ethofumesate in soil to concentration in aqueous 0.01 M CaCl₂ solution (R_{TDS} value). At the beginning of the study (DAT-0) R_{TDS} values were 3.53, 4.30, 3.26, and 7.76 mL/g for soils Laacher Hof AXXa, Hoefchen am Hohenseh 4a, Wurmwielse, and Dollendorf II, respectively. With increasing incubation time (i.e. ageing) of the soils, these values increased until DAT-91 to 8.59, 6.74, and 9.75 mL/g for soil Laacher Hof AXXa, Hoefchen am Hohenseh 4a, and Wurmwielse. For soil Dollendorf II the R_{TDS} value first increased to 10.83 mL/g at DAT-30 and then decreased to 6.14 mL/g.

Regarding the aging time at study end, the mean R_{TDS} value increased by a factor of 2.4, 1.6, and 3.0 in the soils Laacher Hof AXXa, Hoefchen am Hohenseh 4a, and Wurmwielse, respectively. In soil Dollendorf II the mean R_{TDS} value increased by a factor of 1.4 until DAT-30 and then decreased again.

The study was well conducted and points to potential effects of ageing on ethofumesate mobility in soils.

B.8.1.2.3. Summary: adsorption and desorption in soil

Ethofumesate was rapidly and strongly adsorbed to soil in laboratory tests with K_{foc} ranging between 97 and 208 mL/g (geomean 118 mL/g; $n = 12$). An additional time-dependent sorption study was submitted by the notifier Taskforce. The increase of sorption over time was defined as the ratio of concentration of [Phenyl-UL-14C]Ethofumesate in soil to the concentration in aqueous 0.01 M $CaCl_2$ extracts (R_{TDS} value). At study end (91 days), the mean R_{TDS} value increased by a factor of 1.4-3.0 indicating effects of ageing on adsorption of ethofumesate. Adsorption to soil of the metabolites NC 8493 and NC 20645 was investigated. Due to the fast degradation of these metabolites, K_{oc} could not be determined for NC 8493 with batch equilibrium tests and was instead estimated via EPI WIN to 20.82 mL/g. For NC 20645 (ethofumesate-carboxylic acid) the K_{foc} could be determined in 4 of 5 investigated soils. The adsorption to soil was low (geomean K_{FOC} : 5.1 mL/g).

B.8.1.3. Mobility in soil

B.8.1.3.1. Column leaching studies

B.8.1.3.1.1. Column leaching of the active substance

| | |
|---------------------|--|
| Reference: | KEMIFAM PRO FL: SOIL LEACHING IN THREE SOILS, SPONSOR: KEMIRA |
| Notifier: | Taskforce |
| Author(s), year: | Burgener, A.;1995 |
| Report/Doc. number: | A62937 / W 548 / M-146411-01-1 |
| Guideline(s): | None |
| GLP: | yes |
| Deviations: | |
| Validity: | Not valid |
| Status: | Previous evaluation in DAR for original approval / baseline dossier. |

Study summary based on previous draft assessment report

Materials and Methods

The mobility of ethofumesate (690 g/ha), phenmedipham (450 g/ha) and desmedipham (90 g/ha) in the formulation Kemifam Pro FL was investigated in three German standard soils (for soil properties, see table below) in a column leaching study according to BBA Guidelines IV 4-2.

Table 8-112: Soil characteristics

| Soil | O C (%) | pH | sand (%) | silt (%) | clay (%) | MHC (%) | CEC meq/100 g |
|------------|---------|-----|-------------|-------------|-------------|------------|------------------|
| Speyer 2.1 | 0.70 | 6.1 | 92 | 4.4 | 3.5 | n.r. | 4.9 |
| Speyer 2.2 | 2.3 | 6.0 | 89 | 5.6 | 5.1 | n.r. | 9.7 |
| Speyer 2.3 | 1.3 | 6.9 | 80 | 11 | 8.3 | n.r. | 9.5 |

n.r. = not reported

The formulation (rate as above) was applied to triplicate untreated saturated soil columns, 30 cm in height and 5 cm diameter. A volume of 393 mL of distilled water was added over two days, simulating 200 mm rainfall. The leachates were extracted with *n*-hexane prior to analysis with GC.

Results

The mean recovery efficiency of the method of analysis was 94±8% for ethofumesate, 88±8% for phenmedipham and 99% for desmedipham. No detectable amounts, or <1% of applied ethofumesate, was found in the leachates. Phenmedipham and desmedipham was present as hydrolysis products, but only in trace amounts (<2% of applied).

Comments RMS

Instead of a solution simulating artificial rain (0.01 M CaCl₂), water was used for saturation of the columns and for leaching. The LOD corresponded to 1% of AR, which is above the 0.5% recommended by OECD312. No analysis of residues in the soil columns was reported, no mass balance was derived.

The study is not valid.

| | |
|---------------------|---|
| Reference: | LEACHING OF PHENMEDIPHAM AND ETHOFUMESATE AS ACTIVE INGREDIENTS IN A FORMULATION WITH THE TRADE NAME BETANAL TANDEM WP, IN AN EXPERIMENT ACCORDING TO GUIDELINE IV 4-2 OF THE GERMAN BBA |
| Notifier: | Taskforce |
| Author(s), year: | Andre, W.;1991 |
| Report/Doc. number: | A62598 / W 203 / M-146075-01-1 |
| Guideline(s): | None |
| GLP: | No |
| Deviations: | |
| Validity: | Not valid |
| Status: | Previous evaluation in DAR for original approval / baseline dossier. |

Study summary based on previous draft assessment report

Materials and Methods

The mobility of ethofumesate (19.3% w/w) and phenmedipham (29.7% w/w) in the formulation Betanal Tandem WP + Powerpack was investigated in three German standard soils (for soil properties, see table below) in a column leaching study according to BBA Guidelines IV 4-2.

Table 8-113: Soil characteristics

| Soil | Org. C (%) | pH | sand (%) | silt (%) | clay (%) | MHC (%) | CEC meq/100 g |
|------------|---------------|-----|-------------|-------------|-------------|------------|------------------|
| Speyer 2.1 | 0.75 | 5.4 | 84 | 11 | 4.8 | n.r. | 3 |
| Speyer 2.2 | 2.7 | 6.0 | 75 | 17 | 5.7 | n.r. | 10 |
| Speyer 2.3 | 1.1 | 6.6 | 57 | 27 | 9.7 | n.r. | 8 |

n.r. = not reported

The formulation was applied at a rate of 3 kg Betanal Tandem/ha and 3 l Powerpack/ha (corresponding to 0.89 and 1.14 kg phenmedipham and ethofumesate/ha) to duplicate water saturated soil columns, 35 cm in height and 5 cm in diameter. A volume of 370-390 mL of distilled water was added over two days, simulating ca. 200 mm rainfall. The experiment was carried out in the dark at 20±2°C. The leachates were extracted with ethylacetate (for phenmedipham) and dichloromethane (for ethofumesate) prior to analysis with HPLC and GC, respectively.

Results

The mean recovery efficiency of the method of analysis was 103±2% for ethofumesate. No detectable residues of phenmedipham were found in the leachates. Ethofumesate was recovered in the leachates at concentrations corresponding to 1.6% of applied amounts in Speyer 2.2, 1.3% in Speyer 2.2, and 2.9% in Speyer 2.3.

Comments RMS

Instead of a solution simulating artificial rain (0.01 M CaCl₂), water was used for saturation of the columns and for leaching. No analysis of residues in the soil columns was reported, no mass balance was derived.

The authors themselves state that “[the] results however don't correlate to the sorption characteristics of the soils, so that the leaching rate perhaps could be an artefact do to the artificial structure of the soil layer.”

The study is not valid.

| | |
|---------------------|--|
| Reference: | LABORATORY LEACHING OF ETHOFUMESATE FROM A ONE-PACK WETTABLE POWDER FORMULATION (CR 14381) WITH LENACIL IN THREE STANDARD SOILS FROM WEST GERMANY |
| Notifier: | Taskforce |
| Author(s), year: | Reary, J. B.;1981 |
| Report/Doc. number: | A83312 / W 56 / M-155581-01-1 |
| Guideline(s): | BBA: 37 |
| GLP: | No |
| Deviations: | |
| Validity: | Not valid |
| Status: | Previous evaluation in DAR for original approval / baseline dossier. |

Study summary based on previous draft assessment report

Materials and Methods

The mobility of ethofumesate applied as a wettable powder formulation containing 30% ethofumesate and 12 % lenacil was investigated in three German standard soils (for soil properties, see table below) in a column leaching study according to BBA Leaflet 37 (1980).

Table 8-114: Soil characteristics

| Soil | Org. C (%) | pH | < 0.02 mm (%) |
|------|---------------|-----|------------------|
| 2.1 | 0.60 | 7.6 | 10.4 |
| 2.2 | 1.7 | 6.5 | 16.9 |
| 2.3 | 0.5 | 7.8 | 22.9 |

The formulation was applied at a rate corresponding to 7.5 kg a.s./ha to duplicate columns. A volume of approximately 400 mL of leachate could be collected from each soil column. The leachates were extracted with dichloromethane prior to analysis with HPLC and GC, respectively.

Results

The mean recovery efficiency of the method of analysis was $114 \pm 28\%$ for ethofumesate. Less than 0.2% of the applied ethofumesate were collected in the leachate.

Comments RMS

Instead of a solution simulating artificial rain (0.01 M CaCl_2), water was used for leaching. The soils were not appropriately characterized. Texture is not fully reported. There is no information whether columns were saturated prior to the leaching experiment. The recoveries are questionable. The study is not valid.

| | |
|---------------------|---|
| Reference: | SOIL PERCOLATION EXPERIMENTS WITH NORTON (TRAMAT) IN SPEYER STANDARD SOILS FROM W. GERMANY |
| Notifier: | Taskforce |
| Author(s), year: | Harris, R. J.; 1975 |
| Report/Doc. number: | A83291 / W 35 / M-155560-01-1 |
| Guideline(s): | BBA: 37 |
| GLP: | No |
| Deviations: | |
| Validity: | Not valid |
| Status: | Previous evaluation in DAR for original approval / baseline dossier. |

Study summary based on previous draft assessment report

Materials and Methods

The mobility of ethofumesate applied as EC formulation containing 20% ethofumesate was investigated in three German standard soils (for soil properties, see table below) in a column leaching study according to BBA Leaflet 37 (1973).

Table 8-115: Soil characteristics

| Soil | OC (%) | pH | < 0.02 mm (%) |
|------|-----------|-----|------------------|
| 2.1 | 0.80 | 7.0 | 4.2 |
| 2.2 | 2.58 | 6.8 | 10.1 |
| 2.3 | 1.0 | 5.2 | 19.5 |

The formulation was applied at a rate corresponding to 2 kg a.s./ha to duplicate columns. A volume of approximately 400 mL of distilled water was added to each soil column. The leachates were extracted with dichloromethane prior to analysis with HPLC and GC, respectively.

Results

The recovery efficiency of the method of analysis was ranging between 55 % (Soil 2.1) and 112 % (soil 2.3). The limit of detection is 0.4% of the AR. Less than 0.3%, 0.2% and 0.5% of the applied ethofumesate were collected in the leachates of soils 2.1., 2.2, 2.3., respectively.

Comments RMS

The soil characterisation is incomplete, texture is missing. Distilled water and not 0.01 M CaCl₂ was used. Radioactivity in soil sections is reported, but the recoveries and validation of the analytical method are not reported. The study is not valid.

| | |
|---------------------|--|
| Reference: | THE LEACHING OF 14C-NC 8438 IN FOUR SOIL TYPES |
| Notifier: | Taskforce |
| Author(s), year: | Adcock, J. W.; Pearce, J.C.;1975 |
| Report/Doc. number: | A83270 / W 14 / M-155539-01-1 |
| Guideline(s): | No |
| GLP: | No |
| Deviations: | |
| Validity: | Not valid. |
| Status: | Previous evaluation in DAR for original approval / baseline dossier. |

Study summary based on previous draft assessment report

Materials and Methods

The mobility of ¹⁴C-NC8438 was investigated in four soils (for soil properties, see table below) in a column leaching study.

Table 8-116: Soil characteristics

| Soil | OC (%) | pH | sand (%) | silt (%) | clay (%) | MWHC (%) |
|-------------------|-----------|-----|-------------|-------------|-------------|-------------|
| Agricultural sand | 0.9 | 4.7 | 91 | 2.0 | 6.0 | 18 |
| Clay loam | 2.2 | 7.2 | 41 | 20 | 37 | 24 |
| Silt loam | 2.5 | 7.2 | 5.0 | 73 | 20 | 47 |
| Sandy loam | 1.9 | 6.5 | 56 | 24 | 18 | 49 |

n.r. = not reported

The test compound was applied at a rate of approximately 1.4 kg as/ha to single wetted soil columns, 30 cm in height and 3.0 cm in diameter. Distilled water was added over a period of 15 - 20 days, simulating 508 mm of rainfall. After leaching, the columns were divided into four depth segments (7.5 cm each), which were extracted

with methanol:water (9:1). The leachates and soil extracts were analysed with LSC. Bound radioactive residues were determined by combustion of soil samples.

Results

Mass balances were established for each column. Between 89% and 100% of the applied radioactivity could be recovered. The distribution of radioactivity at the end of the leaching period is summarised in the table below.

Table 8-117: Distribution of radioactivity and material balance (% of applied) in soil columns and leachates after application of 1.4 kg ^{14}C -ethofumesate and 508 mm of distilled water over 15-20 days.

| Soil depth | Agricultural sand | | Clay loam | | Silt loam | | Sandy loam | |
|----------------|----------------------|-------|----------------------|-------|----------------------|-------|----------------------|-------|
| | (%) | | (%) | | (%) | | (%) | |
| | extract ¹ | bound | extract ¹ | bound | extract ¹ | bound | extract ¹ | bound |
| 0 - 7.5 cm | 4.4 | 0.41 | 21 | 1.5 | 32 | 0.77 | 14 | 1.9 |
| 7.5 - 15 cm | 3.6 | 0.37 | 33 | 0.54 | 41 | 0.88 | 47 | 1.5 |
| 15 - 23 cm | 7.3 | 0.33 | 16 | 1.2 | 8.1 | 0.52 | 21 | 0.65 |
| 23 - 30 cm | 16 | 0.25 | 15 | 0.69 | 0.83 | 0.21 | 1.0 | - |
| Leachate | 67 | | 7.0 | | 4.5 | | 4.2 | |
| Total recovery | 100 | | 96 | | 89 | | 91 | |

¹ soil samples extracted with methanol:water (9:1) for 16 hours.

Comments RMS

Distilled water was used instead of 0.01 M CaCl₂ for saturating the columns and for the leaching experiments. The use of a background electrolyte is essential for studies investigating the adsorption of chemicals in soils. No replicates of soil columns were set up and therefore the reliability of the experiment is questionable. The study is not acceptable.

| | |
|---------------------|--|
| Reference: | SOIL LEACHING OF NC 8438 AND METABOLITES |
| Notifier: | Taskforce |
| Author(s), year: | Adcock, J. W.; Warner, P. A.; 1974 |
| Report/Doc. number: | A83268 / W 12 / M-155537-01-1 |
| Guideline(s): | No |
| GLP: | No |
| Deviations: | |
| Validity: | Not valid |
| Status: | Previous evaluation in DAR for original approval / baseline dossier. |

Study summary based on previous draft assessment report**Materials and Methods**

The mobility of ^{35}S - and ^{14}C labelled ethofumesate in formulated Nortron was investigated in a sandy loam from Colorado. The experiment was set up in triplicate columns (ca. 30 cm in length). ^{14}C - and ^{35}S -ethofumesate were applied to the soil and aged aerobically for 30 days prior introduction to the top of the leaching columns. A final concentration in the soil of 3 mg a.s. / kg was produced, regarded as being equivalent to a field application of ca. 3.3 kg/ha. Columns were kept at 20°C for 45 days to. Soils were leached with distilled water. Aliquots (100 g) of each radiolabelled soil and the leachates were extracted with dichloromethane and analysed by TLC.

Results

Radioactivity in the column segments decreased from the top layer (47.5%) to the bottom layer (13.7%); 7.2 % of the radioactivity were found in the leachate.

Comments RMS

The study design and the reporting of data were deficient, lacking important information such as soil characteristics. The degradation of ethofumesate during the aerobic ageing period (e.g. mineralization, bound residues) was not determined. Material balances were not established. Recovery efficiencies of the method are not adequately reported. Water was used instead of 0.01 M CaCl_2 . The study is not valid.

| | |
|---------------------|--|
| Reference: | SOIL LEACHING OF RADIOLABELLED NC 8438. Summary |
| Notifier: | Taskforce |
| Author(s), year: | Adcock, J. W.; Challis, I. R.; Warner, P. A.; 1974 |
| Report/Doc. number: | A83265 / W 9 / M-155536-01-1 |
| Guideline(s): | No |
| GLP: | No |
| Deviations: | |
| Validity: | Not valid |
| Status: | Previous evaluation in DAR for original approval / baseline dossier. |

Study summary based on previous draft assessment report**Materials and Methods**

The mobility of ethofumesate ^{35}S - and ^{14}C labelled ethofumesate in formulated Nortron was investigated in a sandy loam from Colorado. The experiment was set up in triplicate columns (ca. 30 cm). ^{14}C - and ^{35}S -ethofumesate were applied to the soil and aged aerobically for 45 days prior to introduction to the top of the leaching columns.

A final concentration in the soil of 3 µg ethofumesate/g was produced, regarded as being equivalent to a field application of ca. 3.3 kg/ha. Columns were kept at 20°C for 45 days. Soils were leached with distilled water. At the end of the 45 day leachate period, the soil was extracted from each column and sectioned into equal quarters. Each quarter was placed in a soxhlet apparatus, -extracted overnight with a methanol-water mixture (9:1), and radioassayed. Subsequently, the soil was air-dried and combusted in a Schoniger flask.

Results

About 5% and 7% of the applied ^{14}C and ^{35}S radioactivity were found in the leachate, respectively. The majority of radioactivity was found in the top ca. 9 cm and decreased to below background in the bottom layer.

Comments RMS

The degradation of ethofumesate during the aerobic ageing period (e.g. mineralization, bound residues) was not determined. Validation and recoveries of the analytical method are not reported. Mass balance is not reported. Water was used for saturation and leaching instead of 0.01M CaCl_2 . The study is not valid.

| | |
|---------------------|--|
| Reference: | THE LEACHING OF ^{14}C-ETHOFUMESATE AND ITS BOUND RESIDUE IN CLAY SOIL FROM THE NETHERLANDS |
| Notifier: | Taskforce |
| Author(s), year: | Drake, C. H.; Hemmings, P. A.; Fordham, L.; Adcock, J. W.; 1977 |
| Report/Doc. number: | A83274 / W 18 / M-155543-01-1 |
| Guideline(s): | No |
| GLP: | No |
| Deviations: | |
| Validity: | Not valid |
| Status: | Previous evaluation in DAR for original approval / baseline dossier. |

Study summary based on previous draft assessment report

Materials and Methods

The mobility of the aged residues of ^{14}C -ethofumesate (radiochemical purity >95%) was investigated in a clay soil (for soil properties, see table below) in a column leaching study.

Table 8-118: Soil characteristics

| Soil | Org. mtr (%) | pH | sand (%) | silt (%) | clay (%) | MHC (%) | CEC meq/100 g |
|-----------------------|-----------------|-----|-------------|-------------|-------------|------------|------------------|
| Northern Holland clay | 2.9 | 7.0 | n.r. | n.r. | 45 | n.r. | n.r. |

n.r. = not reported

^{14}C -ethofumesate was applied to the soil at a rate of 5.1 ppm dry soil and aged aerobically at $20\pm 2^\circ\text{C}$ and 55% of field capacity in the soil for 150 days. After ageing, a 22 mm layer of treated soil was introduced to the top of four leaching columns previously saturated with distilled water (31 cm high with dry soil, 36 cm with water saturated soil, 3.3 cm i.d.).

The soil columns were leached with de-ionised water over 48 days, in amounts corresponding to ca. 200 mm of rain. Leachate was collected seven times during the study, and analysed with LSC. After the leaching period, each column was divided into four segments and the distribution and characterisation of radioactivity determined by methanol/water (9:1) extraction, LSC and TLC.

Results

The mean recovery of radioactivity after the 150 days ageing period was 53% ($^{14}\text{CO}_2$ not included), of which the extractables accounted for 5.3% and bound residues for 48% of applied radioactivity. The amounts of radioactivity in the percolate after the leaching period were indistinguishable from background levels. A mean of 97% of the recovered radioactivity was situated in the upper 9 cm of the soil columns.

Comments RMS

Soil characteristics were incompletely reported, texture is missing. The amounts of evolved $^{14}\text{CO}_2$ and the formation of bound residues during the ageing and leaching periods were not determined, and no material balance could be established. Columns were leached with water instead of 0.01 M CaCl_2 .

The study is not valid.

| | |
|---------------------|---|
| Reference: | THE LEACHING OF ETHOFUMESATE FROM EC AND SC FORMULATION OF NORTON (TRAMAT) IN THREE STANDARD SOILS FROM W. GERMANY |
| Notifier: | Taskforce |
| Author(s), year: | Harris, R. J.;1978 |
| Report/Doc. number: | A83307 / W 52 / M-155576-01-1 |
| Guideline(s): | BBA: 37 |
| GLP: | No |
| Deviations: | |
| Validity: | Not valid |
| Status: | Previous evaluation in DAR for original approval / baseline dossier. |

Study summary based on previous draft assessment report

Materials and Methods

The mobility of ethofumesate was investigated using one 20% EC and one 50% SC formulation of Nortron/Tramat and three German standard soils in a column leaching study according to BBA Guidelines Leaflet No 37.

Table 8-119: Soil characteristics

| Soil | Org. C (%) | pH | < 0.02 mm (%) |
|------|---------------|-----|------------------|
| 2.1 | 0.30 | 6.8 | 8.8 |
| 2.2 | 1.9 | 5.8 | 18.8 |
| 2.3 | 0.7 | 7.7 | 23.8 |

The formulations were applied to the columns of soil at or near the normal application rate (2 kg a.i./ha). The columns of soil (300 mm long x 50 mm diameter) were leached with 200 mm (400 ml) of water over 2.5 days (for the EC formulation) and 1.5 days for the SC formulation. The residue was dissolved with swirling and ultrasonification in 0.5 ml ethyl acetate. The extracts were chromatographed on various Carbowax 20 M columns (2.5% or 4%) at temperatures between 205 and 235°C. Detection was by means of a flame photometric detector employing a sulphur emission filter. The detection limit was 2 mg /L. The applied analytical method for soil was cross referenced to R.J. Harris, Fisons Report RESID/75/31 (June 1975) "Analytical method for residues of NC 8438 in soil treated with NORTRON".

Results

Recoveries determined in fortification experiments with leachate from untreated columns ranged between 70 and 104%. Recoveries determined in fortification experiments with soil ranged between 60% and 105%. Less than 0.5% of the applied radioactivity was found in the leachates of each column. Mass balances were below 71 % for 4 out of 6 columns.

Comments RMS

Test conditions, such as temperature were not reported, and soil texture is missing. The saturation of columns is not reported. Water was used instead of 0.01 M CaCl₂. The unsatisfactory total recovery and the recovery efficiencies of the methods of analysis, especially for soil, make the results unreliable. The study is not valid.

B.8.1.3.1.2. Column leaching of metabolites, breakdown or reaction products

| | |
|---------------------|--|
| Reference: | AGED SOIL LEACHING OF [14C]- ETHOFUMESATE |
| Notifier: | Taskforce |
| Author(s), year: | Mackie, J. A.; Hall, B. E.;1992 |
| Report/Doc. number: | A83391/ W 136 / M-155659-01-1 |
| Guideline(s): | US EPA Pesticide Assessment Guidelines Subdivision N, Paragraph 163-1 (October 1982) |
| GLP: | Yes |
| Deviations: | |
| Validity: | Valid |
| Status: | Previous evaluation in DAR for original approval / baseline dossier. |

Study summary based on previous draft assessment report

Materials and Methods

The mobility of the aged residues of ^{14}C -ethofumesate (radiochemical purity >98.9%) was investigated in a sandy loam soil (for soil properties, see table below) in a column leaching study according to US EPA Guidelines 163-1.

Table 8-120: Soil characteristics

| Soil | Org. mtr (%) | pH | sand (%) | silt (%) | clay (%) | MC at 33 kPa (%) | CEC meq/100 g |
|------------|-----------------|-----|-------------|-------------|-------------|------------------------|------------------|
| Loamy sand | 3.4 | 7.9 | 78 | 9.0 | 13 | 17 | 14 |

n.r. = not reported

^{14}C -ethofumesate was applied to the soil at a rate of 7.25 mg as/kg and aged aerobically at $25\pm 1^\circ\text{C}$ and 75% of FC at 33 kPa in the soil for 30 days. After ageing, 200 g of the treated soil was introduced to each of the duplicate water saturated leaching columns (40 cm high, 4.5 cm i.d.). The nominal application rate was calculated to 9.1 kg as/ha. During incubation, evolved $^{14}\text{CO}_2$ was collected in ethanolamine.

The soil columns were leached with 0.01 M CaCl_2 daily for 17-19 days, in total amounts corresponding to ca. 510 mm of rain. Leachate was collected daily and analysed with LSC. After leaching, the columns were divided into 5 cm segments and the distribution and characterisation determined by solvent extraction (acetonitrile and acetonitrile:water), LSC, TLC and HPLC.

Results

Total recovery after the ageing period was 100% of applied radioactivity, of which the parent compound accounted for 60%. Evolved CO_2 accounted for ca. 5%, and unextractables for ca. 32% of applied radioactivity.

After leaching, total recovery was 86% of applied radioactivity. A mean of 2.8% of applied radioactivity, consisting of ethofumesate and NC20645, was found in the leachate. For total radioactivity, 72% of applied remained in the soil columns (31% extractable, 42% unextractable), the majority (38 and 24% in the two columns, respectively) was situated in the upper 10 cm at the end of the leaching period. The parent compound was almost evenly distributed in the columns.

Table 8-121: Percentage recovery of applied radioactivity from sandy loam soil treated with [¹⁴C]-Ethofumesate

| Sampling Occasion | Time Point | % Applied Radioactivity Recovered From | | | | | |
|-------------------------|------------|--|---------------------|-------------------|---------|----------------|----------------|
| | | Acetonitrile | Acetonitrile: water | Ethanolamine Trap | Residue | Apparatus Wash | Total Recovery |
| Termination of Ageing | 30 day A | 66.55 | 3.38 | 5.46 | 30.28 | 0.09 | 105.76 |
| | B | 52.28 | 2.65 | 5.24 | 34.42 | 0.23 | 94.82 |
| | Mean | 59.42 | 3.02 | 5.35 | 32.35 | 0.16 | 100.29 |
| Termination of Leaching | 47 day A | 38.18 | 3.03 | 10.29 | 43.44 | 0.10 | 95.04 |
| | B | 44.81 | 2.80 | 8.38 | 38.42 | 0.23 | 94.64 |
| | Mean | 41.50 | 2.92 | 9.34 | 40.93 | 0.17 | 94.84 |

Table 8-122: Percentage recovery of applied radioactivity from sandy loam soil treated with [¹⁴C]-Ethofumesate aged residues after leaching

| Column | % Applied Radioactivity Recovered from | | | | | | |
|--------|--|------------------|----------------------------------|------------------------------------|----------------------|----------------|----------------|
| | Leachate | Segment Extracts | Ethanolamine Trap (Ageing Phase) | Ethanolamine Trap (Leaching Phase) | Soil Segment Residue | Apparatus Wash | Total Recovery |
| A | 2.38 | 30.40 | 5.51 | 3.93 | 42.78 | 2.04 | 87.04 |
| B | 3.11 | 31.06 | 5.70 | 3.93 | 40.09 | 1.86 | 85.75 |
| Mean | 2.75 | 30.73 | 5.61 | 3.93 | 41.44 | 1.95 | 86.40 |

Table 8-123: Characterisation of radioactivity in selected leachates following the application of aged [¹⁴C]-Ethofumesate by HPLC

| Leachate from Day | % of Radioactivity in Region of Interest (T) | % Ethofumesate* | % of Radioactivity in Region of Interest (T) | % NC 20645* |
|-------------------|--|-----------------|--|-------------|
| 5 | ND | - | ND | - |
| 10 | ND | - | ND | - |
| 13 | ND | - | ND | - |
| 17 | 57.35 | 0.30 | 42.65 | 0.22 |

Comments RMS

The study followed the respective US EPA guidance and is also in accordance with the OECD 312 guidance. The soil is well characterized, 0.01 M CaCl₂ was used for saturation and leaching of the columns. A mean of 2.7% AR (mainly consisting of ethofumesate and NC20645) was detected in the leachate, whereas 31% AR where retained in the top 10 cm. In the leachate of day 17, ethofumesate accounted for 0.3% AR and the metabolite NC 20645 for 0.22% AR.

The study is acceptable.

B.8.1.3.2. Lysimeter studies

| | |
|---------------------|--|
| Reference: | ETHOFUMESATE SC 50% W/V CR 19035/1 and CR 18654/1 LEACHING IN SOIL LYSIMETERS MAINTAINED UNDER OUTDOOR CONDITIONS |
| Notifier: | Taskforce |
| Author(s), year: | Allen, R.; MacKenzie, E.; Hibbert, L.; Lander, G.;1995 |
| Report/Doc. number: | A89221 / W 171 / M-164392-01-1 |
| Guideline(s): | BBA Guideline, Part IV, 4 -3 |
| GLP: | Yes |
| Deviations: | |
| Validity: | Valid |
| Status: | Previous evaluation in DAR for original approval / baseline dossier. |

Study summary based on previous draft assessment report**Materials and Methods**

The leaching behaviour of ethofumesate in soil lysimeters was studied on [benzene ring-U-¹⁴C] ethofumesate. The radiochemical purity was >98%. The study was carried out for a period of two years (April, 1992 to April, 1994) on a silty sand in three lysimeters. The study was carried out according to general agriculture practice, cultivating sugar beet the first year and wheat the second year, also including fertilisation and the use of other pesticides in 1993 and 1994 (e.g. Tilt turbo, Asset, pirimicarb and Roundup). Ethofumesate was applied once on three lysimeters (April 16 in 1992, first year) at a dose of 1.25 kg as/ha before the emergence of the sugar beet. The lysimeter holdings were made of fibre glass and the inner size of the lysimeters was 80 cm by diameter and 1 meter by depth. The surface area of the lysimeter was 0.5 m².

Table 8-124: Soil characteristics down to 110 cm. (UK particle size distribution)

| Horizon and depth (cm) | Org. C (%) | pH in water | Coarse sand (0.6-2 mm) (%) | Sand (0.2-0.6 mm) (%) | Fine sand (0.1-0.2 mm) (%) | Silt (2-60 µm) (%) | Clay <2 µm (%) |
|------------------------------|---------------|----------------|----------------------------------|-----------------------------|----------------------------------|--------------------------|----------------------|
| Ap (0-31) | 1.02 | 6.1 | 58 | 24 | 1 | 7 | 8 |

| | | | | | | | |
|--------------|------|-----|----|----|---|---|---|
| Bw (31-53) | 0.11 | 6.5 | 70 | 23 | 1 | 1 | 4 |
| Cu (53-77) | 0.08 | 6.5 | 70 | 23 | 1 | 2 | 3 |
| Cu2 (77-110) | 0.02 | 6.4 | 73 | 22 | 1 | 1 | 3 |

During the two years, about 43 leachate samples were collected from each lysimeter. At a few occasion during the summer periods, no sampling was possible because of too small leaching volumes. Total radioactivity was measured on all samples by LSC, whereafter the samples were kept frozen until further treatment. Six samples from each of the three lysimeters, covering the two main radioactive peaks during the two years of the study were treated through a cleaning up procedure, where, prior to analysis by HPLC, the samples were filtered and concentrated by means of dry freezing (lyophilisation). The concentrates were re-dissolved and chromatographed through a Sephadex LH-20 column. The eluted fractions were characterised by UV or by radioactivity counter. The results indicated that leachate samples from the three test lysimeters were fairly identical. Therefore, the lysimeters leachate sample containing the largest amount of radioactivity was investigated further by analysing the 4 main Sephadex eluting peaks by HPLC. Twenty leachate samples from the same lysimeter, collected over the study period, were analysed by HPLC after filtration and lyophilisation.

Results

Total leaching from the three lysimeters, measured as total radioactivity, was between 2.0 and 2.2 % of applied dose.

Table 8-125: Average seasonal concentrations and quantities of total radioactive residues residues in leachate from lysimeters 4,9,10 following application of ¹⁴C-ethofumesate ata a rate of 1.25 kg/ha pre-emergence to sugar beet in April 1992

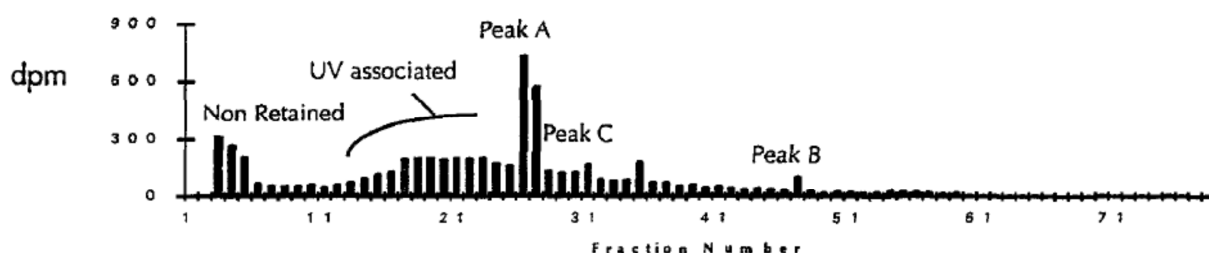
| Season | Lysimeter 4 | | | Lysimeter 9 | | | Lysimeter 10 | | |
|--------------------------------|---------------|-------------|--------------|---------------|-------------|--------------|---------------|-------------|--------------|
| | Concentration | | % of applied | Concentration | | % of applied | Concentration | | % of applied |
| | (µg/l) | (g/ha) | | (µg/l) | (g/ha) | | (µg/l) | (g/ha) | |
| Spring 1992 (Apr, May) | 0.077 | 0.022 | 0.002 | 0.235 | 0.076 | 0.006 | 0.000 | 0.000 | 0.000 |
| Summer 1992 (Jun, Jul, Aug) | 0.301 | 0.041 | 0.003 | 0.517 | 0.044 | 0.004 | 0.001 | 0.000 | 0.000 |
| Autumn 1992 (Sep, Oct, Nov) | 2.316 | 1.095 | 0.088 | 2.906 | 0.813 | 0.065 | 0.710 | 0.594 | 0.048 |
| Winter 1992/93 (Dec, Jan, Feb) | 5.958 | 7.512 | 0.605 | 6.290 | 6.806 | 0.548 | 4.520 | 4.803 | 0.387 |
| Spring 1993 (Mar, Apr, May) | 4.206 | 2.299 | 0.185 | 5.736 | 3.713 | 0.299 | 5.742 | 3.279 | 0.264 |
| Summer 1993 (Jun, Jul, Aug) | No leachate | No leachate | No leachate | No leachate | No leachate | No leachate | No leachate | No leachate | No leachate |
| Autumn 1993 (Sep, Oct, Nov) | 3.807 | 3.631 | 0.292 | 4.916 | 4.208 | 0.339 | 5.979 | 5.262 | 0.424 |
| Winter 1993/94 (Dec, Jan, Feb) | 3.712 | 6.906 | 0.556 | 4.410 | 7.107 | 0.572 | 5.094 | 8.407 | 0.677 |
| Spring 1993 (Mar, Apr) | 1.931 | 3.094 | 0.249 | 2.698 | 4.257 | 0.343 | 3.089 | 4.708 | 0.379 |
| Year 1 (Apr 1992-Apr 1993) | 4.074 | 9.423 | 0.759 | 4.574 | 9.181 | 0.739 | 2.611 | 6.550 | 0.528 |
| Year 2 (Apr 1993-Apr 1994) | 3.161 | 15.178 | 1.222 | 4.002 | 17.843 | 1.437 | 4.634 | 20.504 | 1.651 |
| Overall | 3.457 | 24.601 | 1.981 | 4.180 | 27.025 | 2.177 | 3.902 | 27.054 | 2.179 |

* a.s. equivalents

According to the results from the HPLC analysis, the radioactivity detected was not ethofumesate. Substances reported to have been detected in leachates were mainly the metabolite NC 20645, NC 17900 and NC 20645, the

two last were detected once each. Radioactivity in plant material after harvest was between 0.37 to 0.56% of applied dose, of which most of it was detected in the sugar beets. At termination of the study, radioactive residues in the soil column were totally 45-53% of applied dose in the three lysimeters. Of this, 44-50% was detected in the top 20 cm of the lysimeters, of which ethofumesate represented 2.4-4.2%. No analysis was made regarding ethofumesate below 20 cm as the amount of radioactivity was less than 1%. The amount of radioactivity decreased rapidly below 20 cm.

Table 8-126: HPLC analysis of concentrated leachate from lysimeter 9 (sample collected on 25 January 1993)



Comments RMS

The lysimeter study was carried out according to recommended methods e.g. the BBA Lysimeter guideline, Part IV, 4-3. However, during the previous evaluation, questions were raised on the reliability of the analytical method and the conclusions to be drawn from the study. The analytical method was accepted by the Member States' experts. However, they also highlighted that – given that the study was conducted with less than the maximum rate of application - only under these specified conditions no leaching of ethofumesate was taking place. It has to be stressed that during the previous evaluation, leaching was predicted in model calculations and therefore definitive conclusions on the groundwater leaching potential could not be drawn. In the present re-evaluation, model calculations clearly show that no unacceptable leaching of ethofumesate to groundwater takes place.

The main focus of the lysimeter study was on the assessment of ethofumesate leaching potential whereas metabolites detected in leachate were quantified but only identified by co-chromatography in case the metabolites were already known from laboratory studies and reference substances were available. The highest concentration of an individual peak was detected in lysimeter 9. This zone of radioactivity detected in HPLC chromatography called "Peak A" accounted for at maximum 0.5 µg/L (annual mean, calculated as a.s. equivalent) , but the structure was not identified at that time. This metabolite was identified in a non-guideline study by Stupp et al.(2013), which simulated the conditions of the former lysimeter.

The study is acceptable.

| | |
|---------------------|---|
| Reference: | MOBILITY AND DEGRADATION IN SOIL IN OUTDOOR LYSIMETER 14C-Ethofumesate |
| Notifier: | Taskforce |
| Author(s), year: | Burgener, A.; 1994 |
| Report/Doc. number: | A87603 / M-161530-01-1 |
| Guideline(s): | BBA Guideline, Part IV, 4 -3 |
| GLP: | No |
| Deviations: | |
| Validity: | Valid |
| Status: | Previous evaluation in DAR for original approval / baseline dossier. |

Comments RMS

This was an interim report superseded by Burgener A. (1997).

| | |
|---------------------|---|
| Reference: | Report amendment to 14C-ethofumesate: Mobility and Degradation in soil in outdoor lysimeters |
| Notifier: | Taskforce |
| Author(s), year: | Burgener, A.;1997 |
| Report/Doc. number: | A91247/ W 214-2 / M-167946-02-1 |
| Guideline(s): | BBA Guideline, Part IV, 4 --3 |
| GLP: | Yes |
| Deviations: | |
| Validity: | Valid |
| Status: | Previous evaluation in DAR for original approval / baseline dossier. |

Study summary based on previous draft assessment report

Materials and Methods

The leaching behaviour of ethofumesate in lysimeters, using [benzene ring-U-¹⁴C] ethofumesate, was studied at RCC research station at Itingen in Switzerland on a low organic content sandy soil, the German Borstel soil (see table below).

Table 8-127: Soil characteristics by depth of the sandy soil used in lysimeter study. (USDA)

| Horizon (cm) | Org. C (%) | pH (KCl) | sand (%) | silt (%) | clay (%) | MWHC g water/ | FC g water/ | Soil density |
|-----------------|---------------|-------------|-------------|-------------|-------------|------------------|----------------|--------------|
|-----------------|---------------|-------------|-------------|-------------|-------------|------------------|----------------|--------------|

| | | | | | | 100 g soil | 100 g soil | |
|--------|------|-----|------|-----|-----|------------|------------|------|
| 0-30 | 1.05 | 6.1 | 88.0 | 6.4 | 5.6 | 34.5 | 17.9 | 1.34 |
| 30-60 | 0.49 | 5.9 | 90.1 | 7.3 | 2.6 | 28.6 | 15.5 | 1.50 |
| 60-90 | 0.14 | 6.1 | 93.3 | 3.5 | 3.2 | 23.2 | 11.6 | 1.62 |
| 90-120 | 0.00 | 7.3 | 99.7 | 0.0 | 0.3 | 23.6 | 7.4 | 1.41 |

The study was carried out according BBA guideline Part IV, 4-3. The radiochemical purity of the test substance was 98.8%. Unlabelled ethofumesate (chem. purity $\geq 97\%$) and metabolites NC 8493 and NC 9607 (both with a chem. purity of $>95\%$) were used as reference standards. [^{14}C]-Ethofumesate was applied to two lysimeters having an inner diameter of 115 cm and a surface area of 1 m². The length of the soil column was 120 cm. [^{14}C]-Ethofumesate was applied, formulated as KEMIRON FLOW (500 g as/l), to both lysimeters (19 and 20) in May 1993 at a dose corresponding to 1.5 kg as/ha and in May 1994 with the same dose to one of the lysimeters (20). A third lysimeter was used as a reference with no application of ethofumesate. Lysimeters were cultivated with fodder beet 1993 and 1994, and with winter wheat in 1995. Leachates were collected, when possible, once a month for a total period close to three years. After stripping off $^{14}\text{CO}_2$, leachates were analysed by TLC to determine total ^{14}C and by HPLC, coupled with radioactivity and UV detection, to determine ^{14}C -ethofumesate and the five metabolites NC 8493, NC09607, NC20645 (as potassium salt), NC10458 and NC17900. At the termination of the study, total radioactivity was determined in each soil layer (approximately 10 cm thick) and extracts of the upper three to four 10 cm layers were analysed by LSC, HPLC and combustion to determine total radioactivity, ethofumesate and metabolites, and bound residues. Total radioactivity was determined in plants.

Results

Table 8-128: Results from determination of ^{14}C equivalents in leachates, soil and plants.

| Parameters | Lysimeter 19 | Lysimeter 20 |
|--|-------------------------------------|----------------------------------|
| Total precipitation, mm (L) | 3281 | 3281 |
| Total volume leached, (L); (% of precipitation) | 1222 (37%) | 1286 (39%) |
| Effective dose, total mg as (/m²) | 128 | 115 + 128 = 243 |
| [^{14}C] ethofumesate equivalents | | |
| total leached (excluding CO ₂), % of applied | 0.75 | 1.1 |
| mean annual conc. (excl. CO ₂), µg/L | | |
| year 1 | 0.61 | 0.98 |
| year 2 | 0.76 | 2.6 |
| year 3 | 1.02 | 3.2 |
| highest conc. (excl. CO ₂), µg/L | 1.1 (year 3) | 4.2 (year 3) |
| CO ₂ (carbonates), % of applied (years 1-3) | 0.04 | 0.05 |
| Total radioactivity in plants, year 1-3, % of applied | 0.78 | 0.84 |
| Total ^{14}C in soil column after termination, % of applied | %; (column layer) 31; (0-118 cm) | (column layer) 30; (0-118 cm) |
| Total ^{14}C , as % of applied dose, in | | |
| Layer 1 | 24; (0-10 cm) | 25; (0-15 cm) |
| Layer 2 | 2.6; (10-19 cm) | 1.6; (15-24 cm) |

| | | |
|---|-------------------|-------------------|
| Layer 3 | 1.2; (19-28 cm) | 1.1; (24-33 cm) |
| Layer 4 | 0.85; (28-38 cm) | 0.9; (33-42 cm) |
| Layers 5-8 | 1.8; (38-76 cm) | 1.1; (42-78 cm) |
| Layers 9-12 | 0.26; (76-118 cm) | 0.31; (78-118 cm) |
| Total ^{14}C Recovered, % of applied | 32 | 32 |
| Calculated total loss of ^{14}C by volatilisation and mineralization to CO_2, % of applied | 67.6 | 67.6 |

The results from the HPLC analysis of the four concentrated leachates of each lysimeter show that ethofumesate was not detectable in any of them. Determination limit was 0.01 µg/l. One metabolite was tentatively identified as NC 20645, 2-(2-hydroxy-5-methane-sulfonylhydroxyphenyl)-2-methylpropionic acid. After three years, at termination of the study, residues of radioactivity were concentrated in the top 10-15 soil layer, ca. 24% of the total dose applied. Ethofumesate was the identified residue that was present at the highest concentration in the top 19 cm, approximately 4 % of applied dose.

The unresolved radioactivity increased towards the study end in one lysimeter.

Table 8-129: Radioactive fractions of four concentrated typical leachates of lysimeter 19, given in % AR (above) and µg/l parent equivalents/l leachate (below)

| Sampling date Lys 19 | Days after appl. | Recovery work-up [%] | Peak 1 | Peak 2 | Peak 3 | Peak 4 NC 20645 | not resolved | TOTAL |
|-------------------------|------------------|----------------------|--------|--------|--------|--------------------|--------------|-------|
| Jan 07, 94 | 242 | 78.7 | 0.0010 | 0.0011 | n.d. | n.d. | 0.0268 | 0.029 |
| Nov 24, 94 | 563 | 93.1 | 0.0002 | 0.0003 | n.d. | n.d. | 0.0145 | 0.015 |
| Apr 10, 95 | 700 | 96.1 | 0.0014 | 0.0003 | 0.0017 | 0.0004 | 0.0206 | 0.024 |
| Jan 02, 96 | 967 | 95.5 | 0.0019 | n.d. | 0.0073 | n.d. | 0.0421 | 0.051 |

n.p. not performed

n.d. not detected

| Sampling date Lys 19 | Days after appl. | Parent equival. µg/l | Peak 1 | Peak 2 | Peak 3 | Peak 4 NC 20645 | not resolved |
|-------------------------|------------------|----------------------|--------|--------|--------|--------------------|--------------|
| Jan 07, 94 | 242 | 0.88 | 0.03 | 0.03 | n.d. | n.d. | 0.82 |
| Nov 24, 94 | 563 | 1.11 | 0.02 | 0.03 | n.d. | n.d. | 1.07 |
| Apr 10, 95 | 700 | 0.89 | 0.05 | 0.01 | 0.06 | 0.01 | 0.75 |
| Jan 02, 96 | 967 | 1.18 | 0.04 | n.d. | 0.17 | n.d. | 0.97 |

n.p. not performed

n.d. not detected

Table 8-130: Radioactive fractions of four concentrated typical leachates of lysimeter 20, given in % AR (above) and µg/l parent equivalents/l leachate (below)

| Sampling date Lys 20 | Days after appl. | Recovery work-up [%] | Peak 1 | Peak 2 | Peak 3 | Peak 4 NC 20645 | not resolved | TOTAL |
|-------------------------|------------------|----------------------|--------|--------|--------|--------------------|--------------|-------|
| Jan 07, 94 | 242 | 100.2 | 0.0008 | 0.0005 | 0.0010 | n.d. | 0.0264 | 0.029 |
| Jan 13, 95 | 613 | 100.8 | 0.0007 | n.d. | 0.0008 | n.d. | 0.0139 | 0.015 |
| Apr 10, 95 | 700 | 90.3 | 0.0003 | n.d. | 0.0025 | 0.0005 | 0.0210 | 0.024 |
| Sep 15, 95 | 858 | 79.2 | n.d. | n.d. | 0.0054 | 0.0008 | 0.0452 | 0.051 |

n.p. not performed
n.d. not detected

| Sampling date Lys 20 | Days after appl. | Parent equival. µg/l | Peak 1 | Peak 2 | Peak 3 | Peak 4 NC 20645 | not resolved |
|-------------------------|------------------|----------------------|--------|--------|--------|--------------------|--------------|
| Jan 07, 94 | 242 | 1.40 | 0.04 | 0.02 | 0.06 | n.d. | 1.28 |
| Jan 13, 95 | 613 | 2.78 | 0.12 | n.d. | 0.09 | n.d. | 2.57 |
| Apr 10, 95 | 700 | 4.15 | 0.06 | n.d. | 0.42 | 0.08 | 3.59 |
| Sep 15, 95 | 858 | 4.30 | n.d. | n.d. | 0.45 | 0.07 | 3.78 |

n.p. not performed
n.d. not detected

Comments RMS

The average concentration of ¹⁴C-ethofumesate equivalents in the leachate after CO₂ stripping was 0.75 µg/l (lysimeter 19) and 2.10 µg/l for the twofold treated lysimeter 20. Maximal concentrations were determined on January 2, 1996 (1.15 µg/l, lysimeter 19) and on September 15, 1995 (4.16 µg/l, lysimeter 20). The limit of determination of parent compound was 0.01 µg/L in leachate and 0.3 µg/kg in soil samples. ¹⁴C-ethofumesate was not detected in any of the leachates of both lysimeters.

Four radioactive fractions consisting of discrete peaks were named Peak 1, 2, 3 and 4. The metabolite patterns were similar for both lysimeters. Peak 3 was the most important radioactive fraction and appeared in concentrations up to 0.17 µg/l (lysimeter 19) and up to 0.45 µg/l (lysimeter 20). The radioactive fraction Peak 4 (highest concentration <0.08 µg/l parent equivalents) was tentatively identified as NC 20645 i.e. 2-(2-hydroxy-5-methane-sulfonyloxyphenyl)-2-methypropionic acid. Peak 3 was not further identified. Only 4 leachates were analysed for metabolites, therefore the calculation of yearly averages does not appear appropriate and was not carried out.

The total radioactivity, not identified as ethofumesate, was increasing with time in one lysimeter and reached 3.78 µg/L. The notifier argues that a significant portion of the radioactivity smeared across the chromatogram “mirroring” the UV-background and that this phenomenon was observed more or less at all analyses performed. This UV-mirroring radioactivity was assessed as stemming from the incorporation of ¹⁴C-ethofumesate into soil organic matter. The RMS agrees with this interpretation as this phenomenon has been observed before in lysimeter studies. In addition, the study by Stupp (2013) was conducted in order to assess degradation products of ethofumesate in lysimeter studies.

The study is acceptable.

| | |
|---------------------|---|
| Reference: | [Phenyl-UL-14C]ethofumesate: Investigation of metabolites previously detected in lysimeter leachates by an outdoor experiment with three EU soils |
| Notifier: | Taskforce |
| Author(s), year: | Stupp, H. P.; Junge, T.; 2013 |
| Report/Doc. number: | EnSa-13-0234 / M-461417-01-1 |
| Guideline(s): | Non-Guideline Study, but Principles based on: OECD Test Guideline No. 307 2002 and Regulation (EC) No.1107/2009 of the European Parliament and of the council of 21 October 2009. |
| GLP: | Yes |
| Deviations: | |
| Validity: | Valid |
| Status: | New study |

EXECUTIVE SUMMARY

The objective of the study was to identify a metabolite called “Peak A” detected in leachate in previously performed lysimeter studies (Allen, 1995). The intention of these previous lysimeter studies was to demonstrate that no Ethofumesate reached groundwater. Metabolites detected in leachate were quantified but only identified by co-chromatography in case the metabolites were already known from laboratory studies and reference substances were available. A zone of radioactivity detected in HPLC chromatography called “Peak A” accounted for about 0.5 µg/L (annual mean, calculated as a.i. equivalent), but the structure was not identified at that time. In the present study the lysimeter experiment was re-enacted using plant pots filled with three different soils and incubation under outdoor conditions. The soils were selected to cover different soil types including a typical lysimeter soil (i.e. Laacher Hof AXXa) with about 79% sand. Peak A was selected from the leachate by comparison of the HPLC chromatography behavior in the present study and the previous lysimeter studies. The structure was identified by LC-MS/MS including accurate mass determination. A guideline study is not available for this investigation. The experiments were conducted based on OECD Guideline No. 307, and Regulation (EC)

No.1107/2009 of the European Parliament and of the council of 21 October 2009. The study was conducted in compliance with the GLP standards of OECD, FIFRA and JMAFF.

Three plant pots (30 cm depth, about 40 cm diameter) were filled with three different soils freshly sampled in the field (soil depth 10 cm, on top of a 10 cm graded bed). The soils were taken from agricultural use areas representing different geographical origin and different soil properties, a sandy loam (Laacher Hof AXXa, organic carbon 1.9%, pH 6.2, Monheim, Germany), a sandy loam (Laacher Hof Wurmwielse, organic carbon 1.8%, pH 5.3, Monheim, Germany), and a silt loam (Hoefchen am Hohenseh, organic carbon 2.4%, pH 6.4, Burscheid, Germany) (mean values, long-term average). After a pre-equilibration period, [Phenyl-UL-¹⁴C]Ethofumesate (formulated as suspension concentrate and diluted with water) was applied on the soil surface in the same way as in the previous lysimeter studies. The plant pots were placed in a greenhouse with open roof exposed to rain and sun in summer. The aqueous leachate was collected after 0, 8, 36, 50, 78, 101, 104 and 146 days until no radioactivity was detected in leachate. In addition to rainfall, the soils were irrigated from time to time in order to obtain sufficient leachate. Leachates were analyzed by LSC, by an optimized HPLC method and by the method used in the original lysimeter study. As result a metabolic profile was obtained for the leachate of the three soils. The profile was similar in all soils. Besides Ethofumesate, the known soil metabolite Ethofumesate-carboxylic acid was detected as main metabolite in the eluate. This metabolite was also detected in small amounts in the previous lysimeter study. Applying the HPLC method used in the previous lysimeter study, 2 very minor peaks were selected which had a similar retention behavior as Peak A. The peaks were purified and concentrated, but identification failed due to the low amount formed and probably due to instability during storage before LC-MS(/MS) measurements. After 146 days no significant radioactivity leached indicating that the remaining residues were irreversibly bound to soil.

In order to produce larger amounts of the respective peaks a plant container was filled with about 5 kg soil Laacher Hof AXXa (MID samples). The radioactive application solution was applied and the soil was incubated in a climatic chamber with light exposure, due to bad weather conditions. Fractions of the soil were extracted with acetonitrile /water after 14, 39, 70 and 90 days. The extracts were analyzed by HPLC. The metabolite pattern of the plant pot experiment was reproduced and two minor peaks were detected representing Peak A. Both peaks were sampled, concentrated and analyzed by LC-MS/MS including accurate mass determination. The structures were finally identified as glycoside conjugates of the soil metabolites Ethofumesate-2-hydroxy and Ethofumesate-carboxylic acid.

MATERIALS AND METHODS:

Materials :

Test Material :

[Phenyl-UL-¹⁴C]Ethofumesate

Specific Radioactivity : 3.78 MBq/mg

Soils :

Three different soils were taken from agricultural use areas representing different geographical origin and different soil properties including a typical lysimeter soil.

Soil used for production of larger amounts of metabolites in plant container:

Table 8-131: Soil characteristics

| Parameter | Results/Units |
|---|--|
| Soil Designation | Laacher Hof AXXa Batch used for plant container |
| Geographic Location (City / State / Country) | Monheim / North Rhine-Westphalia / Germany |
| GPS Coordinates | N 51° 04.6' E 006° 55.5' |
| Soil Taxonomic Classification | Loamy, mixed, mesic Typic Argudalf |
| Texture Class | Loamy sand |
| Sand [50 µm – 2 mm] | 79% |
| Silt [2 µm – 50 µm] | 14% |
| Clay [< 2 µm] | 7% |
| pH (soil / 0.01 M CaCl ₂ 1/2) | 6.1 |
| pH (soil / water 1/1) | 6.5 |
| pH (saturated paste) | 6.4 |
| pH (soil / 1 N KCl 1/1) | 5.9 |
| Organic Matter | 3.4% |
| Organic Carbon | 2.0% |
| Cation Exchange Capacity | 8.7 meq/100 g |
| Water Holding Capacity maximum (WHC _{max}) | 46.9 g H ₂ O <i>ad</i> 100 g DW |
| at 1/10 bar (pF 2.0) | 13.7% |
| at 1/3 bar (pF 2.5) | 11.5% |
| Bulk Density (disturbed) | 1.16 g/cm ³ |

Methods :

Study design :

Plant pots were filled with three different soils and incubated under outdoor conditions. After a pre-equilibration period, [Phenyl-UL-¹⁴C]Ethofumesate (formulated as suspension concentrate and diluted with water) was applied on the soil surface in the same way as in the previous lysimeter studies. The plant pots were placed in a greenhouse with open roof exposed to rain and sun in summer. The aqueous leachate was collected after 0, 8, 36, 50, 78, 101, 104 and 146 days until no radioactivity was detected in leachate. In addition to rainfall, the soils were irrigated from time to time in order to obtain sufficient leachate. Only the leachates were investigated.

In an additional test for production of metabolites, a plant container was filled with about 5 kg soil Laacher Hof AXXa (typical lysimeter soil). The radioactive application solution was applied and the soil was incubated in a climatic chamber with light exposure, due to bad weather conditions. Fractions of the soil were extracted with acetonitrile /water.

Experimental Conditions :

The tests were performed under outdoor conditions with additional watering and for the additional test in a climate chamber with light exposure.

Sampling :

The aqueous leachate was collected after 0, 8, 36, 50, 78, 101, 104 and 146 days until no radioactivity was detected in leachate. In case of the additional test fractions of the soil were extracted with acetonitrile /water after 14, 39, 70 and 90 days.

Analytical Procedures :

Leachate and extracts were analyzed by LSC and HPLC using the same methods as in the previous studies in order to compare the metabolic profiles. The selected peaks representative for peak A were fractionated and analyzed by LC-MS/MS including accurate mass determination.

RESULTS AND DISCUSSION

The metabolic profiles of the leachates of the three different soils were very similar (see tables below). Peaks with retention times of Peak A were detected in very low amounts only. In the rest with a plant container and extraction of soils two peaks with retention times similar to Peak A were isolated and identified as glycoside conjugates of the soil metabolites NC 8493 (ethofumesate-2 hydroxy) and NC 20645 (ethofumesate carboxylic acid).

Figure 8-81: HPLC profile comparison of soil leachate and references (HPLC Method 2, same as in original study).

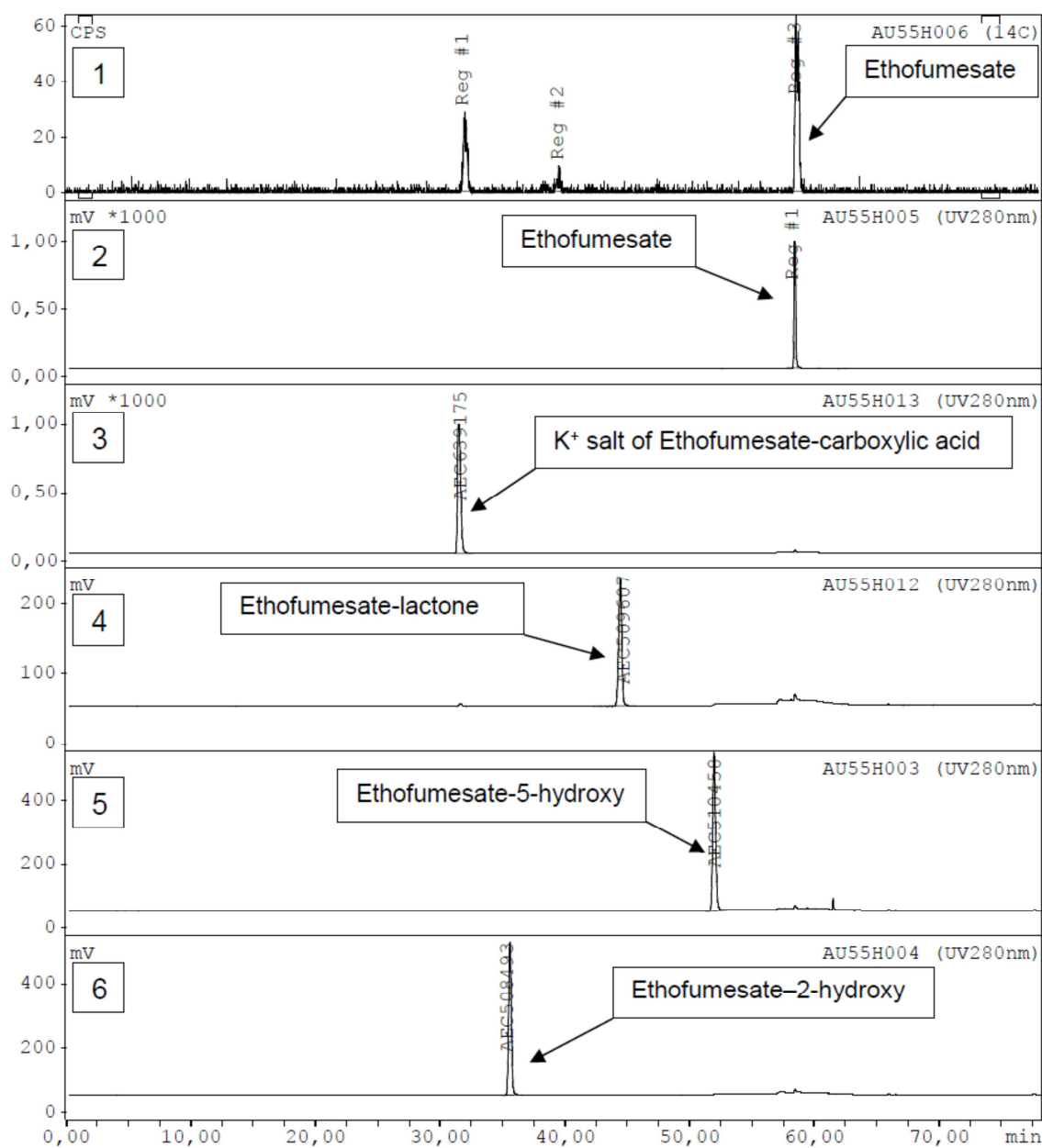


Figure 8-82: HPLC Co-chromatography of Ethofumesate-carboxylic acid and [^{12}C]-reference item (HPLC method, same as in original study).

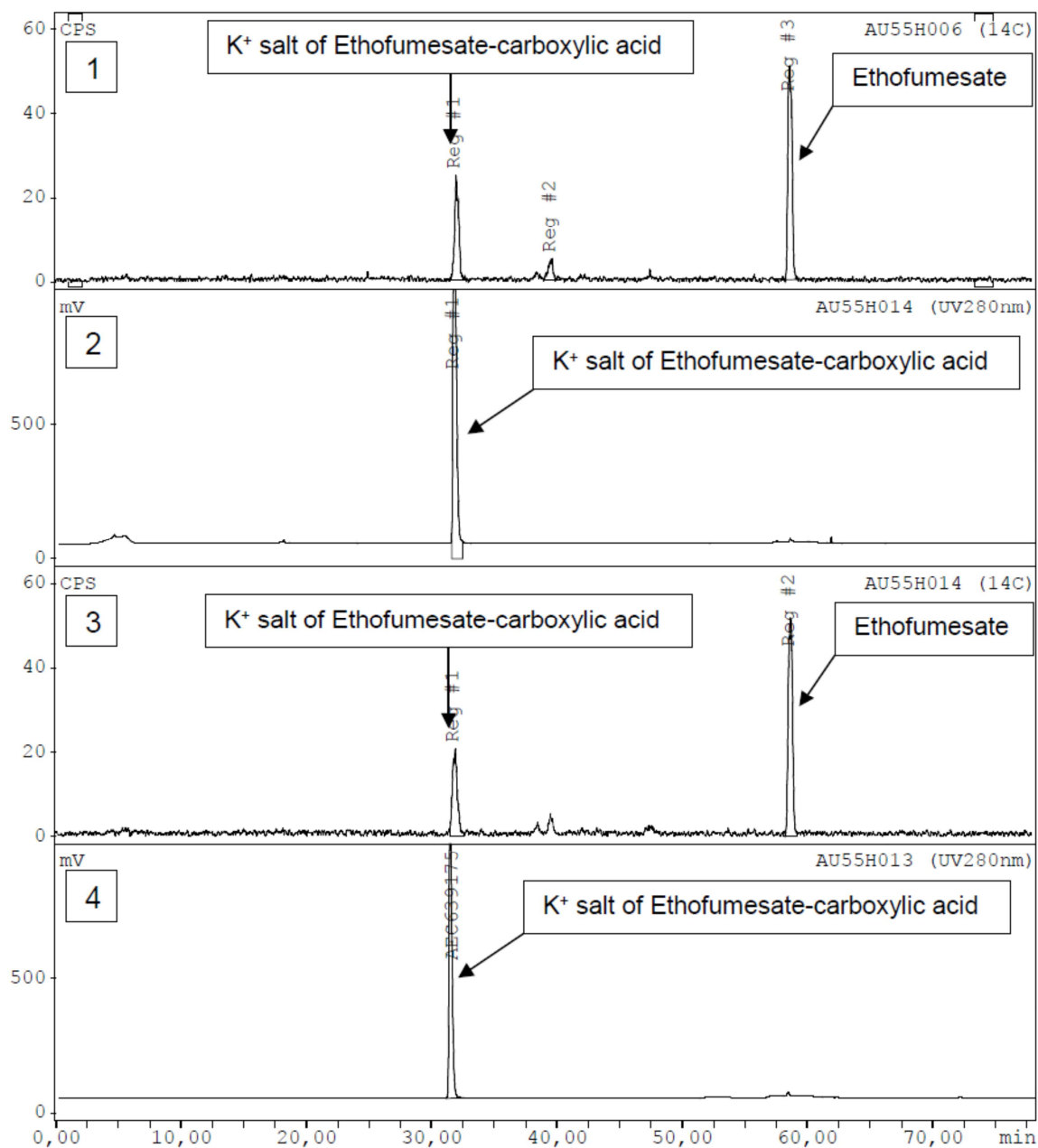


Figure 8-83: HPLC Chromatograms (Method 2, the same method as in the original study) of soil leachates of soil Laacher Hof AX

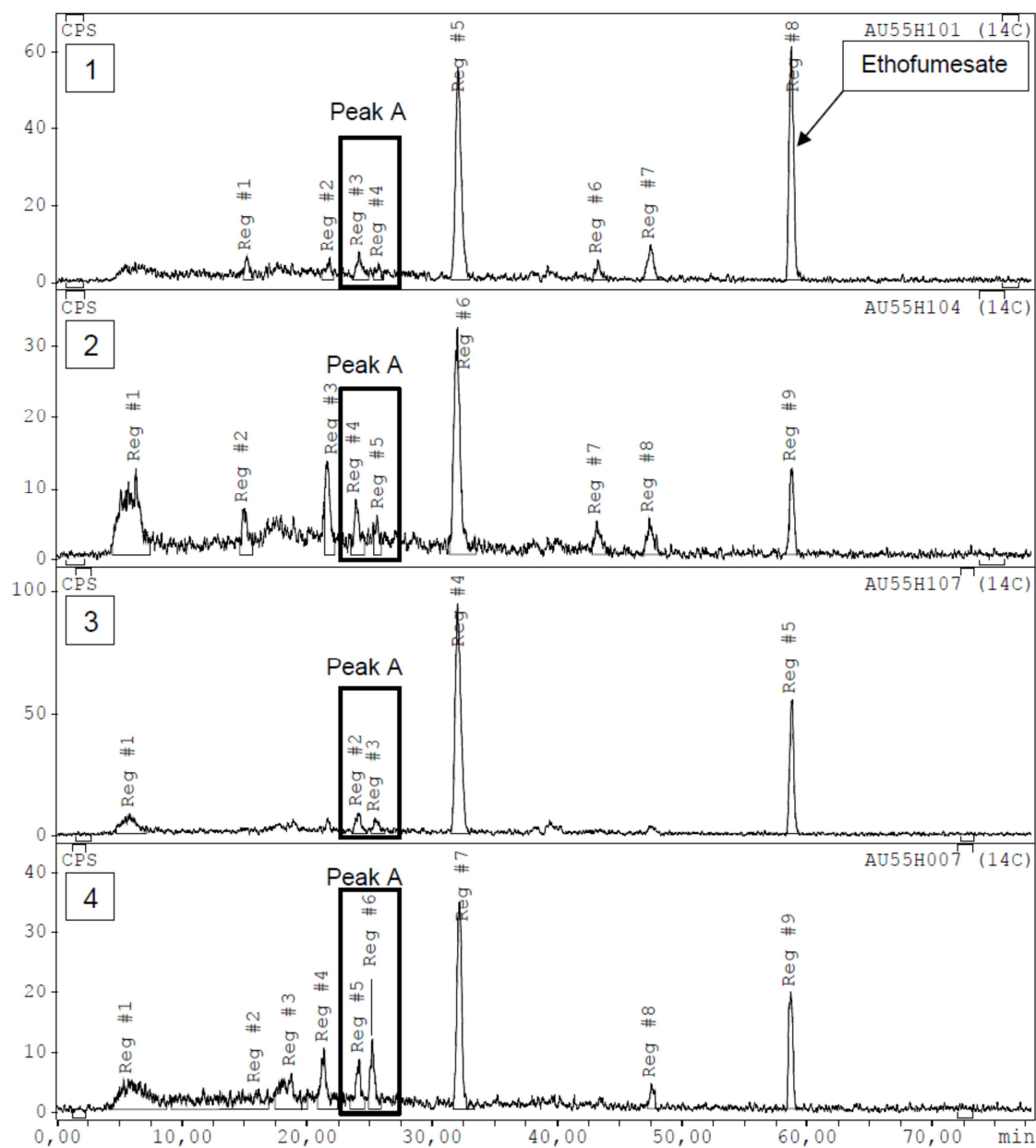


Figure 8-84: HPLC Chromatograms (Method 2, the same method as in the original study) of soil leachates of soil Laacher Hof WW

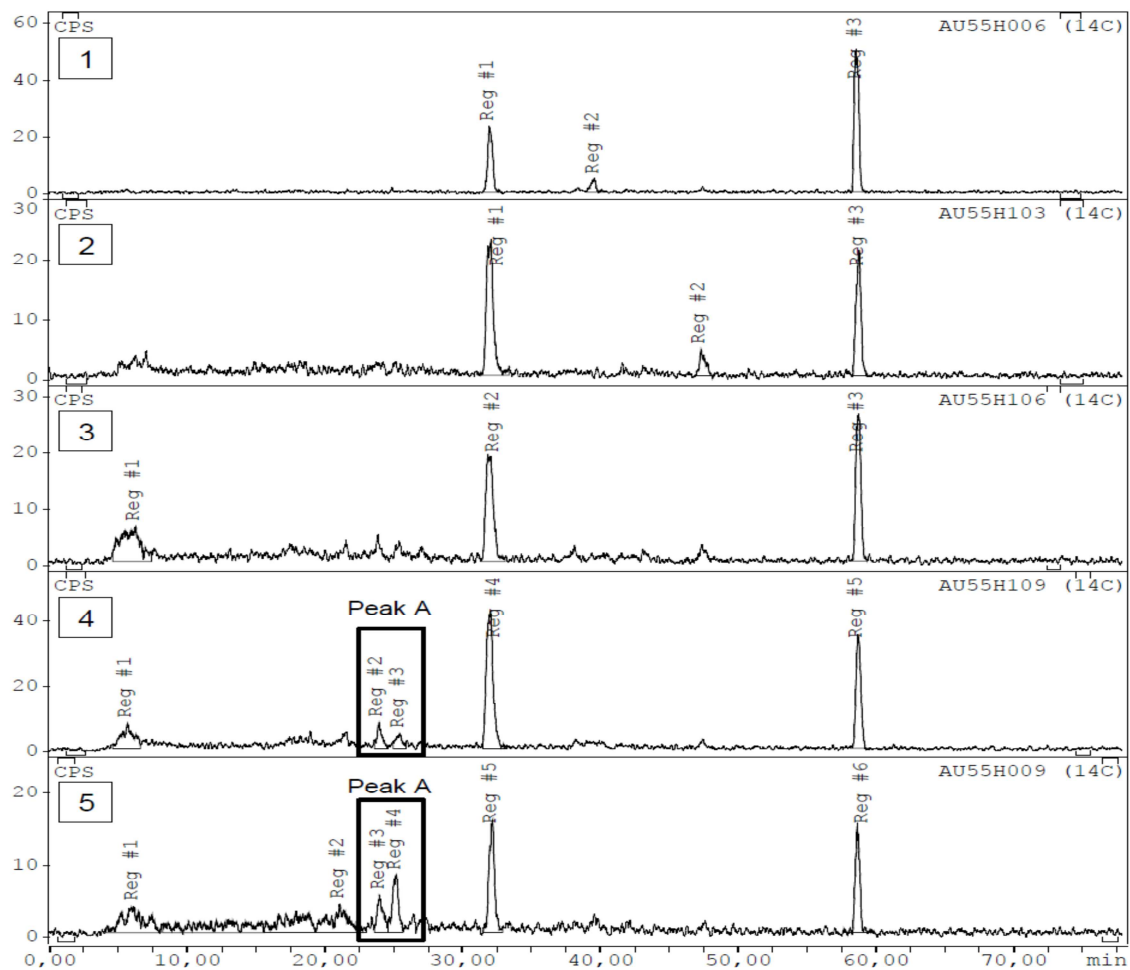


Figure 8-85: HPLC Chromatograms (Method 2, the same method as in the original study) of soil leachates of soil Laacher Hof HH

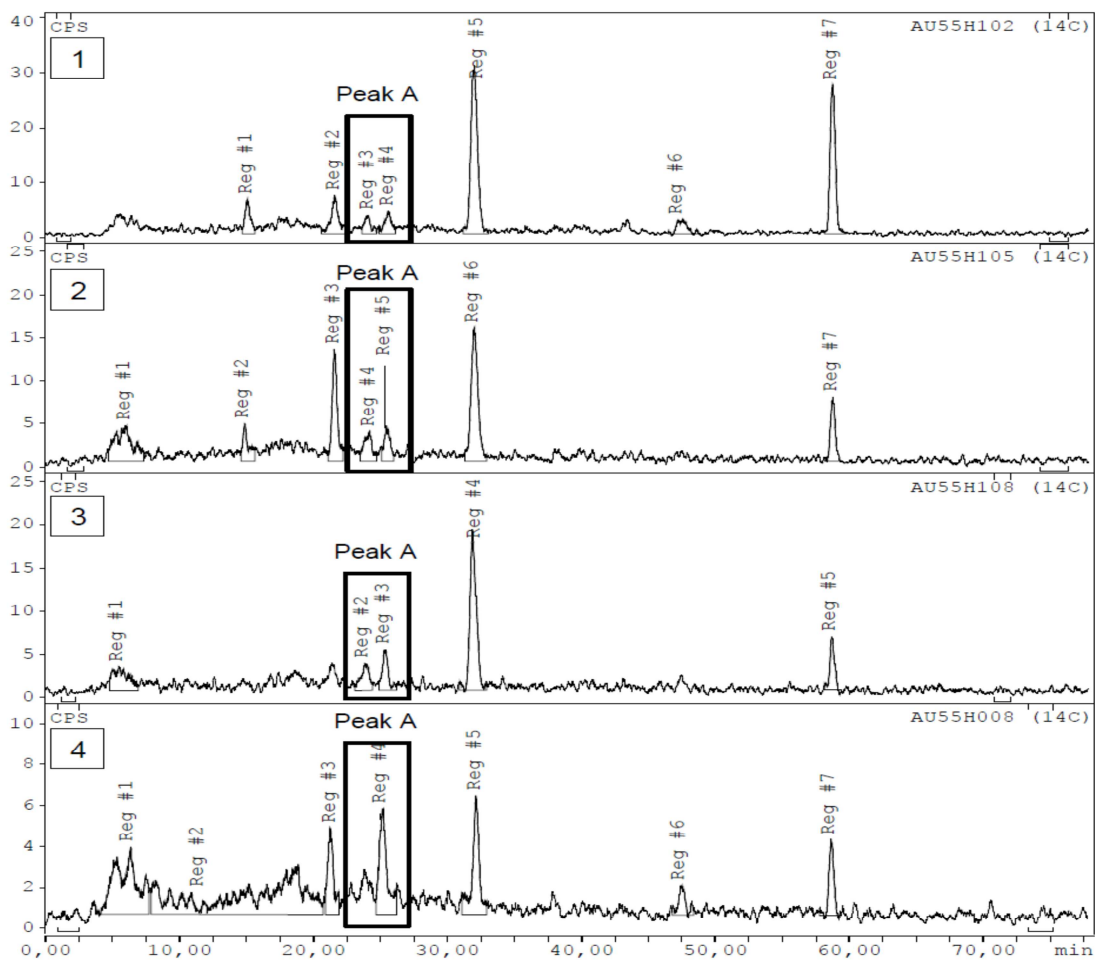


Figure 8-86: Spectra of P3 after isolation

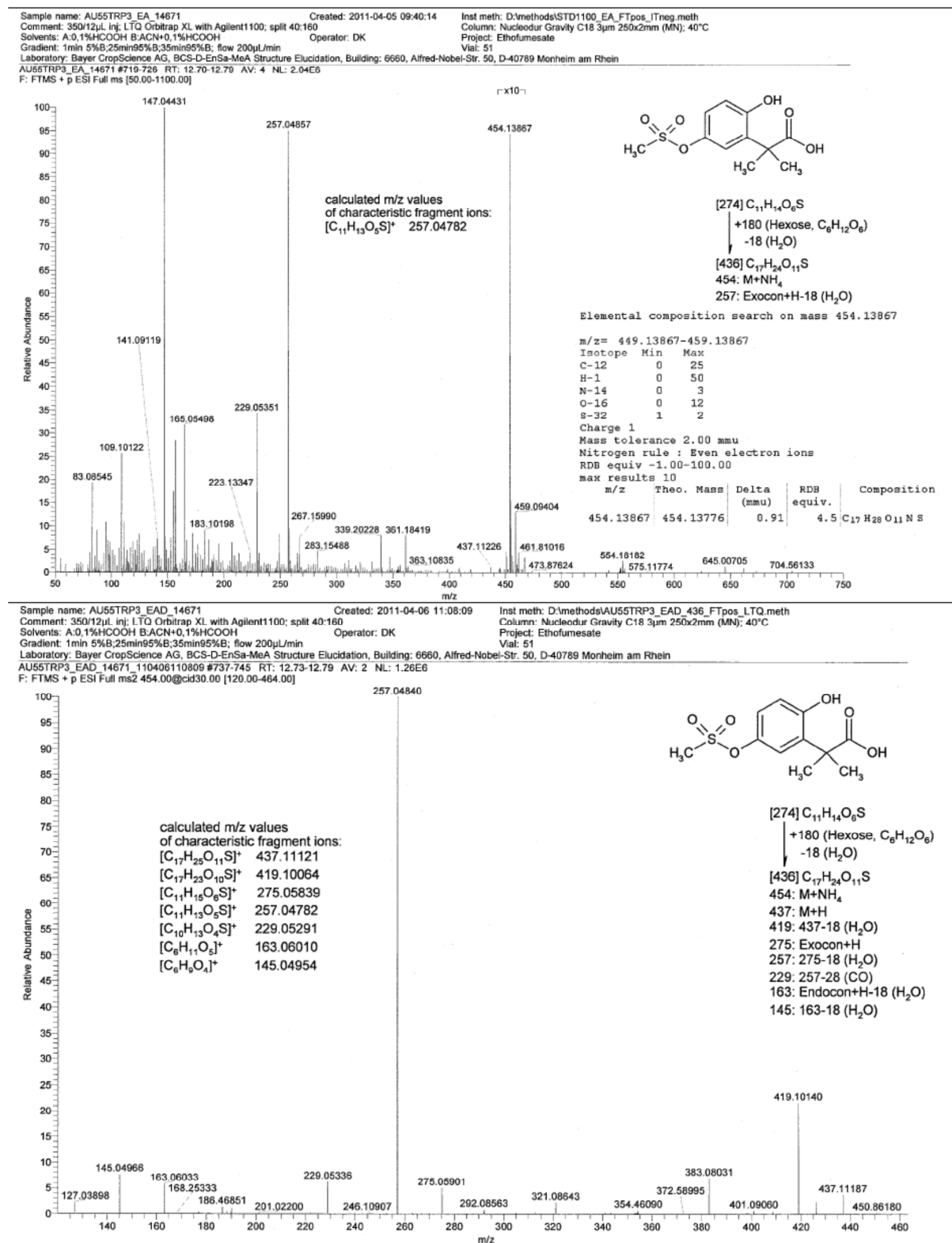
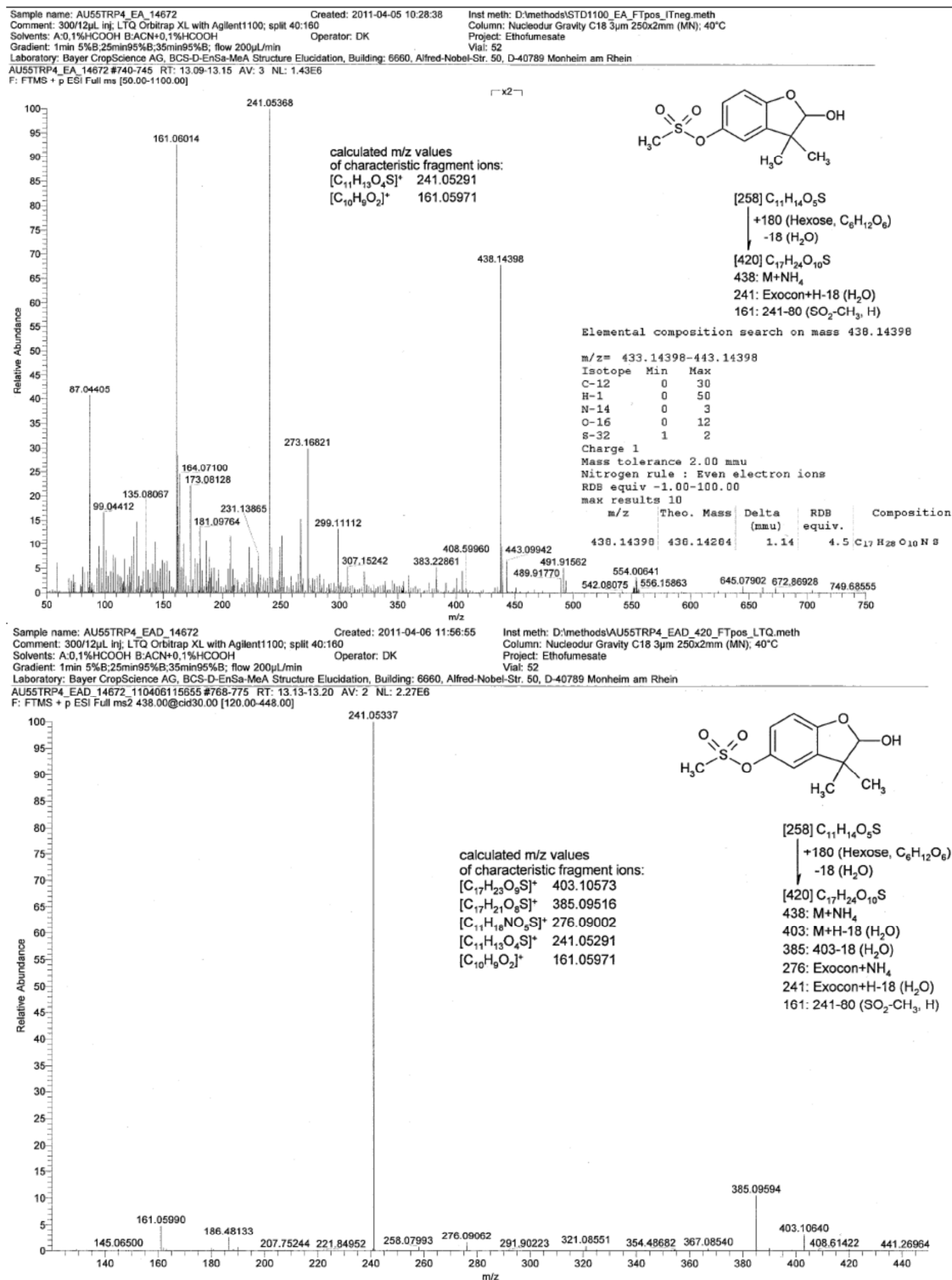


Figure 8-87 Spectra of P4 after isolation.



Enantioselective Degradation:

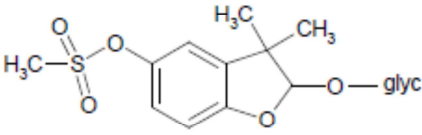
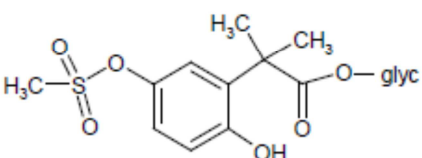
In order to evaluate the degradation of both enantiomers of ethofumesate, the enantiomers were separated by HPLC using a chiral column. The retention times of ethofumesate enantiomers in leachate were compared of with those of authentic reference substances. The analysis of the enantiomers in application solution and the isolated fraction from leachate day 36 of one soil (sample ID: AU55LEP2 (DAT-36)) showed the same ratio of 1 : 1 of each enantiomer in both samples. Therefore, degradation in soil and/or transport processes are considered as similar for both enantiomers.

Conclusion:

Due to the fast degradation of the soil metabolite NC 8493 (ethofumesate –2–hydroxy) in soil and the potential leaching behavior of NC 20645 (ethofumesate carboxylic acid) it is plausible that the relevant metabolite for leaching is NC 20645. This is also confirmed by findings of small amounts of NC 20645 as aglycon in the leachate of the previous lysimeter studies.

Comments RMS

The study provides valuable insights into the metabolite profiles of ethofumesate. The RMS agrees with the notifier that the previously detected Peak A can be attributed to glycosides of NC8493 and NC20645 (see table below).

| | |
|---|---|
| <p>Ethofumesate–2-hydroxy-glycoside</p>  <p>aglycon ethofumesate–2-hydroxy identified, hexose not specified</p> | <p>$C_{17}H_{24}O_{10}S$ 420.4 g/mol</p> |
| <p>Ethofumesate–carboxylic acid glycoside</p>  <p>aglycon ethofumesate–carboxylic acid identified, hexose not specified</p> | <p>$C_{17}H_{24}O_{11}S$ 436.4 g/mol</p> |

The aglycons of both NC8493 and NC20645 were considered in groundwater exposure assessment.

The study is acceptable.

The following two studies were evaluated together.

| | |
|---------------------|---|
| Reference: | ¹⁴C-Ethofumesate and 2-oxo-ethofumesate: Mobility and degradation in soil in field lysimeters. Final report |
| Notifier: | UPL/Agrichem |
| Author(s), year: | Parsons, R. (2003) |
| Report/Doc. number: | Study No. ACE01-012 |
| Guideline(s): | BBA-Guidelines IV, 4-3 OECD 22 |
| GLP: | Yes |
| Deviations: | |
| Validity: | Valid |
| Status: | New study |

| | |
|---------------------|---|
| Reference: | ¹⁴C-Ethofumesate and 2-oxo-ethofumesate: Mobility and degradation in soil in field lysimeters. Final analytical report. |
| Notifier: | UPL/Agrichem |
| Author(s), year: | Parsons, R. (2003) |
| Report/Doc. number: | Study No. ACE-01-012 (Final Analytical Report) |
| Guideline(s): | BBA-Guidelines IV, 4-3 OECD 22 |
| GLP: | Yes |
| Deviations: | |
| Validity: | Valid |
| Status: | New study |

I. MATERIALS AND METHODS

A. MATERIALS

- Test material:** ¹⁴C-Ethofumesate
Radiochemical purity: 99.3%
Specific radioactivity: 162.4 µCi/mg
Batch No.: 00BDR495/2/1
- Test material:** Ethofumesate

Batch No.: KJ 510

Purity: >99%

3. **Test material:** 2-oxo-ethofumesate

Batch No.: KJ 515

Purity: 95%

4. **Soils:** Undisturbed lysimeter cores were collected in Bedfordshire, UK in December 1996. Soil characteristics are presented in the table below.

Table 8-132: Soil physicochemical properties

| Horizon | AP | Bw/Cu | BC/Cu | Cu |
|-----------------------|------|-------|-------|--------|
| Depth [cm] | 0-40 | 40-62 | 62-97 | 97-120 |
| % Sand | 85.9 | 86.4 | 92.1 | 96.4 |
| % Silt | 7.3 | 7.3 | 3.5 | 0.9 |
| % Clay | 6.9 | 6.4 | 4.5 | 2.7 |
| % OC | 1.3 | 0.5 | 0.3 | 0.2 |
| pH (H ₂ O) | 6.1 | 6.2 | 6.3 | 6.5 |

B. STUDY DESIGN

1. Experimental conditions

Two lysimeters, each with a surface area of 0.5 m² and depth of 1.2 m, consisted of undisturbed soil cores enclosed in GRP (glass fibre) cylinders were placed in the ground in Essex, UK and their surfaces were levelled with the surrounding soil. The bottoms of the lysimeters were sealed into gravel filled with galvanised pans which were connected to the leachate collection containers in the pit by underground stainless steel pipes.

Between installation and the initiation of the study typical crops were grown in these lysimeters. Winter wheat was sown in early 2001 and was removed to plant sugar beet required for this work (sowed on 20th April 2001). Before sowing, the soil was forked over to 20 cm. The test and guard crops were netted. After harvest of sugar beet, winter wheat was sowed again on 6th November 2001 and 3rd October 2002.

Solid radiolabelled Ethofumesate was added to blank EC formulation, mixed and suspended in water to give a volume rate of 80 L/ha. Total application rate planned was 1000 g a.s./ha applied as three separate doses of 333 g/ha, using spraying device with moulded full cone nozzles. The applications were done on 15th May, 22nd May and 11th June 2001.

Total rainfall and irrigation for the first year was 806 mm and for the second year 867 mm.

2. Sampling

Sampling of leachate was done monthly or more frequently if necessary, if at least 2 litres had been accumulated in the lysimeters and were then transferred to the laboratory for analysis.

3. Description of analytical procedures

Radioactivity in solid samples was determined after combustion in oxygen using an automatic sample oxidiser. Radioactivity in liquid samples was quantified by LSC. Representative aliquots of leachate were tested for presence of ^{14}C -carbonate with barium chloride. Samples were chromatographed by TLC. The LOD for Ethofumesate and 2-oxo-ethofumesate was 0.006 – 0.017 $\mu\text{g/L}$. These values are derived by assuming 0.8% of the total radioactivity detected by TLC.

Representative leachate samples and also the first soil extracts were analysed by LC-MS/MS for the presence of Ethofumesate and 2-oxo-ethofumesate. The LOD for the procedure was 0.1 $\mu\text{g/L}$.

II. RESULTS AND DISCUSSION

A. MASS BALANCE

Over the whole period of the study the amount of leachate collected represented 16 and 19% of the rainfall and irrigation received by the two lysimeters.

Recovery volumes in the leachate were 0.40 and 0.53% AR for the two lysimeters, respectively.

Table 8-133: Recovery of applied radioactive material

| % AR recovered | Lysimeter A [%] | Lysimeter B [%] |
|-------------------|-----------------|-----------------|
| In leachate | 0.40 | 0.53 |
| In soil | 36.1 | 38.9 |
| In plant material | 1.28 | 1.70 |
| Total | 37.8 | 41.1 |

Table 8-134: Total quantity of the leachate obtained in the two lysimeters

| Leachate quantity | Lysimeter A | | Lysimeter B | |
|-------------------|-------------|--------|-------------|--------|
| | Year 1 | Year 2 | Year 1 | Year 2 |
| [kg] | 32.81 | 133.35 | 51.70 | 163.76 |
| [mm] | 65.62 | 266.70 | 103.40 | 327.52 |

B. FINDINGS

The mean radioactive content of the leachate over the two years of the study was 1.24 and 1.36 µg equivalents/L for the two lysimeters.

The concentration of Ethofumesate and 2-oxo-ethofumesate was equal and was < 0.006 and < 0.017 µg/L parent equivalent total radioactivity for both lysimeters.

Analysis of representative samples of leachate by MS/MS confirmed this observation with no Ethofumesate or 2-oxo-ethofumesate being detected (LOD 0.1 µg/L).

Representative aliquots of leachate were treated with barium chloride to test for the presence of carbonate in the leachate. No radioactivity was shown to be associated with carbonate in the leachate.

The three crops grown in each of the lysimeters, during the study, accounted for 1.28 and 1.70% AR, for lysimeter A and lysimeter B, respectively.

In the soil 36.1 and 38.9% AR was found at the end of the study and about 1.1% of it was extractable.

Table 8-135: Average concentrations in the leachate obtained in the two lysimeters

| Average concentration | Lysimeter A [µg/L parent equivalent total radioactivity] | Lysimeter B [µg/L parent equivalent total radioactivity] |
|--------------------------------|--|--|
| Test substance | | |
| During the first year | < 0.006 | < 0.011 |
| Over 2 years | < 0.011 | < 0.013 |
| 2-oxo-ethofumesate | | |
| During the first year | < 0.006 | < 0.011 |
| Over 2 years | < 0.011 | < 0.013 |
| Non-identifiable radioactivity | | |
| During the first year | 0.51 | 0.92 |
| Over 2 years | 1.24 | 1.36 |

Table 8-136: Non-identifiable radioactivity in each sample collected

NB. No ^{14}C -carbonate was found in the leachate

| Date | $\mu\text{g L}^{-1}$ parent equivalent total radioactivity | |
|--------------------------------|--|-------------|
| | Lysimeter A | Lysimeter B |
| 11 th June 2001 | 0.05 | 0.02 |
| 28 th June 2001 | 0.00 | 0.00 |
| 16 th July 2001 | 0.02 | 0.00 |
| 1 st August 2001 | | 0.00 |
| 19 th December 2001 | | 0.48 |
| 14 th January 2002 | 0.77* | 1.37* |
| 4 th February 2002 | 0.77 | 1.37 |
| 25 th February 2002 | 0.77 | 1.32 |
| 20 th March 2002 | 0.82 | 1.34 |
| 18 th April 2002 | 0.80 | 1.38 |
| 14 th May 2002 | 1.10 | 1.09 |
| 13 th June 2002 | 0.88 | 1.21 |
| 11 th October 2002 | | 2.53 |
| 11 th November 2002 | 1.53 | 2.00 |
| 5 th December 2002 | 1.46 | 1.17 |
| 9 th January 2003 | 1.83 | 1.04 |
| 16 th January 2003 | 1.26 | 1.36 |
| 10 th February 2003 | 1.48 | 1.69 |
| 10 th March 2003 | 1.44 | 2.09 |
| 7 th April 2003 | 1.30 | 2.14 |
| 20 th May 2003 | 1.26 | 1.80 |
| 11 th June 2003 | 1.30 | 1.86 |

* figures for missing samples derived from radioactive contents of higher of the previous or next sample

Table 8-137: Proportions of radioactive components in leachate from lysimeter A following application of [14C]-ethofumesate

| Date | Component/ca Rf | | | | | | | | | | | |
|----------|-----------------|-------|---------------|--------|---------------|--------|--------------------------|--------|---------------------|--------|---------|-------|
| | Peak 1 (origin) | | Peak 2 (0.10) | | Peak 3 (0.24) | | 2-oxoethofumesate (0.50) | | Ethofumesate (0.57) | | Others* | |
| | % C | µg/L | % C | µg/L | % C | µg/L | % C | µg/L | % C | µg/L | % C | µg/L |
| 04/02/02 | 92.9 | 0.743 | <0.8 | <0.006 | <0.8 | <0.006 | <0.8 | <0.006 | <0.8 | <0.006 | 7.1 | 0.057 |
| 25/02/02 | 89.9 | 0.719 | <0.8 | <0.006 | 2.0 | 0.016 | <0.8 | <0.006 | <0.8 | <0.006 | 8.1 | 0.065 |
| 20/03/02 | 94.8 | 0.758 | 2.3 | 0.018 | 1.5 | 0.012 | <0.8 | <0.006 | <0.8 | <0.006 | 1.4 | 0.011 |
| 18/04/02 | 90.7 | 0.726 | <0.8 | <0.006 | <0.8 | <0.006 | <0.8 | <0.006 | <0.8 | <0.006 | 9.3 | 0.074 |
| 14/05/02 | 94.9 | 1.044 | <0.8 | <0.009 | <0.8 | <0.009 | <0.8 | <0.009 | <0.8 | <0.009 | 5.5 | 0.061 |
| 13/06/02 | 92.7 | 0.834 | <0.8 | <0.007 | <0.8 | <0.007 | <0.8 | <0.007 | <0.8 | <0.007 | 7.3 | 0.066 |
| 11/11/02 | 67.9 | 1.019 | 2.4 | 0.036 | 1.8 | 0.027 | <0.8 | <0.012 | <0.8 | <0.012 | 27.9 | 0.419 |
| 05/12/02 | 92.9 | 1.394 | 2.0 | 0.030 | <0.8 | <0.012 | <0.8 | <0.012 | <0.8 | <0.012 | 5.1 | 0.077 |
| 09/01/03 | 92.2 | 1.660 | 2.8 | 0.050 | <0.8 | <0.014 | <0.8 | <0.014 | <0.8 | <0.014 | 5.0 | 0.090 |
| 16/01/03 | 95.2 | 1.238 | <0.8 | <0.010 | 0.8 | 0.010 | <0.8 | <0.010 | <0.8 | <0.010 | 4.0 | 0.052 |
| 10/02/03 | 98.3 | 1.475 | <0.8 | <0.012 | <0.8 | <0.012 | <0.8 | <0.012 | <0.8 | <0.012 | 1.7 | 0.026 |
| 10/03/03 | 95.0 | 1.330 | <0.8 | <0.011 | 1.5 | 0.021 | <0.8 | <0.011 | <0.8 | <0.011 | 3.5 | 0.049 |
| 07/04/03 | 99.1 | 1.288 | <0.8 | <0.010 | <0.8 | <0.010 | <0.8 | <0.010 | <0.8 | <0.010 | 0.9 | 0.012 |
| 20/05/03 | 97.7 | 1.270 | <0.8 | <0.010 | <0.8 | <0.010 | <0.8 | <0.010 | <0.8 | <0.010 | 2.3 | 0.030 |

Results expressed as µg/L

Components separated by normal phase TLC (Toluene : ethyl acetate: acetic acid; 80:15:5, v/v)

* Others represents regions of radioactivity which cannot be assigned to a designated peak

% C %

chromatogram

LOD taken as below the level at which the lowest reported value (Peak 3, 16/01/03, Lysimeter A) is observed.

Table 8-138: Proportions of radioactive components in leachate from lysimeter A following application of [14C]-ethofumesate

| Date | Component/ca Rf | | | | | | | | | | | |
|----------|-----------------|-------|---------------|--------|---------------|--------|--------------------------|--------|---------------------|--------|---------|-------|
| | Peak 1 (origin) | | Peak 2 (0.10) | | Peak 3 (0.24) | | 2-oxoethofumesate (0.50) | | Ethofumesate (0.57) | | Others* | |
| | % C | µg/L | % C | µg/L | % C | µg/L | % C | µg/L | % C | µg/L | % C | µg/L |
| 04/02/02 | 87.8 | 1.229 | <0.8 | <0.011 | <0.8 | <0.011 | <0.8 | <0.011 | <0.8 | <0.011 | 12.2 | 0.171 |
| 18/04/02 | 95.0 | 1.330 | <0.8 | <0.011 | <0.8 | <0.011 | <0.8 | <0.011 | <0.8 | <0.011 | 5.0 | 0.070 |
| 14/05/02 | 84.5 | 0.930 | <0.8 | <0.011 | <0.8 | <0.011 | <0.8 | <0.011 | <0.8 | <0.011 | 15.5 | 0.171 |
| 13/06/02 | 81.4 | 0.977 | <0.8 | <0.011 | <0.8 | <0.011 | <0.8 | <0.011 | <0.8 | <0.011 | 18.6 | 0.223 |
| 11/11/02 | 64.6 | 1.292 | <0.8 | <0.016 | 3.0 | 0.060 | <0.8 | <0.016 | <0.8 | <0.016 | 32.4 | 0.648 |
| 05/12/02 | 87.4 | 1.049 | 3.2 | 0.038 | <0.8 | <0.010 | <0.8 | <0.010 | <0.8 | <0.010 | 9.4 | 0.113 |
| 09/01/03 | 89.9 | 0.899 | 4.2 | 0.042 | <0.8 | <0.008 | <0.8 | <0.008 | <0.8 | <0.008 | 5.9 | 0.059 |
| 16/01/03 | 63.8 | 0.893 | 3.7 | 0.052 | <0.8 | <0.011 | <0.8 | <0.011 | <0.8 | <0.011 | 32.5 | 0.455 |
| 10/03/03 | 90.4 | 1.898 | 1.7 | 0.036 | <0.8 | <0.017 | <0.8 | <0.017 | <0.8 | <0.017 | 7.9 | 0.166 |
| 07/04/03 | 73.9 | 1.552 | <0.8 | <0.017 | 1.9 | 0.040 | <0.8 | <0.017 | <0.8 | <0.017 | 24.2 | 0.508 |
| 20/05/03 | 85.3 | 1.535 | <0.8 | <0.014 | 4.2 | 0.076 | <0.8 | <0.014 | <0.8 | <0.014 | 10.5 | 0.189 |

Results expressed as µg/L

Components separated by normal phase TLC (Toluene : ethyl acetate: acetic acid; 80:15:5, v/v)

* Others represents regions of radioactivity which cannot be assigned to a designated peak

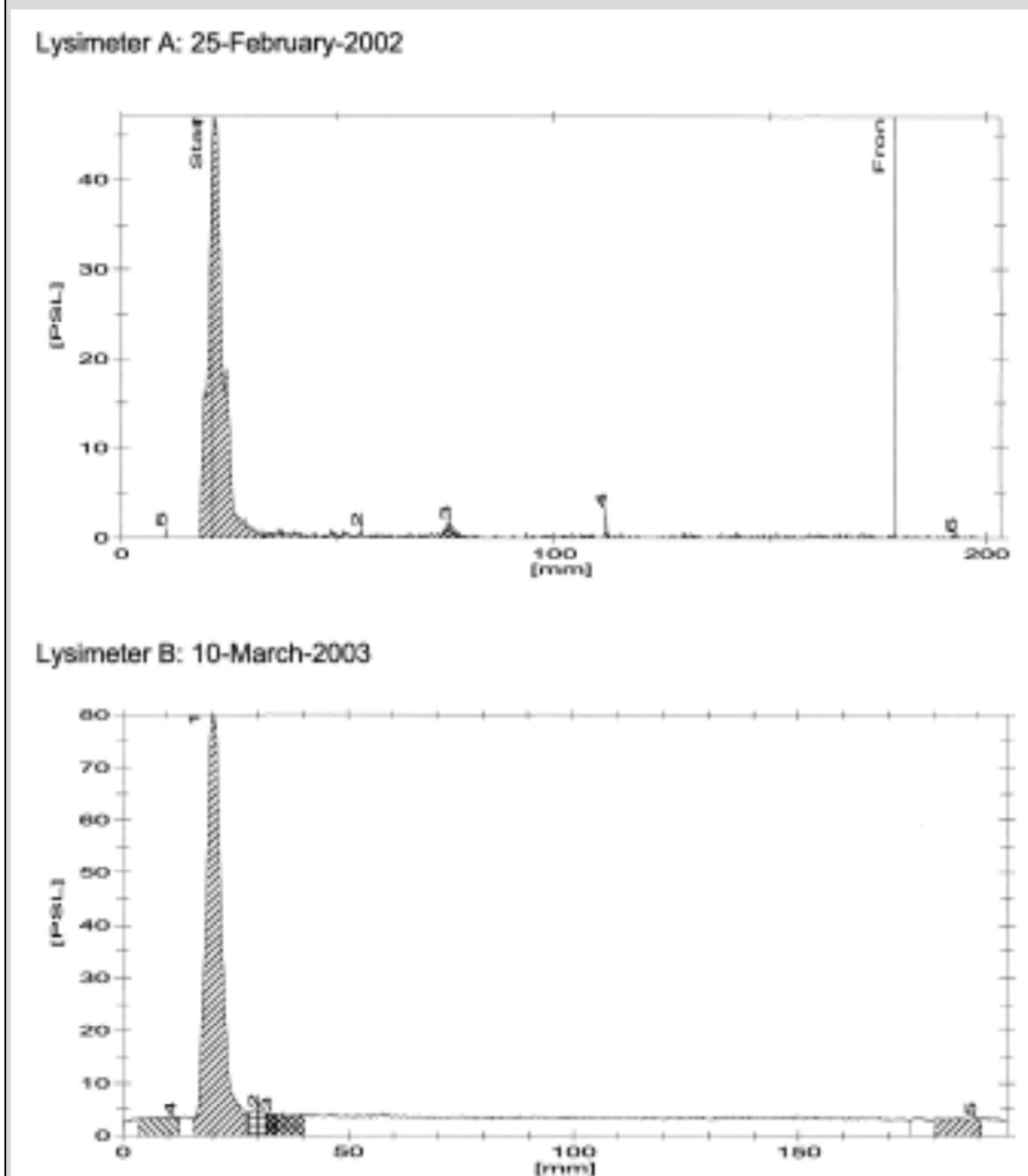
III. CONCLUSIONS

Certain amount of radio-labelled material was found in leachates and soil during the study. However, this was evidently neither Ethofumesate nor its major metabolite, 2-oxo-ethofumesate. The results indicated that neither Ethofumesate nor 2-oxo-ethofumesate exhibits appreciable soil mobility.

Comments RMS

The study was well conducted and reported. Ethofumesate and NC9607 (2-oxo-ethofumesate) were not detected in any of the samples (LOD 0.006 - 0.017 µg/L). The radioactivity in leachates was predominantly associated with polar radioactivity, generally 90% sample radioactivity (range 63.8 - 98.3% sample radioactivity, 0.9 - 1.5 µg/L) at the origin. The RMS agrees with this interpretation (see figure below). This radioactivity was not further resolved.

Figure 8-88: Representative 2D-radiochromatogram showing leachate from lysimeters treated with [¹⁴C]-ethofumesate



| | |
|---------------------|---|
| Reference: | Ethofumesate: Mobility and degradation in soil in outdoor lysimeters |
| Notifier: | UPL/Agrichem |
| Author(s), year: | Diehl, M. (2005) |
| Report/Doc. number: | RCC Study No. 836695 |
| Guideline(s): | BBA Guideline, Part IV, 4 –3 OECD Draft Guideline, March 1998 Dutch Guideline, Section G; Appendix G.1.3.a; July 1992 |
| GLP: | Yes |
| Deviations: | |
| Validity: | Valid |
| Status: | New study |

I. MATERIALS AND METHODS

A. MATERIALS

1. **Test material:** Ethofumesate technical
 - Lot No.:** EFS-117 (RCC No.: 125208/A)
 - Purity:** 98.95%
 - CAS No.:** 26225-79-6

2. **Test material:** ¹⁴C-Ethofumesate
 - Batch No.:** CFQ12729 (RCC No.: 125325/A)
 - Radiochemical purity:** >98.6%
 - Specific radioactivity:** 3.621 MBq/mg

3. **Formulation:** Ethofumesate 200 g/L EC
 - Lot No.:** 028091 (RCC No.: 118719/C)

4. **Reference Item:** 2-ketoethofumesate (RCC Code R1)
 - Batch No.:** EPP AJR KET04 (RCC No.: 125208/C)
 - Purity:** >98%

- 5. Soils:** The undisturbed soil monoliths were excavated near Neustadt, Germany. The soil sampled was a sandy soil with low organic carbon content. The soil has not been exposed to any pesticide treatment for at least five years before sampling. The physical and chemical soil properties are given in the table below.

Table 8-139: Soil characterization

| Parameter | Horizon | Horizon | Horizon | Horizon |
|---|------------|----------|----------|-----------|
| | 0-30 cm | 30-60 cm | 60-90 cm | 90-120 cm |
| Soil type (USDA) | loamy sand | sand | sand | sand |
| pH [KCl] | 5.60 | 5.36 | 4.95 | 5.09 |
| CaCO ₃ [%] | 1.40 | 1.50 | 1.60 | 1.80 |
| Organic carbon [%] | 1.77 | 0.30 | 0.08 | 0.00 |
| Cation exchange capacity [meq/100 g dry soil] | 7.12 | 3.16 | 0.93 | 0.68 |
| Particle size [µm] | | | | |
| <0.002 clay [%] | 6.47 | 3.67 | 0.93 | 0.71 |
| 0.002-0.0 silt [%] | 12.65 | 6.17 | 0.40 | 0.22 |
| >0.05 sand [%] | 80.88 | 90.16 | 98.67 | 99.07 |
| | | | | |
| MWHC [g/100 g dry soil] | 30.94 | 25.19 | 23.89 | 25.24 |

B. STUDY DESIGN

1. Experimental conditions

Two lysimeters containing sandy soil monoliths of low organic carbon content (depth 120 cm, surface area 1.0 m²) surrounded by a small field plot of about 2.2 by 4 meters were chosen in order to simulate actual field conditions as closely as possible. The control lysimeter was used to measure the background radioactivity level in the leachates and also for soil temperature determination.

Fertilisation, seed-bed preparation and sowing were carried out at times normal for sugar beet and were in accordance with good agricultural practice. Shortly before sowing of sugar beet, the topsoil of lysimeters and the surrounding plot was weeded manually. The topsoil was then ploughed using a spade to a depth of about 10 cm and finally prepared for sowing using a hoe. Before sowing of sugar beet the base fertiliser together with potassium- and N-fertilisation were applied.

Pest control measures were not required to ensure normal growth of the plants.

Control plants (sugar beet) were grown in the surrounding area and were identical to those in the lysimeters and handled in the same way.

Three treatments were carried out in the two lysimeters at the growth stages BBCH 10, 12 and 15-16, respectively, at application rate at about 200 g a.s./ha for the first application and at about 400 g a.s./ha for the last two applications. The application was carried out using a gas (N₂) driven spraying device with a commercial full-nozzle to simulate normal agricultural practice. The soil area covered by weeds was assumed to be about 1%.

After each application, the lysimeters were covered for one day to avoid any outside contamination.

The natural precipitation amounted to 1081.0 and 770.5 mm for the first and second year, respectively. Additional irrigation was performed in order to assure proper plant growth and in case of the second year to reach an annual precipitation rate of 800 mm.

2. Sampling

The leachate samples were collected every week when a sufficient amount of water was available.

3. Description of analytical procedures

The total radioactivity in the leachate was determined by LSC. Lyophilisation was carried out on aliquots of 1000 mL of leachate exceeding a concentration of 0.05 µg parent equivalents/L, after carbon dioxide stripping. The radioactivity in the sample was measured by LSC. After Lyophilisation the solutions were subjected to ultrafiltration to exclude a molecular weight of 500 and radioactivity was re-determined by LSC. The filtrated water phases were concentrated and were submitted to TLC analysis.

An aliquot of up to 400 µL of the concentrated sample was mixed with selected reference items dissolved in methanol or acetone and analysed by TLC and/or HPLC.

Limit of detection (LOD) and limit of quantification (LOQ) was set to be 0.04 µg/L and 0.06 µg/L, respectively.

II. RESULTS AND DISCUSSION

A. MASS BALANCE

The radioactivity recovered in the pooled organic phases amounted to 107% and 105% of the initial radioactivity.

B. FINDINGS

The leachate collected during the first experimental year contained 0.63 and 0.79% AR in lysimeter I and II, respectively. For the second experimental year the leachate collected contained 0.49 and 0.42% AR in lysimeter I and II, respectively.

After 737 days, the overall average concentration of parent equivalents in the leachate was 1.16 µg/L (lysimeter I) and 1.22 µg/L (lysimeter II). Maximal concentrations observed during the study amounted to 2.04 µg/L and 2.29 µg/L for lysimeter I and II, respectively.

TLC analysis of the leachates after ultrafiltration indicated the presence of 12 to 14 radioactive fractions (M1-M14). During the first experimental year, the average concentration of radioactive fractions M1-M14 ranged between 0.003 µg and 0.046 µg parent equivalents/L, for both lysimeters. During the second experimental year, the average concentration of radioactive fractions M1-M12 ranged for both lysimeters between 0.011 µg and 0.094 µg/L.

Table 8-140: Summary of the leached radioactivity for both lysimeters

| Year | Lysimeter I | | | | Lysimeter II | | | |
|----------|------------------|--------------------------------|-----------|-------------------------------|------------------|--------------------------------|-----------|-------------------------------|
| | Volume collected | Leachate total radioactivity * | | ¹⁴ CO ₂ | Volume collected | Leachate total radioactivity * | | ¹⁴ CO ₂ |
| | [L] | [%] | [µg/L] ** | [%] | [L] | [%] | [µg/L] ** | [%] |
| 1 | 633.2 | 0.63 | 1.06 | 0.039 | 672.2 | 0.79 | 1.26 | 0.050 |
| 2 | 398.3 | 0.49 | 1.32 | 0.013 | 392.1 | 0.42 | 1.14 | 0.004 |
| Year 1-2 | 1031.5 | 1.12 | 1.16 | 0.052 | 1064.3 | 1.21 | 1.22 | 0.055 |

* includes volatiles

** as parent equivalents

Analysis of the leachate showed that a major part of the radioactivity is bound to the water dissolved organic matter of the soil. The other part (= leachate after the ultrafiltration) contained at least 14 radioactive fractions and none of each exceeded the yearly mean concentration of 0.1 parent equivalents µg/L. Neither Ethofumesate nor metabolite ketoethofumesate were detected.

Table 8-141: Yearly average values of the radioactive fractions detected in the leachate pools after ultrafiltration

| Pattern Ethofumesate | Yearly average concentrations (µg parent equivalents/L) | | | |
|-------------------------|---|--------|--------------|--------|
| | Lysimeter I | | Lysimeter II | |
| | Year 1 | Year 2 | Year 1 | Year 2 |
| M1 | 0.014 | 0.028 | 0.014 | 0.021 |
| M2 | 0.016 | 0.028 | 0.011 | 0.022 |
| M3 | 0.017 | 0.021 | 0.050 | 0.094 |
| M4 | 0.015 | 0.021 | 0.014 | 0.022 |
| M5 | 0.010 | 0.016 | 0.015 | 0.023 |
| M6 | 0.015 | 0.018 | 0.026 | 0.031 |
| M7 | 0.015 | 0.046 | 0.047 | 0.059 |
| M8 | 0.015 | 0.015 | 0.017 | 0.032 |
| M9 | 0.015 | 0.041 | 0.020 | 0.039 |
| M10 | 0.011 | 0.018 | 0.020 | 0.029 |
| M11 | 0.023 | 0.035 | 0.021 | 0.024 |
| M12 | 0.037 | 0.025 | 0.019 | 0.032 |
| M13 | 0.009 | 0.006 | ** | ** |
| M14 | 0.003 | ** | ** | ** |
| Total | 0.215 | 0.317 | 0.274 | 0.427 |

** not detected

The major part of radioactivity remaining in soil at the end of the experimental period was located in the upper-most layer amounting to 23.8 and 19.8% AR in lysimeters I and II, respectively. The majority of the residues in the layers was shown to be bound residues (at least 85% of the radioactivity in the layer).

Uptake of radioactivity by plants during the whole experimental period was very low not exceeding an amount of 0.35% AR.

III. CONCLUSIONS

The results of this lysimeter study showed that neither Ethofumesate nor its degradation products will be of potential risk for contamination of groundwater. Mineralisation to carbon dioxide and complete incorporation into the soil organic matter will be the main route of disappearance of Ethofumesate from the soil.

Comments RMS

The study is acceptable. Neither Ethofumesate nor its degradation products were detected at concentrations above 0.1 µg/L. Mineralisation to carbon dioxide and complete incorporation into the soil organic matter are thought to be the main route of disappearance of Ethofumesate from the soil.

B.8.1.3.3. Summary: mobility in soil

Due to several experimental deficiencies, only one column study could be regarded as valid. In this study, aged ethofumesate residue (corresponding to a field rate of 7.25 kg/ha) was leached with a solution simulating approximately 500mm of artificial rain. Over the study, 2.7% AR mainly consisting of ethofumesate and NC20645 were found in the leachate.

In the course of the first approval of ethofumesate, 5 lysimeter studies covering a period of two or three years with either one or two applications of ethofumesate were evaluated. Spring application rates of 1.25 and 1.5 kg/ha were studied in lysimeters planted with sugar or fodder beet followed by wheat. Mean annual precipitation ranged between 857 and 820 mm/year. Ethofumesate was not detected in the leachate of any of the lysimeter and at termination of the studies the majority of the radioactivity remained in the top 30 cm of the soil layers. Concentrations below 0.1 µg/L of NC9607 were observed in some leachates. The majority of the radioactivity in the leachate was attributed to ethofumesate derived fragments metabolized by soil micro-organisms and subsequently incorporated into soil organic matter. However, in one study an individual peak ("Peak A") was identified. The highest maximum concentration was 0.5 µg/L (annual mean, calculated as a.s. equivalent). It was not evaluated whether this peak consisted of one or more components. In a targeted study, the notifier Taskforce could identify the structure of both metabolites potentially representing Peak A as glycoside conjugates of the respective soil metabolites NC 8493 and NC 20645. Two new lysimeter studies were submitted by the notifier UPL. In the first study, Ethofumesate and its degradation products did not exceed 0.1 µg/L in the leachate. In this two year study, unidentified polar material – attributable neither to ethofumesate nor to NC9607 - ranged between 0.7 and 1.89 µg/L parent equivalents. Similar results were obtained in the second lysimeter study, where the concentration in the leachate was similar and the majority of Ethofumesate was incorporated into large organic structures. Furthermore, up to 14 unknown fractions were detected in this two year study and none exceeded 0.1 µg/L (annual average concentrations). Therefore, it can be assumed that also in the first the unidentified polar material belongs to a larger number of fractions.

Groundwater exposure assessments were carried out using FOCUS (FOCUS, 2009) scenarios and the models PEARL 4.4.4 for the active substance ethofumesate and its metabolites NC8493 (soil photolysis, aglycon of lysimeter metabolite) and NC20645 (aglycon of lysimeter metabolite). The potential for groundwater exposure from the representative uses by these compounds above the parametric drinking water limit of 0.1 µg/L was concluded to be low in geoclimatic situations that are represented by all 9 FOCUS groundwater scenarios. The leaching simulations resulted in PEC_{GW} values below 0.1 µg L⁻¹ for ethofumesate and its metabolites NC8493 and NC20645 for all intended uses and all relevant FOCUS scenarios using FOCUS PEARL 4.4.4.

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.8.2.2. Hydrolytic degradation

| | |
|---------------------|--|
| Reference: | THE HYDROLYSIS OF ETHOFUMESATE UNDER ACIDIC, NEUTRAL AND BASIC CONDITIONS |
| Notifier: | Taskforce |
| Author(s), year: | Brown, P. M.; Reary, J. B.; Whiteoak, R. J.;1978 |
| Report/Doc. number: | A83306 / W 51 / M-155575-01-1 |
| Guideline(s): | US EPA Working Group Draft 4/22/77 |
| GLP: | No |
| Deviations: | |
| Validity: | Not valid. |
| Status: | Previous evaluation in DAR for original approval / baseline dossier. |

Study summary based on previous draft assessment report

Materials and Method

Hydrolysis was studied using [benzene ring- ^{14}C] ethofumesate (NC 8438). The purity was not specified. The method used followed the US EPA Working Group draft guidelines of 1977. Results from an earlier study carried out at 20°C at pH 5, 7 and 9 indicated a hydrolytic stability of the substance. The main test was carried out at 25 and 35°C at pH values of approximately 5 (phthalate), pH 7 (phosphate) and pH 9 (borate). The buffer solutions were equilibrated at the appropriate temperature for at least 18 hours before adding the test substance. [^{14}C]-ethofumesate was dissolved in methanol. The final test solutions, 10 and 100 ppm ethofumesate, were prepared in duplicate 50 and 25 mL volumetric flasks, respectively, by dilution in one step with each of the three buffer solutions. The final pH was 5.0, 7.0 and 9.2. The test solutions were kept in the dark at 25±1°C and 35±1°C. After 0, 3, 7, 14, 21 and 36 days, aliquots of 100 µL were removed for analysis and analysed by HPLC/UV-detector for the qualitative determination and by LSC detector for quantification.

Results

Hydrolysis was negligible at pH 7.0 and 9.2. At pH 5.0, radioactivity was detected in two fractions from the HPLC column, of which one was ethofumesate. In an early fraction, radioactivity was identified as the metabolite NC 8493, a dealkylated product of ethofumesate. After 36 days of incubation at 25°C, 98 and 97% of the applied ethofumesate remained in the 100 and 10 ppm samples, respectively, and, NC 8493 was present as 1.4 and 1.6% of the radioactivity, respectively. This indicates that also at pH 5.0 hydrolysis is negligible.

Comments RMS

The study shows that ethofumesate is not expected to hydrolyse at pH 7 to 9 and hydrolysis at pH 5 is very slow. Only one metabolite was detected, NC 8493, which indicates a hydroxylation of the parent compound. However, there is no information whether or not aseptic conditions were kept throughout the study.

The study is considered not valid.

| | |
|---------------------|--|
| Reference: | Ethofumesate Determination of the Physico-Chemical Properties of Ethofumesate |
| Notifier: | UPL/Agrichem |
| Author(s), year: | Macdonald E., Craig, W.B.; 2002 |
| Report/Doc. number: | Report No. 21131 |
| Guideline(s): | OECD 111 |
| GLP: | yes |
| Deviations: | |
| Validity: | Valid |
| Status: | New study |
| Justification: | Since the summary of the hydrolysis study included in the Monograph is insufficiently detailed to fully determine its acceptability, an existing study conducted according to the OECD Guideline 111 is submitted to cover this point and is summarised below. |

I. MATERIALS AND METHODS**A. MATERIALS**

1. Test Material: Ethofumesate

Batch No.: EFS-116

Purity: 99%

CAS No.: 26225-79-6

2. Buffers: 0.1 buffer solutions in Milli-RO water were prepared at pH 4 using mono-potassium citrate and sodium hydroxide, pH 7 using mono-potassium phosphate and sodium hydroxide, pH 9 using boric acid, potassium chloride and sodium hydroxide.

B. STUDY DESIGN**1. Experimental conditions**

The hydrolysis of Ethofumesate was studied at pH 4, pH 7 and pH 9 buffers at $50^{\circ}\text{C} \pm 0.5^{\circ}\text{C}$ for 5 days. The buffers were autoclaved prior to use. Ethofumesate (ca 100 mg) was weighted into a 10 mL volumetric flask and adjusted to volume with methanol. 0.5 mL of Ethofumesate was then transferred to 100 mL amber volumetric flasks and made to volume with buffer. Samples were prepared in triplicate at each pH and were taken for analysis at 0 h, 2.4 h, 24 h and 5 days.

II. RESULTS AND DISCUSSION

A. MASS BALANCE

At each sampling point (2.4 h, 24 h, and 5 days) the recovery levels for each media did not vary by more than $\pm 10\%$ from the recovery value obtained at t_0 .

B. FINDINGS

Ethofumesate was found to be hydrolytically stable at pH 4, 7 and 9 over a period of 5 days.

Table 8-142: Hydrolysis of Ethofumesate at pH 4, 7 and 9

| Sample No. | Concentration | | % Recovery from | | | | | |
|----------------------------|----------------------|-------|-----------------|-------|-----------|-------|---------------------|-------|
| | [$\mu\text{g/mL}$] | | $T_{2.4h}$ | | T_{24h} | | $T_{5 \text{ day}}$ | |
| | Nominal | T_0 | Nominal | T_0 | Nominal | T_0 | Nominal | T_0 |
| pH 4-1 pH 4-2 pH 4-3 | 49.75 | 47.82 | 96.8 | 100.7 | 94.9 | 98.7 | 91.0 | 94.7 |
| pH 7-1 pH 7-2 pH 7-3 | 49.75 | 49.64 | 99.1 | 99.3 | 99.7 | 99.9 | 107.4 | 107.6 |
| pH 9-1 pH 9-2 pH 9-3 | 49.75 | 49.55 | 98.6 | 99.0 | 99.3 | 99.7 | 106.8 | 107.3 |

III. CONCLUSION

In the aqueous hydrolysis study Ethofumesate was found to be hydrolytically stable at pH 4, 7 and 9 over a period of 5 days.

Comments RMS

The study is conducted according to OECD 111 and shows that ethofumesate is hydrolytically stable at pH 4, 7 and 9 over a period of 5 days.

B.8.2.2.1. Direct photochemical degradation

| | |
|---------------------|--|
| Reference: | THE PHOTOLYSIS OF ETHOFUMESATE (SCHERING CODE NO. ZK 49913) IN AQUEOUS SOLUTION |
| Notifier: | Taskforce |
| Author(s), year: | Brehm, M.;1989 |
| Report/Doc. number: | A83339 / W 81 / M-155608-01-1 |
| Guideline(s): | USEPA Subdivision N - Chemistry: Environmental Fate, NTIS PB83-153973 |
| GLP: | yes |
| Deviations: | |
| Validity: | Not valid |
| Status: | Previous evaluation in DAR for original approval / baseline dossier. |

Study summary based on previous draft assessment report

Materials and Methods

Aqueous photolysis of [benzene ring- ^{14}C] ethofumesate was studied in a solution containing ≈ 50 and 10 mg as/l. Acetonitrile, 1%, was used as organic co-solvent. The solution was buffered (double distilled water) and held at pH of 7.0. The solutions were irradiated using a “merry go round” photoreactor and with filtered light from a Hg-arc lamp, resulting in wavelengths >290 nm. The light intensity, measured by chemical actinometry, was in the wavelength range of 290-320 nm. The intensity was increased by a factor of about 3-5 compared to natural light in summer, 40°N, midday and at cloudless sky. A mixture of [^{14}C]-ethofumesate, with a radiochemical purity of 98%, and unlabelled ethofumesate, with a chemical purity of 99.9% W/W, was used. Nine samples of 50 mg as/l, two samples of 10 mg as/L and one sample of double distilled water were continuously irradiated in quartz cuvettes for 71 hours. Test solutions and double distilled water were kept in the dark for 71 hours. The temperature in the irradiated solutions were kept at $27.8 \pm 0.8^\circ\text{C}$ and in the dark samples at $26.5 \pm 1.6^\circ\text{C}$. Aliquots of 200 μL were withdrawn after 2.0, 4.0, 8.0, 23, 30, 50 and 71 hours from the irradiated cuvettes and after 0.0, 30 and 71 hours from the cuvettes kept in the dark. The samples were analysed by HPLC/UV (230 nm) to determine the rate of reaction.

Additionally, for the determination of material balance analysis was carried out by HPLC coupled with a flow through radioactivity detector. The aim was to determine the rate of photolysis and the quantum yield of ethofumesate. The calculated quantum yield was further used to calculate environmental aqueous half-life with the computer program GCSOLAR.

Results

Transformation was only observed in the irradiated samples, which indicates that ethofumesate was transformed by photolysis. The half-lives were calculated according to first order reaction:

$$50 \text{ ppm:l} \quad t_{1/2} = 31 \text{ h}$$

$$10 \text{ ppm:} \quad t_{1/2} = 28 \text{ h}$$

These half-lives correspond to a continuous irradiation coupled with a 3-5 fold intensity compared to natural sunlight (290-320 nm). Considering this, half-life was calculated by the investigator to be 8-13 days under natural conditions.

The results from the material balance showed one main peak in the analysis by HPLC. The recovery of radioactivity was about 100% after 30 hours of irradiation. Thereafter, the recovery decreased to 93% at the end of the test. The decrease was accounted to result from secondary reactions, but was not possible to explain. Standards of four possible metabolites, NC 8493, NC 9607, NC 10458 and NC 1790 were used to identify the peak detected in the HPLC chromatogram, but it was not identical to any of these. The radioactive peak early in the HPLC chromatogram, which amounted to $\approx 41\%$ of the applied activity after 71 hours of illumination, was not identified. It was concluded that the peak probably contained non-specific polar products. No other products were detected.

The quantum yield, Φ , was calculated from the rate of initial transformation of ethofumesate under well defined irradiation conditions and the UV-spectrum of the substance.

$$\Phi = 9.54 \cdot 10^{-2}$$

Table 8-143: GCSOLAR estimated environmental half-lives of ethofumesate in days

| Latitude | 20°N | 40°N | 60°N |
|----------|------|------|------|
| Season | days | days | days |
| spring | 41 | 60 | 120 |
| summer | 37 | 43 | 62 |
| fall | 53 | 111 | 560 |

Comments RMS

The study was conducted in agreement to US EPA Guideline, Subdivision N, § 161-2 (1982) and was well performed and reported. The estimated range of environmental aqueous photolysis half-lives of ethofumesate in

Europe (40-60°N) under summer conditions are approximately 37-62 days according to the used computer program GCSOLAR. In this study, 41% of the radioactivity remain unidentified, the study is not valid.

| | |
|---------------------|--|
| Reference: | DETERMINATION OF THE DIRECT PHOTOTRANSFORMATION OF 14C-ETHOFUMESATE IN A BUFFERED MEDIUM AT PH4 |
| Notifier: | Taskforce |
| Author(s), year: | Knoch, E.; 1994 |
| Report/Doc. number: | A87609 / W 509-1 / M-161541-01-1 |
| Guideline(s): | BBA: IV, 6-1; OECD |
| GLP: | yes |
| Deviations: | |
| Validity: | Not valid |
| Status: | Previous evaluation in DAR for original approval / baseline dossier. |

Study summary based on previous draft assessment report

Materials and Methods

A photolysis test was performed on a buffered solution (pH 4 solution) of approximately 7.0 and 7.6 mg ethofumesate/L with acetone (1% concentration) as a co-solvent. For the irradiation a Heraeus Suntest CPS accelerated exposure machine with 1.8 kW Xenon burner and 290 nm UV-filter was used (max. irradiance 765 W/m²). The system was equipped with a thermostated sample tablet to achieve a constant temperature of 20 °C ± 2 °C for the samples during irradiation.

Comments RMS

As highlighted during the previous evaluation, acetone is not suitable as a co-solvent as it acts as a photosensitiser and may, therefore, strongly influence the photolytic half-life of the compound. The results from these measurements are not used for further assessment.

| | |
|---------------------|---|
| Reference: | TECHNICAL ETHOFUMESATE: DETERMINATION OF PHYSICO-CHEMICAL PROPERTIES |
| Notifier: | Taskforce |
| Author(s), year: | Howarth, R.; Tremain, S. P.; Bartlett, A. J.; 1991 |
| Report/Doc. number: | A87526 / C 500-1 / M-161417-01-1 |
| Guideline(s): | For the hydrolysis part OECD 111 For the photostability study: EPA, Pesticide assessment Guidelines, Subdivision N, Chemistry: Environmental fate For the auto-flammability study: The Official Journal of the European Communities, L251, Vol 27, 19 September 1984. |
| GLP: | yes |
| Deviations: | |
| Validity: | Valid |
| Status: | Previous evaluation in DAR for original approval / baseline dossier. |

Study summary based on previous draft assessment report

Materials and Methods

A hydrolysis test was carried out in accordance with OECD 111 with ethofumesate technical (purity > 98% w/w).

Result:

Ethofumesate is stable to hydrolysis at pH 4, 7 and 9 at 50°C during a test period of 5 days.

Comments RMS

The study shows that ethofumesate is hydrolytically stable.

The photodegradation part of the study is superseded by new aqueous photolysis studies by both notifiers.

| | |
|---------------------|--|
| Reference: | Aqueous photolysis (14C)-ethofumesate |
| Notifier: | Taskforce |
| Author(s), year: | Keirs, D. C.; 2000 |
| Report/Doc. number: | C009667 / M-199018-01-1 |
| Guideline(s): | SETAC: Proc. Env. Fate & Ecotox. (1995) |
| GLP: | yes |
| Deviations: | |
| Validity: | Valid (quantum yield determination part) |
| Status: | Previous evaluation in DAR for original approval / baseline dossier. |

Study summary based on previous draft assessment report

Materials and methods

An aqueous photolysis study in accordance with the SETAC guideline (1995) was conducted with [Benzene ring- 14]-ethofumesate (specific activity and radiochemical activity were $214 \mu\text{Ci}\cdot\text{mg}^{-1}$ and 98%, respectively, and ethofumesate chemical purity was 99.9% w/w). The study was conducted with a p-nitroacetophenone/pyridine actinometer.

Results

A quantum yield of 1.92×10^{-4} molecules degraded per photon absorbed was determined.

Comments RMS:

Study is of acceptable quality and the quantum yield value (1.92×10^{-4} molecules degraded/photon absorbed) can be used for further calculations. The photodegradation part of the study is superseded by two new studies provided by the notifiers as it was characterized by unknown radioactivity of up to 18% in the irradiated samples.

| | |
|---------------------|--|
| Reference: | PR94/023 - Ethofumesate - Direct phototransformation in water |
| Notifier: | Taskforce |
| Author(s), year: | Schneider, E.;1994 |
| Report/Doc. number: | M-468470-01-1 |
| Guideline(s): | OECD 316 – Draft (1980) |
| GLP: | yes |
| Deviations: | |
| Validity: | Not valid |
| Status: | Previous evaluation in DAR for original approval / baseline dossier. |

Study summary based on previous draft assessment report

Materials and Methods

A direct photolysis study was carried out on ethofumesate, chemical purity 99.4%, according to a draft OECD guideline (1990), prepared by Umweltbundesamt Berlin, FRG. The test was carried out in a "merry go round" - photolysis apparatus, using 1 cm quartz cuvettes. A mercury arc lamp (Philips MSR 575) producing a polychromatic light was used. The light intensities in the region 290 to 380 nm was judged by the investigators to be comparable with the energy distribution of sunlight. The test was carried out on an ethofumesate solution containing 50.1 mg as/L (1% methanol). Seven cuvettes were prepared, of which six were irradiated and one was kept as a control in the dark. Samples were taken after 0, 2 h, 3 h, 4 h, 5 h 45 min (2 samples) and 7 h 30 min. The control was stored for 7 h 30 min. After 7 h 30 min 81% of the applied ethofumesate remained in the irradiated sample and 99% remained in the control. An actinometer test was performed using a potassium ferrioxylate actinometer to determine the number of photons generated by seconds by the photolysis system.

Results

The photolysis rate of ethofumesate was $1.17\text{E-}09 \text{ mol/(l} \cdot \text{sec)}$. The mean photolysis half-life of ethofumesate was determined to 4.6 days on a whole year basis according to Frank/Klöpfer. The photolytic half-life for the month May was calculated to be 2.6 days. Quantum yield was calculated using the photolysis rate and total absorbed light intensity at the wavelengths 290-300 nm ($2.60^{12} \text{ P/(cm}^3 \cdot \text{s)}$). The calculated value of the quantum yield, Φ , was 0.270.

Comments RMS

Both notifiers argued that the quality of the study is not sufficient and that a new study - which would also target degradation products of ethofumesate – would supersede this study. We accept this position, especially because no degradation products were identified in this study. For instance, in the last sample (after 7.5 hours) 81.4% of the applied radioactivity were identified as ethofumesate, the rest was not addressed.

| | |
|---------------------|---|
| Reference: | [Phenyl-UL-14C]Ethofumesate: Phototransformation in water |
| Notifier: | Taskforce |
| Author(s), year: | Weuthen, M.; Stupp, H. P.; 2013 |
| Report/Doc. number: | EnSa-12-0228 / M-453458-01-1 |
| Guideline(s): | OECD 316 US EPA OCSP Test Guideline No. 835.2240 Japanese MAFF New Test Guidelines Annex No. 2-6-2; |
| GLP: | yes |
| Deviations: | |
| Validity: | Valid |
| Status: | New study |

MATERIALS AND METHODS

Materials :

Test Material : [Phenyl-UL-¹⁴C]Ethofumesate

Specific activity: 3.78 MBq/mg

Test system :

Sterile phosphate buffer solution (pH 7), 10 mM

Methods :

Study design :

The photochemical reaction was studied in aqueous solution. Samples were continuously exposed to a xenon lamp with < 290 nm cut-off filter (Suntest equipment) for 10 days equivalent to e.g. 34 days under environmental conditions (Phoenix, Arizona, USA). For comparison, control samples were incubated in the dark. The individual test vessels for irradiated and dark samples contained 10 mL of test solution. The irradiated vessels were individually connected to traps for the collection of CO₂ and organic volatiles while the dark control samples were closed with glass stoppers.

Experimental Conditions :

The photochemical reaction was studied in a sterile phosphate buffer solution (pH 7) at 25 ± 2 °C and an initial nominal concentration of 1 mg/L. Samples were continuously exposed to a xenon lamp with < 290 nm cut-off filter (Suntest equipment) for 10 days equivalent to e.g. 34 days under environmental conditions (Phoenix, Arizona, USA). For comparison, control samples were incubated in the dark.

Sampling :

Test solutions were analyzed 0, 1, 2, 3, 7, 9 and 10 days after application

Analytical Procedures :

Test solutions were analyzed in duplicate 0, 1, 2, 3, 7, 9 and 10 days after application by LSC and reversed phase HPLC with radio-detection to determine the degradation of [phenyl-UL-¹⁴C]Ethofumesate as well as the formation and decline of transformation products. Representative samples were additionally analyzed and the result was confirmed with a second separation method (HPLC). The test item in the stock solution was identified by spectroscopic methods.

RESULT AND DISCUSSION

Mass balance and distribution of radioactivity:

Table 8-144: Distribution of residues in % of AR in irradiated samples

| Compound | Environment ¹⁾ Experiment | Sampling Times [days] | | | | | | |
|--------------------------------|---|-----------------------|------|-------|-------|------|-------|-------|
| | | 0 | 3 | 7 | 10 | 24 | 31 | 34 |
| Ethofumesate | Mean | 100.0 | 96.1 | 95.9 | 88.5 | 73.5 | 68.8 | 64.2 |
| A | Mean | n.d. | 0.4 | 0.9 | 1.4 | 2.9 | 3.9 | 4.3 |
| B | Mean | n.d. | 0.3 | n.d. | n.d. | n.d. | n.d. | n.d. |
| C | Mean | n.d. | 0.3 | 0.5 | 0.9 | n.d. | 1.2 | n.d. |
| D | Mean | n.d. | 2.7 | 4.1 | 5.2 | 4.9 | 4.7 | 4.2 |
| E | Mean | n.d. | n.d. | 0.5 | 1.3 | 2.7 | 3.9 | 4.5 |
| F | Mean | n.d. | n.d. | 0.5 | 1.1 | 1.4 | 2.5 | 2.8 |
| G | Mean | n.d. | n.d. | 0.3 | 0.9 | 1.5 | 2.2 | 2.6 |
| H | Mean | n.d. | n.d. | 0.3 | 0.4 | n.d. | 0.9 | n.d. |
| I | Mean | n.d. | n.d. | n.d. | n.d. | 3.6 | 3.5 | 5.9 |
| J | Mean | n.d. | n.d. | n.d. | n.d. | 1.7 | 2.3 | 2.7 |
| K | Mean | n.d. | n.d. | n.d. | n.d. | 1.0 | 1.1 | 1.2 |
| L | Mean | n.d. | n.d. | n.d. | n.d. | 0.9 | 0.9 | 2.0 |
| M | Mean | n.d. | n.d. | n.d. | n.d. | 1.0 | 0.8 | 2.2 |
| N | Mean | n.d. | n.d. | n.d. | n.d. | 0.9 | 0.8 | n.d. |
| O | Mean | n.d. | n.d. | n.d. | n.d. | n.d. | 0.6 | 1.4 |
| P | Mean | n.d. | n.d. | n.d. | n.d. | n.d. | 0.7 | n.d. |
| Q | Mean | n.d. | n.d. | n.d. | n.d. | n.d. | 0.6 | n.d. |
| R | Mean | n.d. | n.d. | n.d. | n.d. | n.d. | 0.6 | n.d. |
| Total ²⁾ | Mean | 100.0 | 99.3 | 102.7 | 99.5 | 95.5 | 96.3 | 94.6 |
| ¹⁴ CO ₂ | Mean | n.a. | 0.2 | 0.2 | 0.7 | 3.3 | 3.8 | 5.4 |
| Volatile organics | Mean | n.a. | 0.0 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 |
| Total recovery % ²⁾ | Mean | 100.0 | 99.6 | 103.0 | 100.2 | 98.9 | 100.2 | 100.2 |

n.d.: not detected

¹⁾ Irradiation equivalent to environmental conditions in Phoenix, Arizona, USA

²⁾ Values were taken from Material Balance

Table 8-145: Distribution of residues in % of AR in non-irradiated samples

| Compound | Experiment | Sampling Times [days] | | | | | | |
|------------------|------------|-----------------------|------|-------|-------|-------|------|-------|
| | | 0 | 1 | 2 | 3 | 7 | 9 | 10 |
| Ethofumesate | Mean | 100.0 | 99.5 | 103.5 | 100.5 | 100.1 | 99.6 | 100.0 |
| Total recovery % | Mean | 100.0 | 99.5 | 103.5 | 100.5 | 100.1 | 99.6 | 100.0 |

Non-extractable and Extractable Residues :

The test was performed in aqueous solution. All residues were extractable.

Mineralization:

Mineralization was at maximum 5.4% of applied radioactivity in the irradiated samples. The mineralization was not determined in dark samples.

Transformation of Test material and Transformation Products :

In the test solutions of the irradiated test systems, the amounts of [phenyl-UL-¹⁴C] Ethofumesate declined from 100.0% at time zero to 64.2% of AR after 10 days of continuous irradiation. No degradation was detected under dark conditions.

Under irradiated conditions a multitude of transformation products was detected in the test solutions and all of them were characterized according to their retention times. The maximum amount of a single transformation product was 5.9% of AR (I, DAT-10). Due to the low amounts of each single transformation product, identification procedures for transformation products were not performed.

Table 8-146: Result synopsis

| | |
|---|---|
| Test medium | Sterile aqueous buffer solution at pH 7 |
| Source of irradiation | Xenon lamp with cut-off filter < 290 nm |
| Experimental DT ₅₀ / DT ₉₀ [days] in Suntest® | 15.6 / 51.8 |
| Environmental DT ₅₀ [days]: Phoenix, Arizona, USA | 53.2 |
| Environmental DT ₅₀ [days]: Tokyo, Japan | 112.9 |
| Dark control DT ₅₀ / DT ₉₀ [days] | 718.9 / 2388.2 |
| Net Experimental DT ₅₀ [days] ¹⁾ | 16.0 |
| Transformation products | |
| - Exposure to light | a) Numerous minor transformation products in solution (Maximum of a single product: 5.9% of AR, DAT-10) b) Max. 5.4% of CO ₂ , DAT-10 |
| - Dark | None |

¹⁾ Calculated from net rate constant (rate constant of irradiated samples – rate constant of dark samples)

Conclusion :

A multitude of minor metabolites are formed under irradiated conditions.

Comments RMS

The study shows that phototransformation of [phenyl-UL-¹⁴C]Ethofumesate in water systems is a relevant process. A multitude of minor metabolites are formed under irradiated conditions. Among these metabolites, compound I occurs at >5% AR at study end.

The study is acceptable.

The relevant endpoints are:

Experimental DT50 15.6 d

Environmental DT50 53.2 d (Phoenix, Arizona, USA)

| | |
|---------------------|---|
| Reference: | Ethofumesate: Assessment of the environmental half-life of the direct photo-degradation in water |
| Notifier: | Taskforce |
| Author(s), year: | Hellpointner, E.; 2013 |
| Report/Doc. number: | EnSa-13-0355 / M-461408-01-1 |
| Guideline(s): | COMMISSION REGULATION (EU) No 283/2013: Data requirements for active substances, in accordance with Regulation (EC) No 1107/2009 of the European Parliament OECD Test Guideline 101, 1981 OECD Test Guideline 316, 2008 |
| GLP: | yes |
| Deviations: | |
| Validity: | Valid |
| Status: | New study |

MATERIALS AND METHODS

Materials :

Test Material : ethofumesate

Certificate No. : AZ 16166

Test system :

The test substance was dissolved in pure water (22.3 mg/L)

Methods :

The UV-VIS absorption properties of ethofumesate were characterized by the extinction in steps of 1 nm from 200 – 800 nm.

The environmental half live was calculated using two different models :

The arithmetic model developed by Zepp and Cline allows for a transfer of laboratory data concerning the direct photo-transformation in water to field conditions. The model estimates on the basis of a clear summer sky with no influence of clouds. The half-lives calculated therefore may be regarded as minimum half-lives depending on frequency and extent of cover of sky by clouds.

In contrast to the model approach by Zepp and Cline, the arithmetic model developed by Frank and Kloeppfer considers the influence of clouded sky for the region Central Europe, i.e. Germany.

RESULT AND DISCUSSION

The absorption spectrum of ethofumesate in pure water shows two absorption maxima at 225 nm ($\epsilon = 6527 \text{ L mol}^{-1} \text{ cm}^{-1}$) and at 278 nm ($\epsilon = 2427 \text{ L mol}^{-1} \text{ cm}^{-1}$).

No absorption was measured from 306 to 800 nm. Therefore, the overlap with the environmentally relevant range of wavelength is weak, and significant light absorption ends at 306 nm with $\epsilon < 10 \text{ L mol}^{-1} \text{ cm}^{-1}$, already. The molar extinction coefficient (ϵ) at 295 nm is $144 \text{ L mol}^{-1} \text{ cm}^{-1}$. Since the old cut-off wavelength for the tiered evaluation of photo-transformation in the EU was 290 nm, this value with $\epsilon = 744 \text{ L mol}^{-1} \text{ cm}^{-1}$ was calculated.

Based on the known quantum yield of $\Phi = 0.0001$ and the molar extinction coefficients determined for the wavelengths of 297.5 to 305 nm, environmental half-lives were calculated:

Table 8-147: Environmental half-lives calculated according to Zepp & Cline

| Season | Environmental DT ₅₀ of Direct Photo-Transformation of Ethofumesate in Pure Water | | | |
|--------|---|------------------------------|------------------------------|------------------------------|
| | 30 th degree lat. | 40 th degree lat. | 50 th degree lat. | 60 th degree lat. |
| Spring | > 1 year | > 1 year | > 1 year | > 1 year |
| Summer | > 1 year | > 1 year | > 1 year | > 1 year |
| Fall | > 1 year | > 1 year | > 1 year | > 1 year |
| Winter | > 1 year | > 1 year | > 1 year | > 1 year |

Marginal conditions: pure surface water at 0-5 cm depth, 10th degree longitude, clear sky, typical ozone concentrations in the atmosphere, half-lives integrated over the entire day.

The column of the 50th degree of latitude is more or less relevant to the conditions of Central Europe.

Table 8-148: Environmental half-lives calculated according to Frank & Kloeppfer

| Month | Photolysis Constant [1/sec] | Environmental DT ₅₀ of Direct Photo-Transformation of Ethofumesate in Pure Water | | |
|-------|--------------------------------|---|----------|----------|
| | | Minimum | Mean | Maximum |
| April | 0.922×10^{-11} | > 1 year | > 1 year | > 1 year |

| | | | | |
|-----------|-------------------------|----------|----------|----------|
| May | 0.183×10^{-10} | > 1 year | > 1 year | > 1 year |
| June | 0.272×10^{-10} | > 1 year | > 1 year | > 1 year |
| July | 0.280×10^{-10} | > 1 year | > 1 year | > 1 year |
| August | 0.243×10^{-10} | > 1 year | > 1 year | > 1 year |
| September | 0.936×10^{-11} | > 1 year | > 1 year | > 1 year |
| October | 0.247×10^{-11} | > 1 year | > 1 year | > 1 year |

(50th degree lat.), no contribution of another mono- or bimolecular elimination process.

Minimum = clear sky

Maximum = clouded sky

Conclusion:

From this investigation it is evident that direct photo-transformation of ethofumesate in water does not contribute significantly to the elimination of this compound from the environment.

Comments RMS

The study shows that the environmental half-life relevant to Central Europe is above 1 year and that therefore photochemical degradation of ethofumesate might play a minor role under such conditions. The study is valid.

| | |
|---------------------|---|
| Reference: | Photodegradation of [14C]Ethofumesate in Water, Based on the OECD 316 Direct Photolysis Guideline Tier II – Generation and Characterization of Photoproducts |
| Notifier: | UPL |
| Author(s), year: | Peizhi, L.; 2013 |
| Report/Doc. number: | 13485.6132 |
| Guideline(s): | OECD 316 |
| GLP: | yes |
| Deviations: | |
| Validity: | Valid |
| Status: | New study |

I. MATERIALS AND METHODS

A. MATERIALS

- Test Material:** $[^{14}\text{C}$ U-ring]Ethofumesate
Lot No.: 11BLY014
Radiochemical Purity: > 98%
Specific activity: 55 mCi/mmol (426,476 dpm/μg)
- Test material (reference):** Ethofumesate

| | |
|---------------------|-----------------------|
| Synonym: | PESTANAL [®] |
| Batch No.: | SZE6128X |
| CAS No.: | 26225-79-6 |
| Purity: | 99.5% |
| Expiry Date: | 8 May 2013 |

- 2. Test material (reference):** NC8493 (a metabolite of Ethofumesate)

| | |
|-----------------------|--|
| Chemical Name: | 2,3-dihydro-2-hydroxy-3,3-dimethyl benzofuran-5-yl methanesulphonate |
| Batch No.: | EEP/VMV 358A |
| CAS No.: | 26322-82-7 |
| Purity: | 99.8% |
| Expiry Date: | 11 May 2012 |

B. STUDY DESIGN

1. Experimental conditions

Test samples were prepared by placing 5.0 mL of sterile purified reagent water in each of the ten 7-mL quartz photolysis tubes for each test substance. A 28-μL aliquot of the secondary radiolabelled stock solution was added to each tube and tube was closed with a sterile cap. Light samples were continuously irradiated under the Suntest sunlight simulator with a xenon arc lamp, which had been filtered to remove wavelengths less than 290 nm. Samples were irradiated continuously for up to 2 days at $25 \pm 1^\circ\text{C}$ and analysed at 0 hours and after 2, 4, 8 and 12 hours of irradiation. Additional samples were taken after 1 and 2 days of irradiation.

The Ethofumesate test solution was scanned from 250 to 800 nm in order to determine absorbance at appropriate wavelength intervals to calculate the direct photolysis rate constant.

2. Description of analytical procedures

At selected time intervals, samples were analysed directly by LSC and by HPLC/RAM to determine the recovery and distribution of radioactivity in the solution.

II. RESULTS AND DISCUSSION

A. MASS BALANCE

Recoveries of applied radioactivity ranged from 92.78% to 99.30%. Negligible quantities of volatile organic compounds were detected.

B. FINDINGS

The average amount of [^{14}C]Ethofumesate declined in sterile water irradiated samples from 97.25% AR at 0 hours to 41.27% AR after 12 hours of irradiation. Ethofumesate was photodegraded to numerous photoproducts and one significant photoproduct was detected, Degradate 1 (13.5 minutes), first detected at 2 hours at an average of 1% AR and increased to a maximum of 9.57% AR at 12 hours. Several minor regions of radioactivity were observed and were less than 5% AR and therefore not considered further. The HPLC fractionation and further analysis of Degradate 1 by TLC showed that it contains at least six components. The proposed molecular structure for the major component of this mixture was 2,3,5-trihydroxy-4-(1-hydroxyethyl)-hexanedioic acid.

Table 8-149: Distribution of radioactivity in the irradiated sterile water samples treated with (^{14}C)ethofumesate as percent of applied radioactivity and as concentration

| Time (hours) | (^{14}C)Ethofumesate ~ 18.3-min % AR | Deg-1 ~13.5-min % AR | Deg-2 ~15.2-min % AR | Deg-3 ~ 16.9-min % AR | Others in AQ (% AR) | Total (% AR) | Total Conc. ($\mu\text{g/mL}$) |
|--------------|---|----------------------------|----------------------------|-----------------------------|------------------------|-----------------|-------------------------------------|
| | | | | | | | |
| 0 | 96.98 | ND | 1 | ND | 0.78 | 98.76 | 10.2 |
| 0 | 94.53 | ND | 0.73 | ND | 1.04 | 99.3 | 10.26 |
| Average | 97.25 | ND | 0.87 | ND | 0.91 | 99.03 | 10.23 |
| 2 | 83.68 | 1.06 | 1.89 | 4.63 | 5.97 | 97.22 | 10.05 |
| 2 | 85.7 | 0.94 | 1.54 | 2.75 | 7.41 | 98.34 | 10.16 |
| Average | 84.69 | 1 | 1.72 | 3.69 | 6.69 | 97.78 | 10.1 |
| 4 | 73.28 | 3.69 | 3.03 | 4.89 | 12.96 | 97.85 | 10.11 |
| 4 | 77.68 | 2.44 | 1.74 | 4.99 | 11.41 | 98.26 | 10.15 |
| Average | 75.48 | 3.06 | 2.39 | 4.94 | 12.18 | 98.05 | 10.13 |
| 8 | 55.78 | 6.47 | 3.37 | 3.89 | 26.82 | 96.34 | 9.95 |
| 8 | 55.97 | 7.17 | 4.19 | 5.09 | 25.46 | 97.88 | 10.11 |
| Average | 55.87 | 6.82 | 3.78 | 4.49 | 26.14 | 97.11 | 10.03 |
| 12 | 39.31 | 9.18 | 4.63 | 4.03 | 34.63 | 91.77 | 9.48 |
| 12 | 43.22 | 9.97 | 4.84 | 4.04 | 32.23 | 94.29 | 9.74 |
| Average | 41.27 | 9.57 | 4.74 | 4.03 | 33.43 | 93.03 | 9.61 |

III. CONCLUSION

The study demonstrated that Ethofumesate degrades quickly by photolysis in sterile water at $25 \pm 1^\circ\text{C}$. Ethofumesate was photodegraded to numerous photoproducts and one significant photoproduct was detected, Degradate 1, peaking with a maximum of 9.57% AR at 12 hours. The HPLC fractionation and further analysis of Degradate 1 by TLC showed that it contains at least six components. The proposed structure for the major component of this mixture was 2,3,5-trihydroxy-4-(1-hydroxyethyl)-hexanedioic acid.

Comment RMS

The study shows that a multitude of minor metabolites are formed under irradiated conditions.

One of the degradates (Degradate 1) occurs at 9.57% after 12 hours. The HPLC fractionation and further analysis of Degradate 1 by TLC showed that it contains at least six components. The proposed molecular structure for the major component of this mixture was 2,3,5-trihydroxy-4-(1-hydroxyethyl)-hexanedioic acid.

The study is valid.

B.8.2.2.2. Indirect photochemical degradation

| | |
|---------------------|--|
| Reference: | Aqueous Photolysis in Natural Water [¹⁴C]-Ethofumesate |
| Notifier: | Taskforce |
| Author(s), year: | Roohi, A.; Doble, M.;2004 |
| Report/Doc. number: | C036311 / M-220409-01-1 |
| Guideline(s): | JMAF: 13 Seisan No. 3186, Oct 2001, 2-6-2, June 26, 2001 |
| GLP: | yes |
| Deviations: | |
| Validity: | Valid |
| Status: | New study |

MATERIALS AND METHODSMaterials :

Test Material : [Phenyl-UL-¹⁴C]Ethofumesate

Specific activity: 2.37 GBq/mmol (8.28 MBq/mg)

Test system :

Natural water from Boarded Barns Pond, Ongar, Essex, UK ; sterile conditions.

Methods :Study design

The study was conducted under sterile conditions at 25 ± 2 °C, with continuous illumination under artificial sunlight for a period of 7 days. The artificial sunlight was provided by a xenon arc lamp with filters to cut off radiation below 290 nm. The 7 day irradiation period was equivalent to 34.2 days natural spring sunlight as defined in the relevant Japanese guidelines. The initial concentration was 1.0 mg/L with 0.5% acetonitrile present as co-solvent. A set of [¹⁴C]Ethofumesate treated flasks were kept in the dark at 25 ± 1 °C for the same study period.

The water was sterilized by filtration and re-aerated by pumping air through a sterile filter connected to a sterile Pasteur pipette which was placed in the bottle of water. For irradiated samples sterile natural water was placed into glass photolysis vessels, each with a threaded cap containing a quartz window. A Heraeus Suntest CPS+ was used equipped with a filter which cut off radiation below 290 nm. Each photolysis vessel had an inlet and an outlet to allow moist, sterile, carbon-dioxide free air to be pumped across the solution surface. An ethylene trap followed by two 2 M KOH traps were used to capture any volatiles liberated. The design used for the non-irradiated samples was very similar but with a solid cap instead of the cap containing a quartz window.

Sampling

After application test solutions were analyzed after 0, 4, 24, 28, 48 and 72 hours (single samples) and 96, 144 (irradiated only) and 168 hours (duplicate samples).

Analytical Procedures :

Test solutions were analyzed by LSC and reversed phase HPLC with radio-detection to determine the degradation of [phenyl-UL-¹⁴C]Ethofumesate as well as the formation and decline of transformation products. Representative samples were additionally analyzed by spectroscopic methods.

RESULT AND DISCUSSION

Mass balance and distribution of radioactivity:

Table 8-150: Distribution of residues in % of AR in irradiated samples

| Compound | Sampling Times [hours] | | | | | | | | |
|---|------------------------|-------|-------|--------|-------|-------|-------|-------|-------|
| | 0 | 4 | 24 | 28 | 48 | 72 | 96 | 144 | 168 |
| Ethofumesate | 96.18 | 92.91 | 80.51 | 84.28 | 72.85 | 61.52 | 27.21 | 19.03 | 15.56 |
| Sum of individual unknown (n ≥ 50) ≤ 7% ¹⁾ | 2.05 | 4.44 | 19.27 | 16.50 | 24.32 | 35.56 | 66.82 | 73.63 | 77.05 |
| Volatile traps | n.a. | n.a. | 0.01 | 0.00 | 0.08 | 0.22 | 0.78 | 1.19 | 1.46 |
| Total recovery % ²⁾ | 98.22 | 97.99 | 100.8 | 101.15 | 97.69 | 97.66 | 95.17 | 94.16 | 94.38 |

n.a.: not analyzed

¹⁾ At the final time-point the number of these minor “unknowns” exceeded 50 in total.

²⁾ Values were taken from Material Balance including acetonitrile rinse (<1%)

Table 8-151: Distribution of residues in % of AR in non-irradiated samples

| Compound | Sampling Times [hours] | | | | | |
|---------------------------------|------------------------|-------|--------|--------|-------|--------|
| | 0 | 24 | 48 | 72 | 96 | 168 |
| Ethofumesate | 98.87 | 97.27 | 98.58 | 98.31 | 96.61 | 98.74 |
| Sum of individual unknown (n=2) | 2.35 | 1.12 | 1.63 | 1.69 | 1.56 | 1.36 |
| Volatile traps | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 |
| Total recovery % ¹⁾ | 101.22 | 99.17 | 100.82 | 100.55 | 98.70 | 100.63 |

n.a.: not analyzed

¹⁾ Values were taken from Material Balance including acetonitrile rinse (< 1%)

Non-extractable and Extractable Residues:

The test was performed in aqueous solution. All residues were extractable.

Mineralization/Volatiles:

The sum of volatiles was at maximum 1.5% (mean of duplicates) of applied radioactivity in the irradiated samples. The mineralization was not determined in dark samples.

Transformation of Test material and Transformation Products: Analysis of the irradiated samples by HPLC showed that Ethofumesate declined from ca. 96% of the applied radioactivity at time zero to 15% at day 7.

A multitude of peaks or zones were formed and detected by HPLC. These peaks or zones were either not identified or only tentatively identified. The maximum of an individual peak or zone was 7.0 % of the applied radioactivity. The number of minor degradates in the irradiated samples increased as the study progressed and the level of ethofumesate declined. By day 7, more than 50 individual components of widely varying polarities were detected. The majority of these minor degradates were present at less than 1% of applied radioactivity.

The number of minor degradates in the irradiated samples increased as the study progressed and the level of ethofumesate declined. By day 7, more than 50 individual components of widely varying polarities were detected. The majority of these minor degradates were present at less than 1% of applied radioactivity.

Conclusion:

It is considered that phototransformation of [phenyl-UL-¹⁴C]Ethofumesate in water systems is a contributor to the elimination of Ethofumesate from the aqueous environment. A multitude of minor metabolites are formed under irradiated conditions.

Comments RMS

The study shows, that phototransformation of [phenyl-UL-¹⁴C] Ethofumesate in water systems is a contributor to the elimination of Ethofumesate from the aqueous environment. A multitude of minor metabolites are formed under irradiated conditions, two of them occur at >5% AR.

The study is acceptable.

B.8.2.3. Route and rate of biological degradation in aquatic systems

B.8.2.3.1. “Ready biodegradability”

| | |
|---------------------|---|
| Reference: | READY BIODEGRADABILITY: 28 DAYS CLOSED BOTTLE TEST WITH ETHOFUMESATE |
| Notifier: | Taskforce |
| Author(s), year: | Bogers, M.;1993 |
| Report/Doc. number: | A87607 / W 507-1 / M-161538-01-1 |
| Guideline(s): | OECD 301D EU 84/449 |
| GLP: | yes |
| Deviations: | |
| Validity: | Valid |
| Status: | Previous evaluation in DAR for original approval / baseline dossier. |

Study summary based on previous draft assessment report

Materials and Methods

A ready biodegradability test of ethofumesate was carried out according to OECD Guidelines 301D: "Ready Biodegradability: Closed Bottle Test" (1981). The purity of ethofumesate was $\geq 97\%$. The test was carried out with a filtered and aerated inoculum from a municipal sewage treatment plant (secondary effluent). The test was carried out at ethofumesate concentrations (nominal) of 1 and 3 mg/L test solution. The following solutions were used as oxygen controls: test medium (Millipore water + nutrients) without inoculum, test medium with inoculum, 2 mg sodium acetate/L with inoculum (as positive control) and finally 2 mg/L sodium acetate + 1 mg ethofumesate/L with inoculum (as inhibition control). The test was carried out at $20 \pm 1^\circ\text{C}$ and test bottles were withdrawn for O_2 determination with an oxygen electrode after 0, 5, 14 and 28 days.

Results

Theoretical oxygen demand (ThOD) for ethofumesate is calculated to 1.84 mg O_2 /L and for sodium acetate 0.781 mg O_2 /l.

Table 8-152: BOD (mg O_2 /L) for ethofumesate, positive control and inhibition control, related to the inoculum control after 28 days incubation at 20°C .

| Test substance | O_2 consumption, mg/L (28 days) | % of ThOD degraded (28 days) |
|---------------------|---|---------------------------------|
| Ethofumesate 1 mg/L | -0.26 | -14 |

| | | |
|---|-------|----|
| Ethofumesate 3 mg/L | -0.23 | -4 |
| Sodium acetate 2 mg/L (positive control) | 1.01 | 65 |
| Sodium acetate 2 mg/L + ethofumesate 1 mg/L | 0.94 | - |

Comments RMS

The study is acceptable.

The test is shortly described but seems to have been carried according to the mentioned OECD Guideline. The results indicate that ethofumesate is not readily biodegradable.

| | |
|---------------------|---|
| Reference: | DETERMINATION OF BIOCHEMICAL AND CHEMICAL OXYGEN DEMAND OF ETHOFUMESATE DISPERSED IN WATER |
| Notifier: | Taskforce |
| Author(s), year: | Wuethrich, V.;1993 |
| Report/Doc. number: | A87608 / W 508-1 / M-161539-01-1 |
| Guideline(s): | DIN: 38409, H-41; EU (=EEC): 79/831, Annex V, Part C, Sect. C.5 + C.6 |
| GLP: | yes |
| Deviations: | |
| Validity: | Valid |
| Status: | Previous evaluation in DAR for original approval / baseline dossier. |

Study summary based on previous draft assessment report**Materials and Methods**

The biological and chemical demand, BOD₅ and COD, respectively, of ethofumesate were determined at RCC, Itingen, Switzerland. The tested batch of ethofumesate had a chemical purity of $\geq 97\%$. The BOD-test was carried out using inoculum from domestic waste-water, which after washing and filtering contained 4 g dry matter per litre, mixed with Sørensen buffer solution (pH 7). The test flasks were incubated in a SAPROMAT D12 (Voith GmbH), which determine the generated amount of CO₂ evolved at the consumption of O₂. Control solutions were test medium and test medium + inoculum (0.2 g/L test solution) Three test flasks with 10.3, 10.3 and 10.2 mg ethofumesate/250 test medium + 50 mg inoculum, were incubated together with the mentioned controls and the positive controls of 50 mg D(+)-Glucose- and 50 mg Sodium-L-glutamate/250 mL test medium (both with 50 mg inoculum) in the test apparatus for 5 days at 20±1°C. There was no description of the COD method used.

Results

COD of ethofumesate was determined to be 157.3 mg O₂/100 mg ethofumesate. In two of the BOD-flasks with ethofumesate no CO₂ was evolved after 5 days of incubation. In the third flask BOD was determined to 4.9 mg O₂/100 mg ethofumesate. The calculated BOD of the control substances were 54.8 and 55.3 mg O₂/100 mg D(+)-Glucose and Sodium-L-glutamate, respectively.

Based on the calculated average BOD-value of ethofumesate the BOD/COD ratio is:

$$\frac{\text{BOD}}{\text{COD}} = \frac{1.6}{157.3} = 0.010$$

Comments RMS

The study is acceptable. The low BOD:COD ratio of 0.01 indicates that ethofumesate is not biologically oxidised when related to its chemical oxygen demand.

| | |
|---------------------|--|
| Reference: | ASSESSMENT OF READY BIODEGRADABILITY OF ETHOFUMESATE |
| Notifier: | Taskforce |
| Author(s), year: | Douglas, M. T.; Sewell, I. G.; 1989 |
| Report/Doc. number: | A83351 / M-155620-01-1 |
| Guideline(s): | OECD 301D |
| GLP: | yes |
| Deviations: | |
| Validity: | Valid |
| Status: | Previous evaluation in DAR for original approval / baseline dossier. |

Study summary based on previous draft assessment report

Materials and Methods

The test was carried out according to OECD Guidelines 301D, the ready biodegradability closed bottle test. The chemical purity of ethofumesate was 99.9%. Sodium benzoate (C₆H₅.COOH) and aniline (C₆H₅.NH₂) were used as reference substances. Activated sludge for the test was taken from a sewage plant treating predominantly domestic sewage. The following solutions were tested: non-inoculated dilution water, inoculated dilution water, inoculated dilution water and filter paper, and three different inoculated samples: 3 mg/L ethofumesate, 3 mg/L sodium benzoate and 2 mg/L aniline. The solutions were filled on dark BOD bottles and kept in a water bath at 20±1°C. Duplicate bottles were withdrawn after 0, 5, 15 and 28 days. The free oxygen content was determined and degradation expressed as % of ThOD(NO₃) was calculated for ethofumesate and the reference substances.

Results

Table 8-153: O₂ depletion (mg O₂/l) and degradation (% of ThOD) after 28 days

| Substance | O ₂ depletion (mg O ₂ /l) | Degradation (% of ThOD) |
|--------------------------|--|----------------------------|
| Ethofumesate (3 mg/l) | 0.575 | 10 |
| Sodium benzoate (3 mg/l) | 4.40 | 88 |
| Aniline (2 mg/l) | 4.17 | 68 |

Comments RMS

The study is acceptable.

The results indicate that ethofumesate is not readily biodegradable.

B.8.2.3.2. Aerobic mineralisation in surface water

| | |
|----------------------------|--|
| Reference: | [¹⁴ C]Ethofumesate – Aerobic Mineralisation in Surface Water |
| Notifier: | UPL/Agrichem |
| Author(s), year: | Caviezel, A., 2013 |
| Report/Doc. number: | 20130080 |
| Guideline(s): | OECD 309 |
| GLP: | Yes |
| Deviations: | |
| Validity: | Valid |
| Status: | New study |
| Justification: | New data requirement |

I. MATERIALS AND METHODS

A. MATERIALS

- Test Material:** [¹⁴C]Ethofumesate
Batch No.: 7350CDB001-1
Radiochemical Purity: 98.7%
Specific Radioactivity: 2.80 MBq/mg
- Test Material:** Ethofumesate

CAS No.: 26225-79-6

Batch No.: SZBB091XV

Purity: 99.6%

3. **Reference Material:** [¹⁴C(U)]Benzoic Acid

Batch No.: 121214

Radiochemical Purity: >99%

Specific Radioactivity: 125 mCi/mmol (37.87 MBq/mg)

4. **Test system:** The test was performed using surface water without sediment (pelagic test). Water was freshly sampled from the pond from Fröschweiher on July 16, 2013. After one day of acclimation, the water was passed through a 0.2 mm sieve.

Table 8-154: Physiochemical parameters of the water system

| System | Fröschweiher |
|---|---------------|
| Water parameters measured at field sampling: | |
| Temperature [°C] | 22.0 |
| pH (water) | 7.68 |
| Oxygen concentration [mg/L] | 4.5 |
| Redox potential (E _h) * [mV] | 329 |
| Sampling depth [cm] | 0 – 20 |
| Colour | Brown |
| Turbidity/Visibility | Approx. 15 cm |
| Water parameters measured post-handling: | |
| TOC [mg/L] | 6.60 |
| DOC [mg/L] | 5.53 |
| BOD | <4.00 |
| Nitrate [mg/L] | 0.97 |
| Nitrite [mg/L] | <0.82 |
| Ammonium [mg/L] | 0.16 |
| Orthophosphate [mg/L] | 1.30 |
| N total [mg/L] | 1.15 |
| P total [mg/L] | 0.42 |

* The measured potential was corrected to E_h of a standard hydrogen electrode by adding 211 mV

B. STUDY DESIGN

1. Experimental conditions

The study was performed in an open gas-flow-through-system consisting of 300 mL Erlenmeyer flasks each containing 100 mL of surface water. The flasks with surface water were equilibrated for less than one week.

Samples were incubated in the dark at a temperature of $21.1 \pm 0.1^\circ\text{C}$ under aerobic conditions. Each flask was aerated with moistened air. The samples were continuously and gently stirred to maintain particles and micro-organisms in suspension. After treatment, samples (except for those taken immediately after treatment, i.e. day 0) were connected to a volatile trapping system equipped with two absorption traps, one containing ethylene glycol and the other 2N NaOH (in this sequence) to trap organic volatiles and $^{14}\text{CO}_2$, respectively. Another set of samples (high dose) were maintained under sterilised conditions.

Two untreated control samples were used to measure physico-chemical parameters during the test. In addition, two samples were treated with [^{14}C -U]benzoic acid in order to test the microbial activity of the test water.

2. Sampling

Samples (duplicates for the high and low dose and single samples for the sterilised systems) were taken immediately after treatment (day 0) and after 7, 14, 21, 28, 42 and 62 days of incubation. Single samples treated with the reference test item [^{14}C (U)]benzoic acid were taken for analysis after 7 and 14 days.

Trapping solutions of samples were taken on the corresponding sampling day. Trapping solutions were in addition exchanged after 34 days of incubation.

The oxygen concentration and pH of the treated samples and the two untreated samples were measured at each sampling interval.

3. Description of analytical procedures

At each sampling interval, the volume of the water phase was recorded and the radioactivity present was determined by LSC using at least two replicates. Aliquots of the water phases were then submitted for HPLC analysis. At two sampling intervals, aliquots were removed from the water phase in order to obtain the remaining concentration of benzoic acid in the test system.

The volumes of the trapping solutions were recorded. Thereafter, radioactivity present in the trapping solutions was determined by LSC. In case when multiple trapping solutions are collected for a given sample during the incubation period, the total amount of volatile radioactivity is calculated as the sum of radioactivity in the corresponding trapping solutions.

The limit of detection (LOD) in samples was set to twice the background radioactivity or 42 dpm and the respective limit of quantification (LOQ) was set to three times the background radioactivity or 63 dpm per measurement sample aliquot.

II. RESULTS AND DISCUSSION

A. MASS BALANCE

The mean radioactivity in the aqueous phases was between 96.7 and 100.3% of applied radioactivity for the high dose samples and between 95.3 and 100.8% of applied radioactivity for the low dose samples. For the sterilised samples (high dose) the mean recovery in the aqueous phase was between 96.3 and 101.6% AR.

The total radioactivity recovery including volatiles was between 95.3% and 101.8% AR throughout the study for all doses.

B. FINDINGS

HPLC analysis of the radioactivity in the water phase showed only [¹⁴C]Ethofumesate and, thus, stability of the test item for 62 days of incubation in natural surface water. The mineralisation was marginal with maximum 1.1% (high dose) and 0.8% (low dose) at the end of the incubation period.

Table 8-155: Radioactivity in surface water following application of [¹⁴C]Ethofumesate in % of applied radioactivity

| Fröschweiher [%AR] | Replicate | Incubation time in days | | | | | | |
|-----------------------|-----------|-------------------------|------|-------|-------|-------|------|-------|
| | | 0 | 7 | 14 | 21 | 28 | 42 | 62 |
| High dose | | | | | | | | |
| Aqueous phase | A | 98.2 | 97.2 | 100.7 | 100.6 | 98.1 | 97.3 | 98.2 |
| | B | 96.8 | 96.3 | 99.9 | 98.2 | 100.7 | 96.5 | 98.2 |
| | Mean | 97.5 | 96.7 | 100.3 | 99.4 | 99.4 | 96.9 | 98.2 |
| 14CO2 | A | n.p. | 0.1 | 0.2 | 0.3 | 0.9 | 0.7 | 1.1 |
| | B | n.p. | 0.1 | 0.1 | 0.3 | 0.4 | 0.6 | 1.1 |
| | Mean | n.p. | 0.1 | 0.1 | 0.2 | 0.7 | 0.6 | 1.1 |
| Other volatiles in EG | A | n.p. | <0.1 | <0.1 | 0.1 | 0.2 | <0.1 | <0.1 |
| | B | n.p. | <0.1 | <0.1 | 0.1 | 0.1 | <0.1 | <0.1 |
| | Mean | n.p. | <0.1 | <0.1 | 0.1 | 0.1 | <0.1 | <0.1 |
| Total | A | 98.2 | 97.2 | 100.9 | 101.0 | 99.2 | 98.0 | 99.2 |
| | B | 96.8 | 96.4 | 100.0 | 98.6 | 101.2 | 97.1 | 99.3 |
| | Mean | 97.5 | 96.8 | 100.4 | 99.8 | 100.2 | 97.6 | 99.2 |
| Mean ± SD | | 98.8 ± 1.6 | | | | | | |
| High dose - Sterile | | | | | | | | |
| Aqueous phase | - | 96.8 | 96.7 | 99.6 | 99.1 | 101.6 | 96.3 | 98.8 |
| 14CO2 | - | n.p. | 0.1 | 0.1 | <0.1 | 0.1 | 0.1 | 0.1 |
| Other volatiles in EG | - | n.p. | <0.1 | <0.1 | <0.1 | 0.1 | <0.1 | <0.1 |
| Total | - | 96.8 | 96.8 | 99.7 | 99.2 | 101.8 | 96.3 | 98.9 |
| Mean SD | | 98.5 ± 2.0 | | | | | | |
| Low dose | | | | | | | | |
| Aqueous phase | A | 96.5 | 97.5 | 100.1 | 99.7 | 100.7 | 97.2 | 97.5 |
| | B | 94.1 | 98.3 | 100.0 | 96.5 | 100.9 | 96.4 | 100.1 |
| | Mean | 95.3 | 97.9 | 100.0 | 98.1 | 100.8 | 96.8 | 98.8 |
| 14CO2 | A | n.p. | 0.1 | 0.1 | 0.4 | 0.4 | 0.4 | 0.8 |
| | B | n.p. | 0.1 | 0.2 | 0.1 | 0.6 | 0.4 | 0.8 |
| | Mean | n.p. | 0.1 | 0.2 | 0.2 | 0.5 | 0.4 | 0.8 |
| Other volatiles in EG | A | n.p. | 0.1 | <0.1 | 0.4 | 0.4 | <0.1 | <0.1 |
| | B | n.p. | <0.1 | <0.1 | <0.1 | 0.1 | <0.1 | <0.1 |
| | Mean | n.p. | <0.1 | <0.1 | 0.2 | 0.2 | <0.1 | <0.1 |
| Total | A | 96.5 | 97.6 | 100.2 | 100.5 | 101.5 | 97.6 | 98.4 |
| | B | 94.1 | 98.4 | 100.2 | 96.6 | 101.5 | 96.9 | 100.9 |
| | Mean | 95.3 | 98.0 | 100.2 | 98.6 | 101.5 | 97.2 | 99.6 |
| Mean SD | | 98.5 ± 2.0 | | | | | | |

n.p. Not performed

As [¹⁴C]Ethofumesate was stable, a degradation rate was not calculated.

III. CONCLUSIONS

The rate of biodegradation of Ethofumesate was investigated in natural pond surface water using the [¹⁴C]labelled test item incubated at 21.1 ± 0.1 °C under aerobic conditions.

Ethofumesate was stable for 62 days of incubation. The mineralisation was marginal with maximum 1.1% (high dose) and 0.8% (low dose) at the end of the incubation period.

Comment RMS

In contrast to the study submitted by the notifier Taskforce, ethofumesate was stable for 62 days and mineralisation was low (1.8% in the high dose test, 0.8% in the low dose test).

The study is valid.

| | |
|---------------------|---|
| Reference: | [14C]Ethofumesate: Aerobic mineralization in surface water |
| Notifier: | Taskforce |
| Author(s), year: | Fahrbach, M. (2012) |
| Report/Doc. number: | M-439697-01-1 |
| Guideline(s): | OECD 309 |
| GLP: | Yes |
| Deviations: | |
| Validity: | Valid |
| Status: | New study |
| Justification: | New data requirement |

MATERIALS AND METHODS**Materials :**

| | |
|-------------------------|--|
| Test Material : | [Phenyl-UL- ¹⁴ C]Ethofumesate |
| Specific Radioactivity: | 3.78 MBq/mg |

Test Water :

The test water was freshly sampled from a pond (Möhlin, AG, Switzerland) and consisted of natural water sampled at a depth of about 30 cm and filtered through a 0.2 mm sieve. The test water was acclimated under aerobic conditions and continuous agitation in the dark prior to treatment. At the day of application and at each sampling interval, the pH, redox potential and oxygen concentration of the water was measured in blank control duplicates (FB) and in the treated flasks

Table 8-156: Water characteristics

| Pond | Test Water | |
|--|--|-----------------------------|
| | Field sampling | Determined before treatment |
| Origin/Source | Fröschweiher pond, Möhlin AG/Switzerland | |
| Temperature [°C] | 13.8 | - |
| Colour | yellow-brown | - |
| pH | 6.95 | - |
| Redox Potential* [mV] | 512.0 | - |
| Oxygen content [mg/L] | 9.93 | - |
| BOD [mg/L] | - | 1552.0 |
| TOC [mg C/L] | - | 8.76 |
| DOC [mg C/L] | - | 7.76 |
| N _{tot} [mg/L] | - | 155.8 |
| P _{tot} [mg/L] | - | 0.13 |
| NO ₃ ⁻ [mg/L] | - | 1.61 |
| NO ₂ ⁻ [mg/L] | - | <0.83 |
| NH ₄ ⁺ [mg/L] | - | 0.27 |
| Dissolved orthophosphate (PO ₄ ³⁻) [mg/L] | - | 0.002 |

BOD: Biological oxygen demand

TOC: Total Organic Carbon

DOC: Dissolved Organic Carbon

*: The measured redox potential value was converted to the standard hydrogen electrode by the addition of + 211 mV (Ag/AgCl electrode, WTW SenTix® ORP, 20 °C).

-: Not determined

Methods :

Study design

A volume of 300 mL pelagic was filled in all-glass metabolism flasks (inner diameter: about 5.3 cm, volume: ca. 500 mL). Each flask was equipped with a gas inlet and outlet and one absorption trap containing 60 mL of 2N sodium hydroxide to trap CO₂ and one absorption trap containing 50 mL ethylene glycol to trap organic volatiles, respectively.

The ¹⁴C-labelled test item was applied to the water surface of each sample at two concentrations: 9.9 µg/L (low concentration, FTL) and 101.4 µg/L (high concentration, FTH), respectively. Several samples were treated with a higher test item amount (extended concentration, FTH, 1524 µg/L) in order to facilitate the production and isolation of metabolites. In addition, reference control samples (FC) were treated with [ring-¹⁴C(UL)]Benzoic acid at a concentration of 11.0 µg/L in order to confirm the microbial activity. Furthermore, sterile controls (FS) and solvent controls were established.

During the incubation period, the samples were incubated in the dark and continuously agitated using magnetic stirrers. A stream of air was allowed to pass through the samples. Organic volatiles and ^{14}C -carbon dioxide were collected in ethylene glycol and sodium hydroxide traps, respectively.

Experimental Conditions

The time course and concentration dependency of the biodegradation of [^{14}C]Ethofumesate in aerobic surface water (“pelagic test”) was investigated at 20 ± 3 °C in the dark

Sampling :

Duplicate samples of each Ethofumesate concentration were taken for analysis after 0, 7, 14, 21, 28, 58 and 88 days of incubation.

Analytical Procedures :

The test water was removed from the metabolism flasks. The glass material and the magnetic stirrer bars were rinsed with methanol. The test water was first submitted to LSC measurement for determination of its radioactivity content before being analyzed by HPLC and/or 1D-TLC and radiodetection either directly or after the water was concentrated under reduced pressure at 38 °C using a rotary evaporator (e.g. 75 mL were concentrated to 5.6 mL).

RESULT AND DISCUSSION

Mass balance and Distribution of Radioactivity :

Table 8-157: Material Balance in the Pond Test Water (Low Concentration, FTL) after Treatment with [^{14}C]Ethofumesate. Values Are Given in Percent of the Applied Radioactivity

| Pond System Pelagic Low Conc. (% of applied) | Sample | Incubation Time in Days | | | | | | | |
|---|-------------|-------------------------|----------------|----------------|----------------|----------------|----------------|----------------|-------------|
| | | 0 | 7 | 14 | 21 | 28 | 58 | 88 | Sterile* |
| Radioactivity in water | A | 99.0 | 95.7 | 97.1 | 100.1 | 97.5 | 96.1 | 96.3 | 98.6 |
| | B | 98.9 | 97.8 | 98.9 | 98.1 | 99.3 | 98.6 | 95.2 | 98.6 |
| | Mean | 99.0 | 96.7 | 98.0 | 99.1 | 98.4 | 97.3 | 95.7 | 98.6 |
| $^{14}\text{CO}_2$ | A | n.p. | <0.1 | 0.2 | 0.1 | 0.2 | 0.9 | 0.3 | 0.2 |
| | B | n.p. | <0.1 | <0.1 | 0.9 | 0.1 | 0.9 | 1.3 | 0.2 |
| | Mean | n.p. | <0.1 | 0.1 | 0.5 | 0.2 | 0.9 | 0.8 | 0.2 |
| Organic Volatiles | A | n.p. | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | 0.1 | 0.1 |
| | B | n.p. | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | 0.1 |
| | Mean | n.p. | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | 0.1 |
| Total | A | 99.0 | 95.7 | 97.3 | 100.2 | 97.8 | 96.9 | 96.7 | 98.9 |
| | B | 98.9 | 97.8 | 98.9 | 99.0 | 99.4 | 99.5 | 96.5 | 98.9 |

| | Mean | 99.0 | 96.8 | 98.1 | 99.6 | 98.6 | 98.2 | 96.6 | 98.9 |
|--------------------|------|-------------|------|------|------|----------|------------|------|------|
| MEAN +/- SD | | 98.1 | | | | ± | 1.3 | | |

* Only replicate B (sterile control) was used for evaluation due to technical problems.

n.p.: Not performed.

SD: Standard Deviation.

Table 8-158: Pattern of [¹⁴C]Ethofumesate and its Metabolites in the Pond Test Water (Low Concentration, FTL). Values Are Given in Percent of the Applied Radioactivity

| Pond System Pelagic Low Conc. (% of applied) | Sample | Incubation Time in Days | | | | | | | |
|---|-------------|-------------------------|-------------|-------------|-------------|-------------|-------------|-------------|----------------|
| | | 0 | 7 | 14 | 21 | 28 | 58 | 88 | Sterile** |
| Parent | A | 99.0 | 95.7 | 94.8 | 95.0 | 94.8 | 86.9 | 61.7 | 93.9 |
| | B | 98.9 | 97.8 | 96.1 | 94.8 | 90.8 | 86.6 | 55.1 | 93.9 |
| | mean | 99.0 | 96.7 | 95.5 | 94.9 | 92.8 | 86.7 | 58.4 | 93.9 |
| M1 (BCS-CU88901) | A | * | * | 2.2 | 5.1 | 2.7 | 9.2 | 8.7 | <LOQ |
| | B | * | * | 2.7 | <LOQ | 3.8 | 10.4 | 27.9 | <LOQ |
| | mean | * | * | 2.5 | 4.2 | 3.2 | 9.8 | 18.3 | <LOQ |
| M2 (BCS-CW35117) | A | * | * | * | * | * | * | 19.1 | <LOQ |
| | B | * | * | * | * | 4.7 | * | 7.7 | <LOQ |
| | mean | * | * | * | * | 2.4 | * | 13.4 | <LOQ |
| M3 | A | * | * | * | * | * | * | 5.0 | * |
| | B | * | * | * | * | * | * | <LOQ | * |
| | mean | * | * | * | * | * | * | 4.0 | * |
| non-resolved*** | A | --- | --- | --- | --- | --- | --- | 1.8 | 0.3 |
| | B | --- | --- | --- | --- | --- | 1.6 | 1.3 | 0.3 |
| | mean | --- | --- | --- | --- | --- | 0.8 | 1.6 | 0.3 |

*: Not detected

**: Only replicate B was used for evaluation due to technical problems. The sterile sample was used to examine abiotic degradation or other non-biological removal of the test item. The sample was worked-up on the last sampling interval (day 88). The sterile samples were autoclaved (121°C; 20 min) to stop the biological activity.

***: Adsorbed radioactivity which remained as origin on the TLC plate

<LOQ: Below Limit of Quantification

Table 8-159: Material Balance in the Pond Test Water (High Concentration, FTH) after Treatment with [¹⁴C]Ethofumesate. Values Are Given in Percent of the Applied Radioactivity

| Pond System Pelagic High Conc. (% applied) | Sample | Incubation Time in Days | | | | | | |
|---|--------|-------------------------|------|------|------|------|------|------|
| | | 0 | 7 | 14 | 21 | 28 | 58 | 88 |
| Radioactivity in water | A | 93.5 | 90.8 | 95.4 | 95.1 | 95.6 | 94.2 | 92.8 |
| | B | 97.0 | 95.4 | 96.7 | 96.8 | 96.7 | 93.7 | 93.5 |
| | Mean | 95.2 | 93.1 | 96.0 | 95.9 | 96.1 | 94.0 | 93.1 |
| ¹⁴ CO ₂ | A | n.p. | <0.1 | <0.1 | <0.1 | 0.1 | 0.3 | 0.9 |
| | B | n.p. | <0.1 | <0.1 | <0.1 | <0.1 | 0.3 | 0.8 |
| | Mean | n.p. | <0.1 | <0.1 | <0.1 | 0.1 | 0.3 | 0.8 |
| Organic Volatiles | A | n.p. | <0.1 | <0.1 | <0.1 | <0.1 | 0.1 | <0.1 |
| | B | n.p. | <0.1 | <0.1 | <0.1 | <0.1 | 0.2 | <0.1 |
| | Mean | n.p. | <0.1 | <0.1 | <0.1 | <0.1 | 0.2 | <0.1 |
| Total | A | 93.5 | 90.9 | 95.5 | 95.2 | 95.7 | 94.6 | 93.7 |
| | B | 97.0 | 95.4 | 96.7 | 96.9 | 96.8 | 94.2 | 94.3 |
| | Mean | 95.2 | 93.1 | 96.1 | 96.0 | 96.2 | 94.4 | 94.0 |
| MEAN +/- SD | | 95.0 ± | | | | | 1.7 | |

n.p.: Not performed.

SD: Standard Deviation.

Table 8-160: Pattern of [¹⁴C]Ethofumesate and its Metabolites in the Pond Test Water (High Concentration, FTH). Values Are Given in Percent of the Applied Radioactivity

| Pond System Pelagic High Conc. (% of applied) | Sample | Incubation Time in Days | | | | | | |
|--|--------|-------------------------|------|------|------|------|------|------|
| | | 0 | 7 | 14 | 21 | 28 | 58 | 88 |
| Parent | A | 93.5 | 90.8 | 93.3 | 91.2 | 92.4 | 81.7 | 79.3 |
| | B | 97.0 | 94.1 | 94.9 | 90.5 | 94.6 | 85.8 | 79.4 |
| | mean | 95.2 | 92.5 | 94.1 | 90.9 | 93.5 | 83.8 | 79.3 |
| M1 (BCS-CU88901) | A | * | * | 2.1 | 3.0 | 3.2 | 4.6 | 8.8 |
| | B | * | 1.2 | 1.7 | 6.3 | * | 4.9 | 14.1 |
| | mean | * | <LOQ | 1.9 | 4.6 | 1.6 | 4.7 | 11.4 |
| M2 (BCS-CW35117) | A | * | * | * | 0.9 | * | 7.8 | 4.7 |
| | B | * | * | * | * | 2.1 | 3.0 | * |
| | mean | * | * | * | <LOQ | 1.0 | 5.4 | 2.4 |

Not detected

<LOQ: Below Limit of Quantification

Non-extractable and Extractable Residues:

All residues were extractable.

Mineralization:

The maximum of formed $^{14}\text{-CO}_2$ was 0.9% of AR and 0.8% for the low and high concentration, respectively.

Transformation of Test material and Transformation Products :

^{14}C]Ethofumesate was degraded slowly in the test water. In the low concentration samples (FTL) a significant degradation of the test item was observed after a lag phase of approximately 60 days. Immediately after application, its concentration in the water phase represented on average 99.0% (low concentration, FTL) and 95.2% (high concentration, FTH) of the applied radioactivity decreasing to 58.4% and 79.3% after 88 days, respectively. The parent remained almost stable in the sterile control (FS) after an incubation period of 88 days.

Two major metabolites, designated M1 (R1 = BCS-CU88901; NC 20645, ethofumesate-carboxylic acid NC20645) and M2 (BCS-CW35117), were formed. Metabolite M1 reached maximum values of 18.3% (low concentration, FTL) and 11.4% (high concentration, FTH) of applied at the end the incubation period. Metabolite M2 reached maximum levels of 13.4% on day 88 at the low concentration (FTL). Metabolite M2 was identified as ethofumesate-acetic acid by LC-MS analysis and chromatographic behavior. At the high concentration (FTH) metabolite M2 reached its maximum on day 58 with 5.4% of applied radioactivity. In the low concentration samples (FTL) one additional minor radioactive fraction, designated M3 was detected. Metabolite M3 did not exceed 4.0% of the applied radioactivity in the low concentration samples and was not identified

Conclusion:

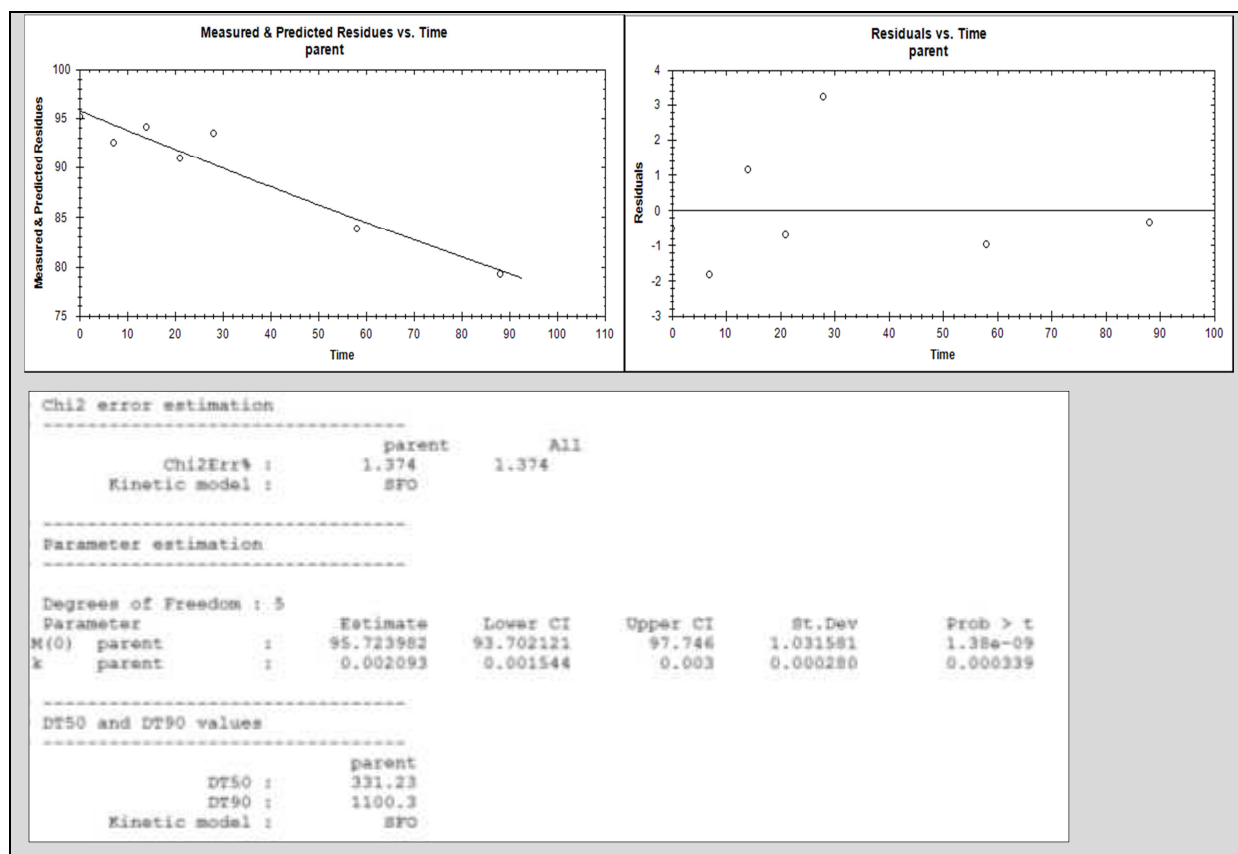
In aerobic surface water ethofumesate was degraded slowly. At the lower test item concentration the test item was degraded faster after a lag-phase of about 60 days. This indicates that the rate of Ethofumesate degradation in water is concentration dependent. Two predominant metabolites and one minor metabolite were formed, NC 20645 (ethofumesate carboxylic acid, reference substance BCS-CU88901) and BCS-CW35117 (ethofumesate acetic acid). The formation of carbon dioxide due to mineralization was low.

Comments RMS

The study is fully acceptable.

In contrast to the study presented by the notifier UPL, two major metabolites (NC 20645 and CW35117) were formed. Metabolite NC20645 reached maximum values of 18.3% (low concentration test, FTL) and 11.4% (high concentration test,, FTH) of applied radioactivity at the end the incubation period. Metabolite CW35117 reached maximum levels of 13.4% on day 88 at the low concentration test (FTL). Both metabolites were considered in the risk assessment.

Degradation rates were calculated by the RMS. The SFO model gave acceptable fits (see graphs and tables below).



B.8.2.3.3. Water/sediment study

| | |
|---------------------|--|
| Reference: | DEGRADATION OF ETHOFUMESATE IN A SEDIMENT/WATER MICROSYSTEM |
| Notifier: | Taskforce |
| Author(s), year: | Celorio, J. I.;1984 |
| Report/Doc. number: | A83284 / W 28 / M-155553-01-1 |
| Guideline(s): | None |
| GLP: | no |
| Deviations: | |
| Validity: | Not valid |
| Status: | Previous evaluation in DAR for original approval / baseline dossier. |

Study summary based on previous draft assessment report

Materials and Methods

The aerobic transformation of U-phenyl-labelled ^{14}C -ethofumesate (purity >97%) was investigated in a sediment/water system originating from a natural pond in Northern Berlin according to Dutch Registration Guidelines, Section G. 2, 1980. For sediment characteristics, see table below.

Table 8-161: Sediment characteristics

| Sediment | Org. C (%) | pH | clay (%) | silt (%) | sand (%) | MHC (%) | CEC (meq/100 g) |
|---------------------|---------------|-----------|-------------|-------------|-------------|------------|--------------------|
| Hubertussee sand | 11 | 5.8 | 7.9 | 2.9 | 89 | n.r | n.r |
| water phase | | 6.0 - 7.0 | | | | | |
| n.r. = not reported | | | | | | | |

Sediment was introduced to a depth of ca. 7 cm (97 g) in 500 mL glass cylinders (5 cm i.d.). Surface water was added to a depth of 15 cm (ca. 343 ml). The systems were treated with 12.6 mg ^{14}C -ethofumesate/kg sediment (corresponding to a field rate of 6.1 kg as/ha). The test systems were aerated with carbon dioxide free air and incubated at $22\pm 2^\circ\text{C}$ in the dark after 3 days of equilibration. Volatile transformation products were trapped in 1, 2-ethanediol, NaOH and H_2SO_4 . Single samples (whole cylinders) were taken for analysis at 0, 2, 8, 15, 30, 42, 63 and 84 days after treatment. The sediment was extracted with acetone, acetonitrile/water (4:1, Soxhlet) and NaOH. Radioactivity in the water phase and in the sediment extracts were quantified by LSC and identified by TLC. Non-extractable residues were combusted and measured by LSC.

Results

After 84 days of incubation, 25% of the applied radioactivity (14% unaltered parent compound) was recovered in the water phase, and 59 % in the sediment (51% unaltered parent compound). The material balance of applied ^{14}C -radioactivity is given in the table below.

Table 8-162: Material balance of applied ^{14}C -ethofumesate after 84 days of incubation in water/sediment systems maintained at $22\pm 2^\circ\text{C}$.

| System | NC8438 (%) | CO_2 (%) | unextractable (%) | Other ¹ (%) | total (%) |
|---------------------------------|---------------|----------------------|----------------------|---------------------------|--------------|
| Hubertussee (water+sediment) | 65 | 1.7 | 2.4 | 17 | 93 |

¹ includes soxhlet, volatiles (H_2SO_4 + 1, 2-ethanediol), and other TLC radioactive zones.

The dissipation half-life of ethofumesate from the water phase was 13 days. For the whole system, the half-life was calculated to 125 days, based on first order kinetics. The sum of other transformation products than CO_2 reached a maximum of 19% on day 63, but none of them was identified.

Comments RMS

About 17% of the radioactivity remained unidentified. Moreover, CO₂-free air was used for aeration, which in contrast to the requirements by the OECD 308. The waterphase is insufficiently characterized: the only reported parameter was the pH at study beginning; measured with a test strip giving the range from 6-7. There is no information on the storage of sediment or whether it was freshly processed.

The study is not valid.

| | |
|---------------------|---|
| Reference: | DEGRADATION AND METABOLISM OF ¹⁴C ETHOFUMESATE IN AQUATIC SYSTEMS |
| Notifier: | Taskforce |
| Author(s), year: | Kellner, G.;1995 |
| Report/Doc. number: | A87625/ W 526-1 / M-161568-01-1 |
| Guideline(s): | BBA: IV, 5-1 |
| GLP: | yes |
| Deviations: | |
| Validity: | Valid |
| Status: | Previous evaluation in DAR for original approval / baseline dossier. |

Study summary based on previous draft assessment report

Materials and Methods

The aerobic transformation of U-phenyl-labelled ¹⁴C-ethofumesate (radiochemical purity 98.8%) was investigated in two sediment/water systems, according to BBA Guideline Part IV, 5-1, 1990. For sediment and water characteristics, see tables below.

Table 8-163. Sediment characteristics

| Sediment | OC (%) | pH | clay (%) | silt (%) | sand (%) | water content (%) | CEC (mequ/100 g) |
|---------------|-----------|-----|-------------|-------------|-------------|----------------------|---------------------|
| Rhine river | 1.2 | 6.9 | 5.6 | 9.3 | 85 | 39 - 44 | 8.3 |
| Anwiler Teich | 1.4 | 6.9 | 29 | 30 | 42 | 48 - 49 | 23 |

Table 8-164: Water characteristics during the test period

| Water | O ₂ (% of saturation) | pH | redox-potential (mV) | hardness (°dH) | alkalinity (mg CaCO ₃ /l) |
|---------------|-------------------------------------|-----------|-------------------------|-------------------|---|
| Rhine river | 41 - 87 | 7.6 - 8.3 | 93 - 213 | 18 | n.r. |
| Anwiler Teich | 54 - 98 | 7.4 - 8.3 | 107 - 223 | 20 | n.r. |

n.r. = not reported

Sediment was introduced to a depth of ca. 2 cm (190 and 180 g w/w from river and pond, respectively) in 500 mL glass flasks. Surface water was added to achieve a water column of 6 cm height (290 ml). Each test system was treated with 0.14 mg ^{14}C -ethofumesate (corresponding to a field rate of 1.5 kg as/ha). The systems were ventilated with moistened air and incubated at $20\pm 1^\circ\text{C}$ in the dark after two weeks of equilibration. Volatile transformation products were trapped in NaOH and 2-methoxyethanol. Duplicate samples were taken for analysis 0, 0.25, 1, 2, 7, 14, 30, 61 and 103 days after treatment. The sediment was extracted with acetone/water (2:1). Radioactivity in the water phase and in the sediment extracts were quantified by LSC and identified by TLC. Non-extractable residues were combusted and measured by LSC.

Results

After 103 days of incubation, 32 and 27% (13 and 18% parent compound) of applied radioactivity was recovered in the river and pond water phase, respectively, while 57 and 64% (37 and 41% parent compound) was associated to the sediments. The material balance of applied ^{14}C -radioactivity is given in the table below.

Table 8-165: Balance of the radioactivity in the river water and sediment after various time intervals. Values are given in %AR.

| | | INCUBATION TIME IN | | | | | | | | |
|---------------------------------|------|--------------------|-----------|------|--------|------|------|------|------|------|
| | | HOURS | | DAYS | | | | | | |
| | | 0 | 6 | 1 | 2 | 7 | 14 | 30 | 61 | 103 |
| WATER | A | 96.1 | 90.1 | 81.4 | 76.7 | 63.1 | 47.7 | 36.3 | 30.7 | 32.5 |
| | B | 95.7 | 89.0 | 83.7 | 72.9 | 55.6 | 51.9 | 39.0 | 30.6 | 31.1 |
| | Mean | 95.9 | 89.6 | 82.5 | 74.8 | 59.4 | 49.8 | 37.6 | 30.6 | 31.8 |
| SEDIMENT Extractables | A | 1.4 | 7.5 | 16.2 | 19.6 | 32.5 | 44.3 | 53.6 | 49.9 | 42.4 |
| | B | 1.8 | 10.5 | 13.7 | 24.4 | 37.9 | 41.0 | 50.7 | 49.5 | 42.4 |
| | Mean | 1.6 | 9.0 | 14.9 | 22.0 | 35.2 | 42.7 | 52.2 | 49.7 | 42.4 |
| Non- extractables | A | 0.1 | 0.2 | 0.2 | 0.1 | 0.3 | 0.6 | 2.7 | 11.4 | 13.7 |
| | B | 0.1 | 0.3 | 0.3 | 0.3 | 0.2 | 0.6 | 4.3 | 8.6 | 14.8 |
| | Mean | 0.1 | 0.2 | 0.3 | 0.2 | 0.3 | 0.6 | 3.5 | 10.0 | 14.2 |
| TOTAL SEDIMENT | A | 1.6 | 7.6 | 16.4 | 19.7 | 32.7 | 45.0 | 56.3 | 61.3 | 56.1 |
| | B | 1.9 | 10.8 | 14.0 | 24.7 | 38.1 | 41.5 | 55.0 | 58.1 | 57.2 |
| | Mean | 1.7 | 9.2 | 15.2 | 22.2 | 35.4 | 43.3 | 55.6 | 59.7 | 56.6 |
| Volatile Compounds | A | n.d. | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 |
| | B | n.d. | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 |
| | Mean | n.d. | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 |
| ¹⁴ C-CO ₂ | A | n.d. | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | 0.1 | 0.5 | 1.5 |
| | B | n.d. | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | 0.1 | 0.5 | 1.5 |
| | Mean | n.d. | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | 0.1 | 0.5 | 1.5 |
| TOTAL RECOVERY | A | 97.7 | 97.8 | 97.8 | 96.5 | 95.9 | 92.7 | 92.8 | 92.6 | 90.1 |
| | B | 97.6 | 99.8 | 97.7 | 97.7 | 93.7 | 93.5 | 94.1 | 89.2 | 89.9 |
| | Mean | 97.7 | 98.6 | 97.8 | 97.1 | 94.8 | 93.1 | 93.5 | 90.9 | 90.0 |
| MEAN RECOVERY | | ± | Std. Dev. | | 94.9 ± | | 3.2 | | | |

Notes: n.d.: not determined

Table 8-166: Balance of the radioactivity in the pond water and sediment after various time intervals. Values are given in %AR.

| | | INCUBATION TIME IN | | | | | | | | |
|---------------------------------|------|--------------------|-----------|--------|------|------|------|------|------|------|
| | | HOURS | | DAYS | | | | | | |
| | | 0 | 6 | 1 | 2 | 7 | 14 | 30 | 61 | 103 |
| WATER | A | 92.4 | 88.5 | 81.4 | 73.6 | 61.0 | 55.7 | 39.5 | 34.4 | 29.8 |
| | B | 93.3 | 89.0 | 82.2 | 74.1 | 63.1 | 52.0 | 42.6 | 36.8 | 24.1 |
| | Mean | 92.8 | 88.7 | 81.8 | 73.8 | 62.0 | 53.9 | 41.0 | 35.6 | 26.9 |
| SEDIMENT Extractables | A | 1.4 | 7.0 | 13.3 | 21.4 | 33.9 | 37.8 | 51.1 | 50.4 | 36.7 |
| | B | 0.6 | 8.1 | 13.5 | 22.3 | 33.3 | 41.4 | 49.1 | 47.9 | 50.4 |
| | Mean | 1.0 | 7.6 | 13.4 | 21.8 | 33.6 | 39.6 | 50.1 | 49.1 | 43.5 |
| Non- extractables | A | 0.1 | 0.3 | 0.3 | 0.7 | 0.9 | 1.2 | 3.3 | 10.2 | 25.1 |
| | B | 0.1 | 0.4 | 0.2 | 0.5 | 0.9 | 1.1 | 3.6 | 9.1 | 15.9 |
| | Mean | 0.1 | 0.3 | 0.3 | 0.6 | 0.9 | 1.2 | 3.4 | 9.6 | 20.5 |
| TOTAL SEDIMENT | A | 1.5 | 7.3 | 13.6 | 22.0 | 34.8 | 39.0 | 54.4 | 60.6 | 61.8 |
| | B | 0.7 | 8.5 | 13.7 | 22.8 | 34.2 | 42.5 | 52.7 | 57.0 | 66.4 |
| | Mean | 1.1 | 7.9 | 13.7 | 22.4 | 34.5 | 40.8 | 53.5 | 58.8 | 64.1 |
| Volatile Compounds | A | n.d. | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 |
| | B | n.d. | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 |
| | Mean | n.d. | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 |
| ¹⁴ C-CO ₂ | A | n.d. | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | 0.1 | 0.3 | 1.2 |
| | B | n.d. | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | 0.1 | 0.3 | 1.2 |
| | Mean | n.d. | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | 0.1 | 0.3 | 1.2 |
| TOTAL RECOVERY | A | 93.9 | 95.8 | 95.0 | 95.6 | 95.8 | 94.8 | 94.1 | 95.3 | 92.8 |
| | B | 93.9 | 97.5 | 96.0 | 96.9 | 97.4 | 94.6 | 96.4 | 94.1 | 91.7 |
| | Mean | 93.9 | 96.7 | 95.5 | 96.3 | 96.7 | 94.8 | 94.8 | 94.8 | 92.3 |
| MEAN RECOVERY | | ± | Std. Dev. | 95.1 ± | | 1.4 | | | | |

Notes: n.d.: not determined

The radioactivity referred to as “other” includes up to four unknown fractions, of which one amounted to a maximum of 15 and 6.6% (TLC) of applied radioactivity in the river- and pond waters, respectively. No other fraction amounted to more than 3% of applied.

The dissipation half-life of ethofumesate from the river and pond water phase was 11 and 19 days. For the whole systems, the half-lives were calculated to 105 and 153 days. The calculations for the river system was based on 1.5th order kinetics, while the pond calculations were based on first order kinetics.

RMS Comments

The study was conducted in accordance with the referred guidelines, except for the lack of identification of residues. The water:sediment ratio is narrower than required by guideline (3:2 instead of 3:1 to 4:1), but still acceptable. CO₂-free air was used for aeration, however, no alkalization occurred.

The study is acceptable with regard to the degradation of ethofumesate. The kinetic evaluation is reported in Schmitt (2008).

| | |
|---------------------|---|
| Reference: | DEGRADATION OF ETHOFUMESATE IN AEROBIC WATER/ANAEROBIC SEDIMENT SYSTEM |
| Notifier: | Taskforce |
| Author(s), year: | Wahle, U.;1991 |
| Report/Doc. number: | A83402 / W 173 / M-155670-01-1 |
| Guideline(s): | None |
| GLP: | yes |
| Deviations: | |
| Validity: | Not valid |
| Status: | Previous evaluation in DAR for original approval / baseline dossier. |

Study summary based on previous draft assessment report

Materials and Methods

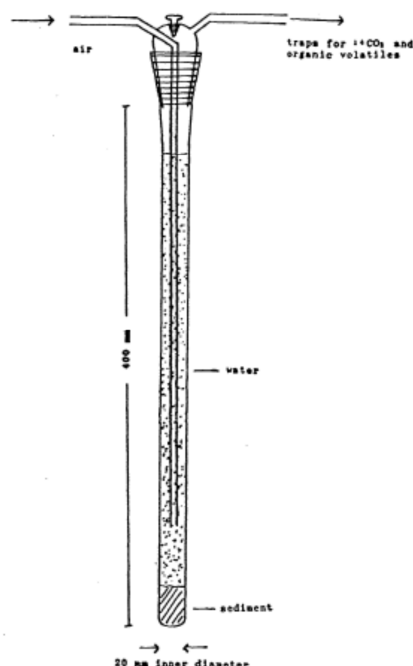
The transformation of ethofumesate (purity 95.5%) was investigated in two sediment/water systems, according to Dutch Registration Guidelines, 1988. For sediment and water characteristics, see table below.

Table 8-167: Sediment characteristics

| System | Org. C (%) | pH | clay (%) | silt (%) | sand (%) | water content (%) | CEC (meq/100 g) |
|--------------------|---------------|-----|-------------|-------------|-------------|----------------------|--------------------|
| I. Loamy sediment | 5 | 7.0 | 18 | 66 | 16 | n.r. | 12 |
| water phase | | 7.5 | | | | | |
| II. Sandy sediment | 1.1 | 8.2 | 5 | 38 | 57 | n.r. | 8.8 |
| water phase | | 7.8 | | | | | |

Sediment was introduced to a depth of ca. 2 cm (10 g dry weight) in incubation vessels (20 mm i.d., 400 mm in height). Surface water was added to a volume of 100 ml. Each test system was treated with 31.3 µg ¹⁴C-ethofumesate (corresponding to 3 mg as/kg dw of sediment or 3.1 kg as/ha). The systems were ventilated with synthetic air and incubated at 20±1°C in 10 h light/14 h dark per day after eight weeks of equilibration. Sterile samples were used as control. Volatile transformation products were trapped in NaOH and ethyleneglycol/NaOH. Duplicate samples were taken for analysis at 0, 3, 7, 21, 42, 63 and 84 days after treatment. The sterile vessels were sampled after 84 days. The sediment was extracted with dichloromethane/water (10:3). Radioactivity in concentrated sediment and water phase extracts were analysed by GC. Evolved CO₂ was analysed by titration of the trapping solutions with HCl (indicator phenolphthalein).

Figure 8-89: Employed incubation apparatus for the water/sediment study.



Results

After 84 days of incubation, 45 and 43% of applied ethofumesate was recovered in the water phase, while 14 and 6.4% was extractable from the loamy and sandy sediments, respectively. In the sterile samples 46 and 71% of the test substance was found in the aqueous phase, and 19 and 13% extractable from the loamy and sandy sediment, respectively. In the aqueous phase of the sandy sediment, 2-oxo-2, 3-dihydro-3, 3-dimethylbenzofuran-5-yl-methanesulfonate (NC9607) accounted for a maximum of 4% of applied (3 and 9 weeks after application). In the loamy sediment, 2-hydroxy-2, 3-dihydro-3, 3-dimethylbenzofuran-5-yl-methanesulfonate (NC8493) was detected (4 - 8% of applied) until 9 weeks after application. No metabolites were detected in the sterile control samples. The half-life for dissipation of ethofumesate from the water phase could be calculated to 55 days ($r^2=0.66$) in the loamy sand system and to 65 days ($r^2=0.76$) in the sandy system. For the whole systems, the half-lives were calculated to 148 and 124 days, respectively, based on first order kinetics.

In the sandy system, the microbial activity was higher at the end of the study than before the incubation was started.

Comment RMS

The test water was insufficiently characterized: only the pH was measured when the water was sampled; TOC and temperature are not reported. The same parameters were also not measured during or at the end of the experiment. The test substance was not radiolabelled, and no conclusions could be made about mineralisation rate, volatiles or bound residues. Due to the test vessel design, the area of the sediment surface was probably not

sufficient to permit exchange between sediment and water. CO₂-free air was used for aeration and due to the lack of measured pH, potential alkalization cannot be ruled out.

The data are not further considered in the assessment of ethofumesate.

| Reference: | RATE OF DEGRADATION OF ETHOFUMESATE IN AN AEROBIC WATER/SEDIMENT SYSTEM |
|---------------------|---|
| Notifier: | Taskforce |
| Author(s), year: | Hillebrand, A. J.; Vonk, J. W.; 1989 |
| Report/Doc. number: | A87605 / W 505-1 / M-161534-01-1 |
| Guideline(s): | None |
| GLP: | No |
| Deviations: | |
| Validity: | Not valid |
| Status: | Previous evaluation in DAR for original approval / baseline dossier. |

Study summary based on previous draft assessment report

Materials and Methods

The aerobic dissipation of ethofumesate (purity >98%) was investigated in two sediment/water systems, according to Dutch Registration Guidelines. For sediment characteristics, see table below. The TNO ditch water, used in both trials, was not characterised.

Table 8-168: Sediment characteristics

| Sediment | OC (%) | pH | clay (%) | silt (%) | sand (%) | water content (%) | CEC (mequ/100 g) |
|-------------|-----------|-----|-------------|-------------|-------------|----------------------|---------------------|
| TNO ditch | 8.4 | 7.4 | 25 | 32 | 30 | n.r | n.r |
| Kromme Rijn | 5.5 | 7.3 | 20 | 25 | 42 | n.r | n.r |

n.r. = not reported

Ditch water was introduced to a volume of 100 mL in cylindrical biometer flasks. Sediment was added to achieve a 1% content of dry solids. The test concentration was 8.0 mg as/l. The flasks were incubated in a shaker at 20°C. Duplicate samples were taken for analysis at 0, 14, 28, 56 and 84 days after treatment. Ethofumesate in water and sediment was extracted with dichloromethane and analysed by GC.

Results

On the day of application, only 69% of the nominally applied test substance was recovered in both test systems. After 84 days of incubation, 58 and 63% of applied ethofumesate remained unaltered in the TNO and Kromme

Rijn systems, respectively. The dissipation half-lives of ethofumesate were estimated to >200 days for both systems.

Comments RMS

The study is characterized by several insufficiencies. The test compound was stored at room temperature without protection from light.

The water:sediment ratio was wide (100:1). No information was given about water characteristics, any equilibration of the systems before application of the test substance, or whether the systems were kept in light or darkness. Mineralisation rate, any transformation products or bound residues are not reported.

The study is not valid.

| | |
|---------------------|---|
| Reference: | Ethofumesate - Fate and behaviour in water/sediment |
| Notifier: | Taskforce |
| Author(s), year: | Blech, S.;1996 |
| Report/Doc. number: | OFC00004877 / M-352106-01-1 |
| Guideline(s): | Richtlinien für die Prüfung von Pflanzenschutzmitteln im Zulassungsverfahren' part IV, 5-1, |
| GLP: | Yes |
| Deviations: | |
| Validity: | Valid |
| Status: | Previous evaluation in DAR for original approval / baseline dossier. |

Study summary based on previous draft assessment report

Materials and Methods

The aerobic transformation of U-phenyl-labelled ¹⁴C-ethofumesate (radiochemical purity >98.5%) was investigated in two sediment/water systems, according to BBA Guideline Part IV, 5-1, 1990. For sediment and water characteristics, see tables below.

Table 8-169: Sediment characteristics at the beginning of the experiment

| Sediment | Org. C (%) | pH | clay (%) | silt (%) | sand (%) | water content (%) | CEC (mval) |
|-----------------|---------------|-----|-------------|-------------|-------------|----------------------|---------------|
| Waldwinkel | 10 | 7.1 | 24 | 62 | 14 | n.r. | 33 |
| Ruckhaltebecken | 0.75 | 7.2 | 12 | 79 | 9.3 | n.r. | 7.9 |

Figure 8-90: Water characteristics at the beginning of the experiment

| Water | O ₂ (% of saturation) | pH | redox-potential (mV) | hardness (mmol/l) | alkalinity (mg CaCO ₃ /l) |
|-----------------|-------------------------------------|-----|-------------------------|----------------------|---|
| Waldwinkel | 91 | 7.7 | 177 | 3.2 | n.r. |
| Ruckhaltebecken | 93 | 8.1 | 117 | 1.8 | n.r. |

n.r. = not reported

Sediment was introduced to a depth of ca. 2.5 cm (140 and 110 g w/w from Waldwinkel and Ruckhaltebecken, respectively) in 500 mL flasks. Surface water was added to achieve a water column of 5.5 - 6.5 cm height. The test systems were treated with 0.4 mg ¹⁴C-ethofumesate/L water (corresponding to a field rate of 1.2 kg as/ha, assuming 0.3 m water depth), pipetted on the water surface of the systems. After one week of equilibration the systems were closed with absorption/ventilation devices and gently shaken (without whirling up the sediment) during incubation at 20±0.5°C in the dark. Volatile transformation products were trapped in NaOH and ethylacetate. Duplicate samples were taken for analysis 0, 1, 2, 7, 14, 30, 60±1, 100±4 and 230±5 days after treatment. The sediment was extracted with acetone and the water with trichloromethane. The radioactivity was quantified by LSC and identified by TLC. Non-extractable residues were combusted and measured by LSC.

Results

After 234 days of incubation in Waldwinkel and 225 days in Ruckhaltebecken, 5.1 and 26% (1.5 and 21% parent compound) of applied radioactivity was recovered in the water phase, while 81 and 58% (53 and 30% parent compound) was associated to the sediments. The material balance of applied ¹⁴C-radioactivity at termination of the study is given in the table below.

Table 8-170: Material balance of applied ¹⁴C-ethofumesate after 234 or 225 days of incubation in water/sediment systems maintained at 20±1°C.

| System | NC8438 (%) | CO ₂ (%) | unextractable (%) | other (%) | total (%) |
|-------------------------|---------------|------------------------|----------------------|--------------|--------------|
| Waldwinkel (234 d) | 54 | 9.4 | 27 | 3.3 | 95 |
| Ruckhaltebecken (225 d) | 51 | 5.7 | 27 | 4.1 | 91 |

The radioactivity referred to as “other” includes a non extractable fraction assigned to metabolites, which amounted to a maximum of 3.6 and 5.9% (TLC) of applied radioactivity in the Waldwinkel and Ruckhaltebecken waters, respectively.

Table 8-171: Water/sediment system 'Waldwinkel' Distribution of radioactivity, summary (mean values) (%):

| days | 0 | 1 | 2 | 7 | 14 | 30 | 59 | 104 | 234 |
|--|------|------|------|------|------|------|------|------|-----|
| water (sum) | 87.9 | 83.1 | 76.7 | 47.5 | 33.2 | 24.2 | 17 | 11.7 | 5.1 |
| extractable part | 87.2 | 81.9 | 75.3 | 46 | 31.7 | 21.3 | 13.4 | 9.4 | 1.8 |
| radioactivity assigned to ethofumesate | 87 | 81.4 | 73.2 | 45.8 | 31.2 | 20.8 | 13.4 | 9.2 | 1.5 |

| | | | | | | | | | |
|---|------|------|-------|------|------|------|------|------|------|
| non extractable part. radioactivity assigned to metabolites (sum) | 0.7 | 1.2 | 1.4 | 1.5 | 1.4 | 2.8 | 3.6 | 2.3 | 3.3 |
| sediment (sum) | 12 | 16.3 | 27.4 | 50.8 | 63.7 | 71.7 | 77.7 | 81.1 | 80.7 |
| extrectable part | 12 | 16.2 | 27.1 | 50.2 | 62.8 | 70.3 | 74.6 | 74.4 | 53.8 |
| radioactivity assigned to ethofumesate | 11.8 | 15.1 | 26.6 | 49.4 | 61 | 66.8 | 71.3 | 72.2 | 52.5 |
| bound residue | 0.1 | 0.1 | 0.2 | 0.2 | 0.2 | 1.4 | 3.4 | 6.7 | 26.9 |
| carbon dioxide | 0 | 0 | 0 | 0 | 0 | 0.2 | 0.4 | 1.5 | 9.4 |
| volatile substances | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| recovery | 99.9 | 99.5 | 104.1 | 98.3 | 96.9 | 96.1 | 95.1 | 94.4 | 95.3 |
| test substance (sum) | 98.8 | 96.5 | 99.8 | 95.2 | 92.2 | 87.6 | 84.7 | 81.4 | 54 |
| not classified radioactivity | 0.4 | 1.6 | 2.6 | 1.1 | 2.3 | 4.1 | 3 | 2.4 | 1.7 |

Table 8-172: Water/sediment system 'Waldwinkel' Distribution of radioactivity, summary (mean values) (%):

| days | 0 | 1 | 2 | 7 | 14 | 30 | 61 | 98 | 225 |
|---|------|-------|------|------|------|------|------|------|------|
| water (sum) | 91 | 88.9 | 90.4 | 76.5 | 66 | 56.3 | 49.6 | 42.5 | 26.4 |
| extractable part | 90.3 | 87.9 | 89.2 | 74.9 | 64.5 | 53.4 | 43.8 | 36.6 | 22.3 |
| radioactivity assigned to ethofumesate | 88.2 | 85.5 | 88.8 | 74.4 | 63 | 52.5 | 43.5 | 36.1 | 21.4 |
| non extractable part, radioactivity assigned to metabolites (sum) | 0.7 | 1.1 | 1.2 | 1.6 | 1.5 | 2.9 | 5.7 | 5.9 | 4.1 |
| sediment (sum) | 6 | 11.4 | 10.6 | 22.5 | 31.5 | 40.4 | 44.5 | 48.4 | 58.4 |
| extrectable part | 5.9 | 11.2 | 10.4 | 22 | 30.8 | 38.8 | 39.5 | 36.4 | 31.6 |
| radioactivity assigned to ethofumesate | 5.6 | 10.7 | 10.2 | 21.8 | 30.2 | 37.7 | 38.6 | 35.2 | 29.9 |
| bound residue | 0 | 0.2 | 0.2 | 0.1 | 0.2 | 1.6 | 5 | 12.1 | 26.9 |
| carbon dioxide | 0 | 0 | 0 | 0 | 0 | 0.1 | 0.6 | 1.5 | 5.7 |
| volatile substances | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.1 |
| recovery | 97 | 100.3 | 101 | 99 | 97.6 | 96.8 | 94.7 | 92.5 | 90.6 |
| test substance (sum) | 93.8 | 96.2 | 98.9 | 96.2 | 93.2 | 90.2 | 82 | 71.3 | 51.3 |
| not classified radioactivity | 2.5 | 2.9 | 0.6 | 0.7 | 2.1 | 2 | 1.2 | 1.7 | 2.6 |

The dissipation half-lives of ethofumesate from the water phases in Waldwinkel and Ruckhaltebecken were 7 (6 - 9) and 50 (42 - 58) days, respectively. For the whole systems, the half-lives were extrapolated to 285 (CL 241 - 329) and 242 (CL 223 - 262) days, according to a Timme model based on the root function of first order.

The microbial biomass of the sediments was 23 and 15 mg/100 g dw in Waldwinkel and Ruckhaltebecken, respectively, at start of the incubation. At termination of the incubation, the corresponding values were 20 and 11 mg/100 g dw.

Comments RMS

The experiment was set up in duplicates but only the mean values reported. The study is valid.

Degradation kinetics for the water and the sediment compartment were re-evaluated by the RMS according to level-I recommendations in FOCUS (2006). For the Waldwinkel study, for the sediment compartment no reliable kinetics could be determined.

System Rückhaltebecken

| Compartment | kinetics | Ethofumesate | | |
|--------------------------|----------|--------------|------|------------------|
| | | DT50 | DT90 | Chi ² |
| | | [d] | [d] | |
| Total system degradation | SFO | 250 | 830 | 1.4 |
| Water dissipation | DFOP | 52 | 457 | 2.4 |
| Sediment dissipation | SFO | 477 | 1584 | 0.5 |

System Waldwinkel

| Compartment | kinetics | Ethofumesate | | |
|--------------------------|----------|--------------|------|------------------|
| | | DT50 | DT90 | chi ² |
| | | [d] | [d] | |
| Total system degradation | SFO | 294 | 976 | 2.3 |
| Water dissipation | DFOP | 7.8 | 101 | 2.2 |
| Sediment dissipation | n.a. | 1000 | 1000 | n.a. |

The details of the kinetic evaluation are shown in the figure below

Figure 8-91: Kinetic evaluation experiment Rückhaltebecken. Water dissipation (SFO)

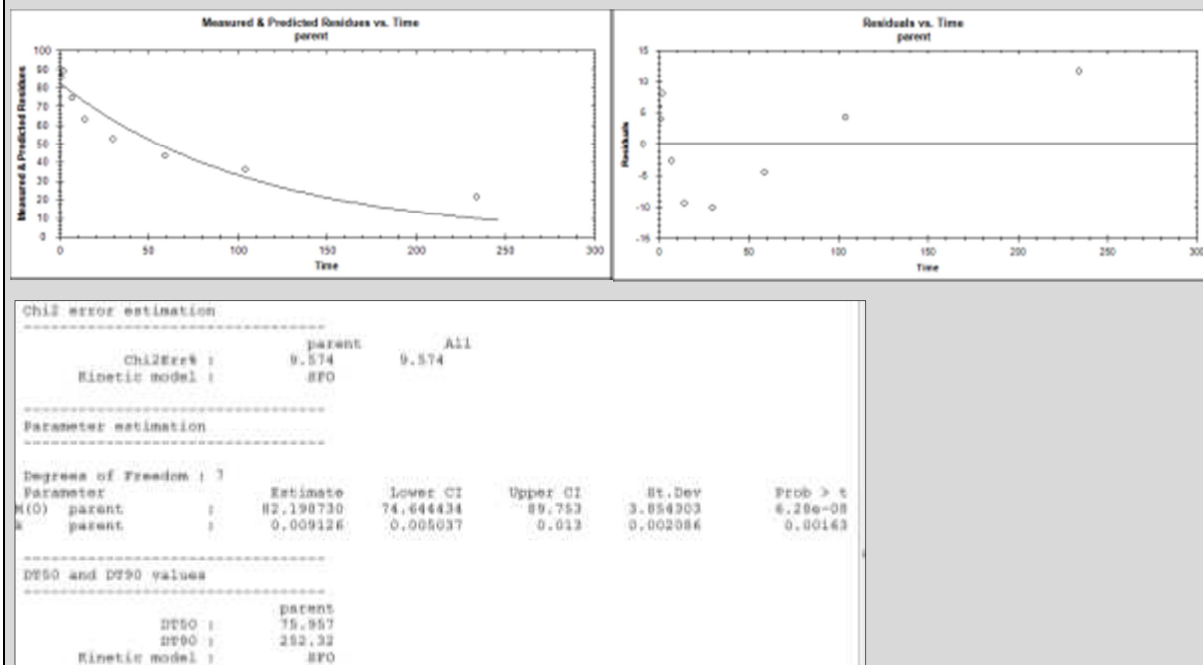


Figure 8-92: Kinetic evaluation experiment Rückhaltebecken. Water dissipation (FOMC)

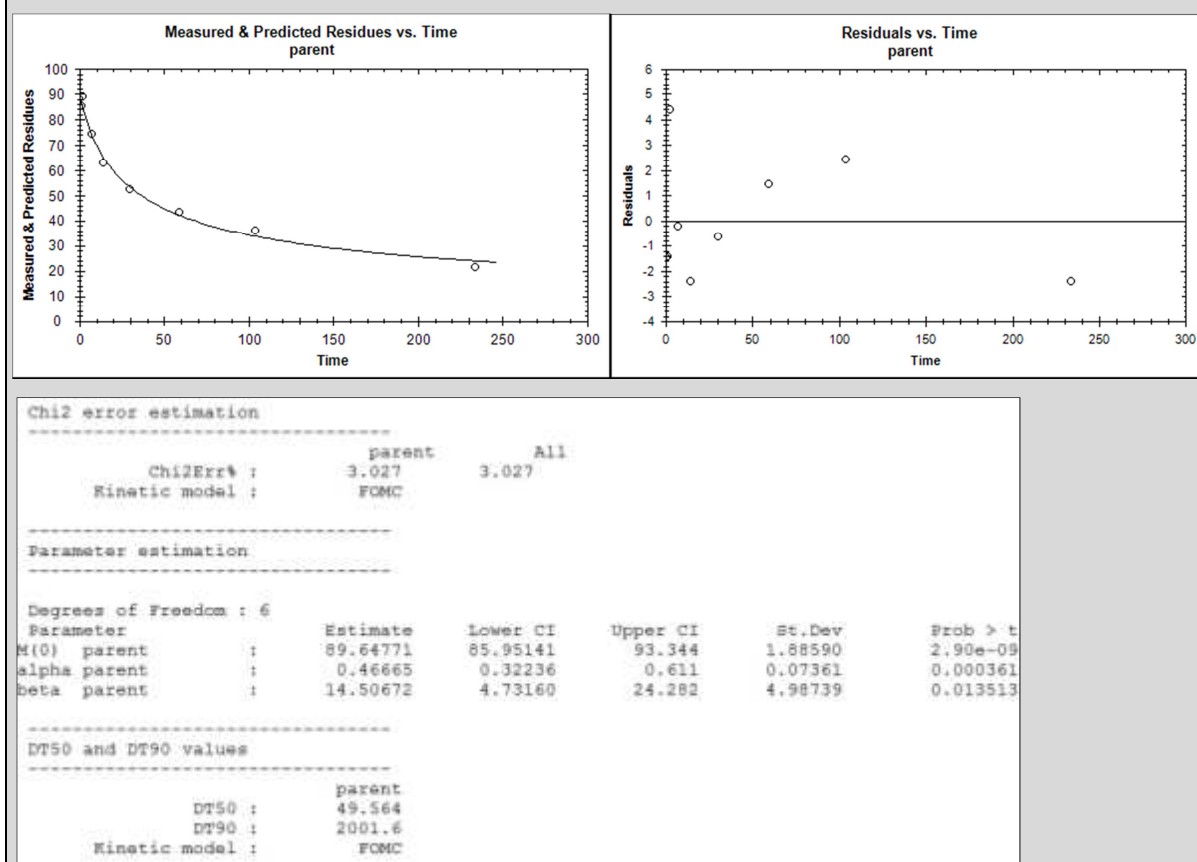
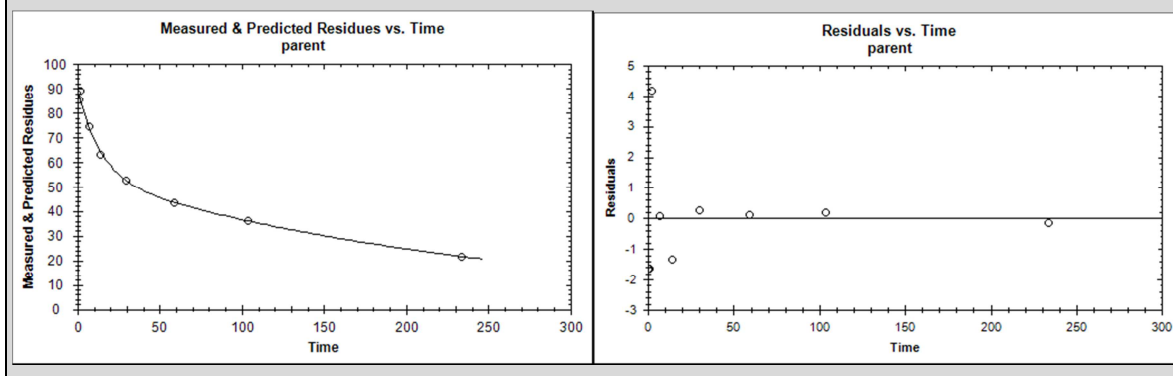


Figure 8-93: Kinetic evaluation experiment Rückhaltebecken. Water dissipation (DFOP)

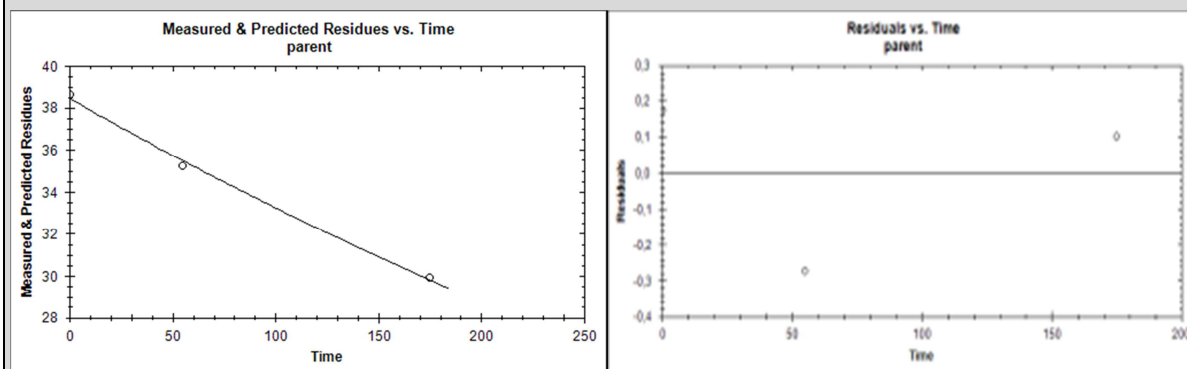


```

# Chi2 error estimation
# -----
#           parent      All
#   Chi2Err% :      2.421      2.421
#   Kinetic model :      DPOP
# -----
# Parameter estimation
# -----
# Degrees of Freedom : 5
# Parameter      Estimate      Lower CI      Upper CI      St.Dev      Prob > t
M(0) parent :      8.983e+01      8.688e+01      92.779      1.505e+00      1.25e-08
k1 parent :      7.114e-02      3.975e-02      0.103      1.601e-02      0.003375
k2 parent :      3.927e-03      2.571e-03      0.005      6.919e-04      0.001182
q parent :      3.987e-01      3.093e-01      0.488      4.563e-02      0.000163
# -----
# DT50 and DT90 values
# -----
#           parent
#   DT50 :      52.036
#   DT90 :      456.81
#   Kinetic model :      DPOP

```

Figure 8-94: Kinetic evaluation experiment Rückhaltebecken. Sediment dissipation (SFO)

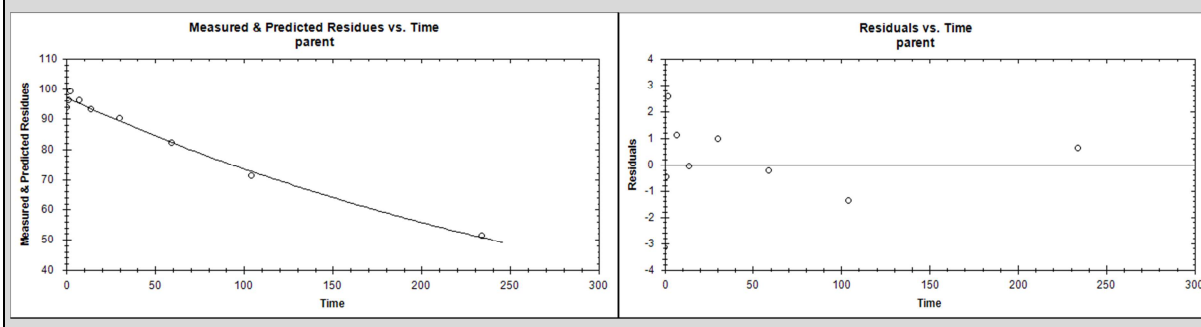


```

# Chi2 error estimation
# -----
#           parent      All
#   Chi2Err% :      0.5028      0.5028
#   Kinetic model :      SFO
# -----
# Parameter estimation
# -----
# Degrees of Freedom : 1
# Parameter      Estimate      Lower CI      Upper CI      St.Dev      Prob > t
M(0) parent :      3.843e+01      3.785e+01      39.001      2.933e-01      0.00243
k parent :      1.453e-03      1.291e-03      0.002      9.275e-05      0.01810
# -----
# DT50 and DT90 values
# -----
#           parent
#   DT50 :      476.96
#   DT90 :      1584.4
#   Kinetic model :      SFO

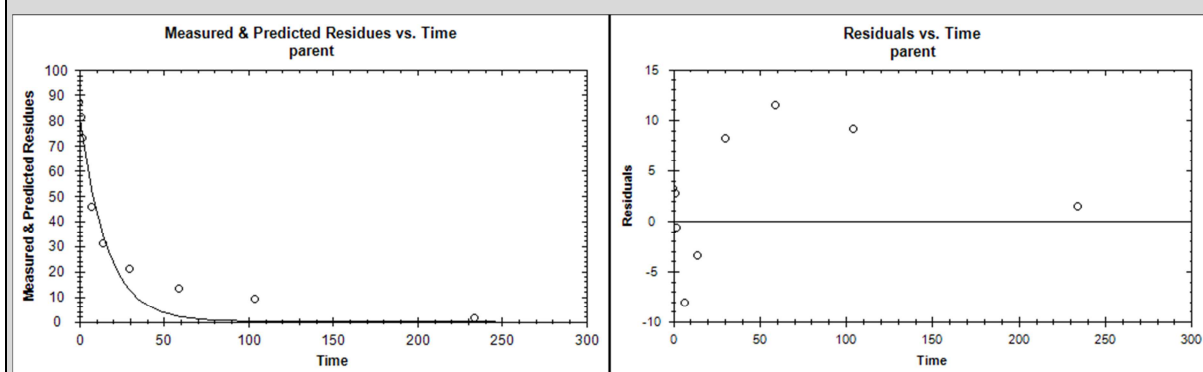
```

Figure 8-95: Kinetic evaluation experiment Rückhaltebecken. Whole system degradation (SFO)



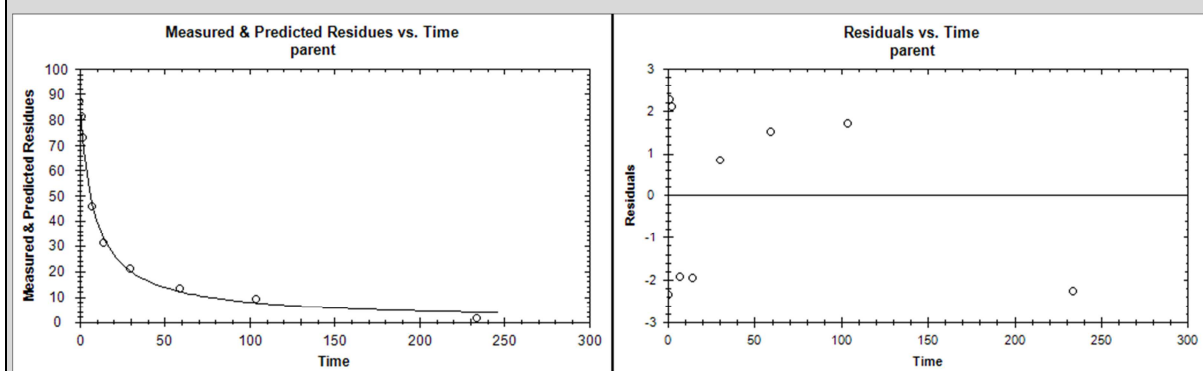
| | | | | | |
|------------------------|---------------|-----------|-----------|----------|-----------|
| Chi2 error estimation | | | | | |
| ----- | | | | | |
| | | parent | All | | |
| | Chi2Err% | 1.434 | 1.434 | | |
| | Kinetic model | SFO | | | |
| ----- | | | | | |
| Parameter estimation | | | | | |
| ----- | | | | | |
| Degrees of Freedom : 7 | | | | | |
| | Parameter | Estimate | Lower CI | Upper CI | St.Dev |
| M(0) | parent | 9.685e+01 | 9.549e+01 | 98.422 | 7.489e-01 |
| k | parent | 2.774e-03 | 2.512e-03 | 0.003 | 1.335e-04 |
| ----- | | | | | |
| DT50 and DT90 values | | | | | |
| ----- | | | | | |
| | | parent | | | |
| | DT50 | 249.90 | | | |
| | DT90 | 830.14 | | | |
| | Kinetic model | SFO | | | |

Figure 8-96: Kinetic evaluation experiment Waldwinkel. Water dissipation (SFO)



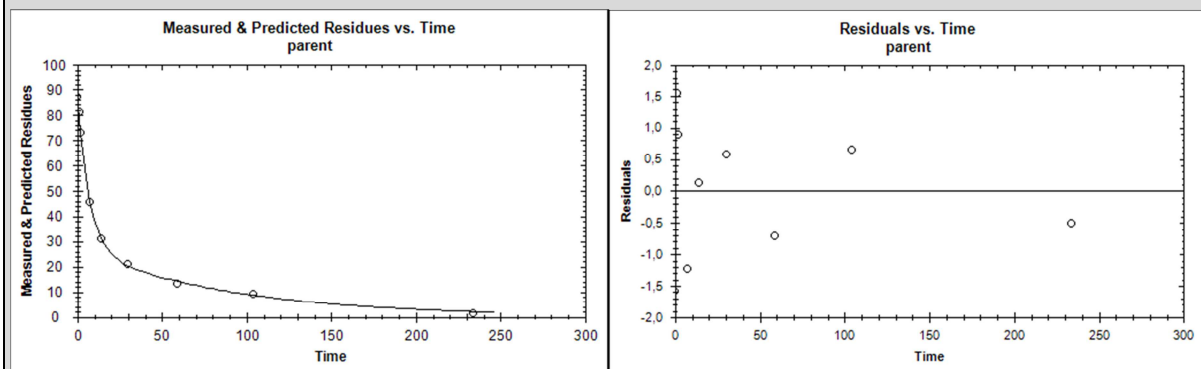
| | | | | | |
|------------------------|--------|----------|----------|----------|---------|
| Chi2 error estimation | | | | | |
| ----- | | | | | |
| | | parent | All | | |
| Chi2Err% | : | 12.80 | 12.80 | | |
| Kinetic model | : | SFO | | | |
| ----- | | | | | |
| Parameter estimation | | | | | |
| ----- | | | | | |
| Degrees of Freedom : 7 | | | | | |
| Parameter | | Estimate | Lower CI | Upper CI | St.Dev |
| (0) | parent | 83.86172 | 74.82694 | 92.897 | 4.60967 |
| | parent | 0.06328 | 0.03766 | 0.089 | 0.01307 |
| ----- | | | | | |
| DT50 and DT90 values | | | | | |
| ----- | | | | | |
| | | parent | | | |
| DT50 | : | 10.954 | | | |
| DT90 | : | 36.388 | | | |
| Kinetic model | : | SFO | | | |

Figure 8-97: Kinetic evaluation experiment Waldwinkel. Water dissipation (FOMC)



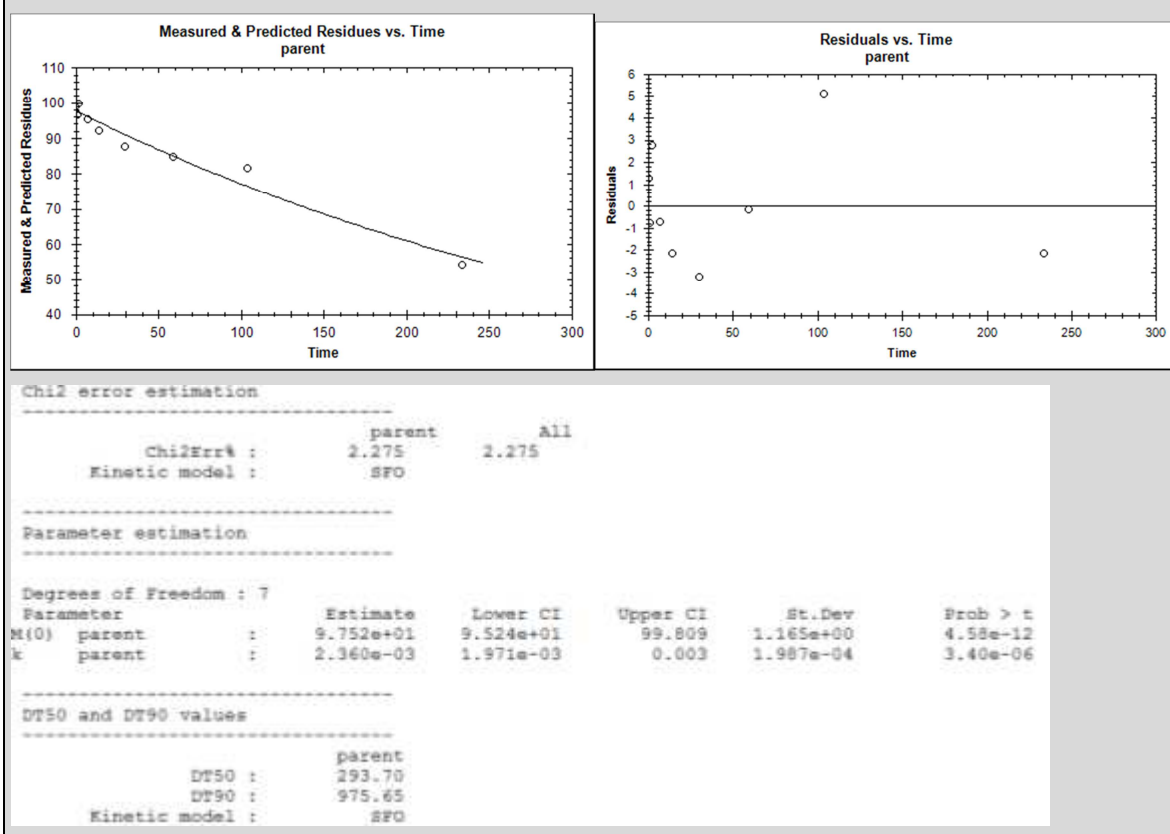
| | | | | | | |
|------------------------|---|----------|----------|----------|--------|----------|
| Chi2 error estimation | | | | | | |
| ----- | | | | | | |
| | | parent | All | | | |
| Chi2Err% | : | 4.034 | 4.034 | | | |
| Kinetic model | : | FOMC | | | | |
| ----- | | | | | | |
| Parameter estimation | | | | | | |
| ----- | | | | | | |
| Degrees of Freedom : 6 | | | | | | |
| Parameter | | Estimate | Lower CI | Upper CI | St.Dev | Prob > t |
| M(0) parent | : | 89.3502 | 84.9302 | 93.770 | 2.2551 | 8.64e-09 |
| alpha parent | : | 0.8904 | 0.6590 | 1.122 | 0.1181 | 0.000141 |
| beta parent | : | 6.8455 | 3.3380 | 10.153 | 1.6875 | 0.003338 |
| ----- | | | | | | |
| DT50 and DT90 values | | | | | | |
| ----- | | | | | | |
| | | parent | | | | |
| DT50 | : | 8.0644 | | | | |
| DT90 | : | 84.031 | | | | |
| Kinetic model | : | FOMC | | | | |

Figure 8-98: Kinetic evaluation experiment Waldwinkel. Water dissipation (DFOP)



```
# Chi2 error estimation
# -----
#
#           parent      All
# Chi2Err% :      2.198      2.198
# Kinetic model :      DFOP
#
# -----
# Parameter estimation
# -----
#
# Degrees of Freedom : 5
#
# Parameter      Estimate      Lower CI      Upper CI      St.Dev      Prob > t
M(0) parent      :      88.573320      86.401196      90.745      1.108247      2.91e-09
k1 parent      :      0.147368      0.121330      0.173      0.013285      5.19e-05
k2 parent      :      0.011131      0.007422      0.015      0.001892      0.00101
q parent      :      0.692920      0.627890      0.758      0.033179      2.33e-06
#
# -----
# DT50 and DT90 values
# -----
#
#           parent
# DT50 :      7.8300
# DT90 :      100.79
```

Figure 8-99: Kinetic evaluation experiment Waldwinkel. Whole system degradation (SFO)



| | |
|---------------------|--|
| Reference: | [Phenyl-UL-14C]Ethofumesate:Aerobic aquatic metabolism |
| Notifier: | Taskforce |
| Author(s), year: | Stupp, H. P. Weuthen, M.;2012 |
| Report/Doc. number: | A87605 / W 505-1 / M-443554-01-1 |
| Guideline(s): | OECD 308 |
| | US EPA OCSPP Test Guidelines No. 835.4300 and 835.4400 |
| GLP: | Yes |
| Deviations: | |
| Validity: | Valid |
| Status: | New study |

MATERIALS AND METHODS

Materials :

| | |
|---------------------|--|
| Test Material : | [Phenyl-UL- ¹⁴ C]Ethofumesate |
| Spec. Radioactivity | 3.78 MBq/mg |

Water / Sediment Test Systems :

The study was carried out with natural water/sediment systems from two locations:

Anglersee (Leverkusen, Germany): This small lake is a reclaimed gravel-pit, which is used for fishing only. The lake is entirely enclosed by a fence.

Hoenniger Weiher (close to Wipperfuerth, Germany): This is an artificially dammed pond in the course of the "Hoenniger Creek" forming "Hoenniger Weiher". On account of its in- and outlet the pond (about 1000 m² in surface area) has strong water current.

Table 8-173: Water characteristic

| Properties of Waters | | |
|--|------------------|-------------------------|
| Parameter | Anglersee | Hoenniger Weiher |
| Temperature [°C] ¹ | 1.0 | 1.0 |
| pH ¹ | 8.6 | 7.2 |
| Total Organic Carbon (TOC) [mg/L] ^{2,3} | < 2 / 3 / 6 | < 2 / 12 / 25 |
| Redox Potential E _h [mV] ^{1,5} | + 435 | + 523 |
| Oxygen Content [%] ¹ | 95 | 96 |

Table 8-174: Sediment characteristics

| Properties of Sediments | | |
|--|--|--|
| Parameter | Anglersee | Hoenniger Weiher |
| Geographic Location | Leverkusen North Rhine-Westphalia, Germany | Wasserfuhr, close to Wipperfuerth North Rhine-Westphalia, Germany |
| Soil Taxonomic Classification (USDA) | Sand | Loamy Sand |
| Sand (2000 – 50 µm) [%] | 95 | 77 |
| Silt (< 50 – 2 µm) [%] | 5 | 23 |
| Clay (< 2 µm) [%] | 0 | 0 |
| pH ¹ | 7.6 | 7.4 |
| pH | 6.8 (CaCl ₂); 7.0 (H ₂ O) | 6.3 (CaCl ₂); 6.5 (H ₂ O) |
| Organic Matter [%] ^{2,3,4} | 0.48 / 0.38 / 7.26 | 2.6 / 2.69 / 2.57 |
| Organic Carbon [%] ^{2,3} | 0.28 / 0.22 / 4.21 | 1.51 / 1.56 / 1.49 |
| Soil Microbial Activity [mg CO ₂ /h/kg sediment (dry weight)] ^{2,3} | 3.75 / 2.08 / 0.83 | 16.25 / 12.50 / 5.42 |
| Cation Exchange Capacity [meq/100 g] ² | 3.5 | 6.3 |
| Redox Potential E _h [mV] ^{1,5} | + 355 | + 469 |
| Moisture [g H ₂ O ad 100 g dry weight] | 23.9 | 50.1 |

¹ day of sampling

² start of acclimation

³ DAT-0 / DAT-125

⁴ %organic matter = %organic carbon x 1.724

⁵ Potential difference between used electrode* and H₂-electrode at 20°C: 210 mV

Theoretical potential of used buffer solution for Pt-Ag/AgCl electrode at 25°C: 220 mV

Methods :

Study design

The test system consisted of special cylindrical glass container (volume about 1000 mL, inner diameter about 10.5 cm, surface area about 86.6 cm², see Figure 4). The vessels were fitted with solid trap attachments

permeable for oxygen but absorbing volatile compounds formed in the test systems to soda lime (CO₂) and polyurethane foam (organic volatiles).

For preparation of the test systems, wet sediment with a mass equivalent to a volume of 175 mL was weighed into each flask and 520 mL of the corresponding water were added. The volume ratio of water to sediment used was approximately 3:1 with a sediment layer of about 2 cm. The flasks were then fitted with trap attachments, stoppers and stirrers.

For acclimation of the test systems and for establishment of phase separation, the test systems were stored under the intended study incubation conditions for 19 days prior to application.

Experimental Conditions:

The test vessels were incubated in a climatic cabinet at about 20.0°C in the dark. Maintenance of aerobic conditions was achieved by a slight continuous movement of the water surface and the use of “open” test systems (so-called bio-meter flasks) with solid trap attachments permeable for air.

Sampling:

Duplicate samples of both test systems were taken and analyzed after 0, 3, 7, 22, 30, 65, 93 and 125 days of incubation

Analytical Procedures :

The water layers were decanted and centrifuged. The volumes of the water layers were determined and aliquots thereof were analyzed by liquid scintillation counting (LSC) to measure the radioactivity content. From day 3 onwards, aliquots of the water phases were taken before to determine the dissolved amount of CO₂. The sediment samples were extracted three times with 80 mL acetonitrile/water (80:20, v:v) at ambient temperature and once under reflux conditions with 80 mL acetonitrile/water (80:20, v:v), too. All extracts were combined and analyzed by LSC. Concentrates of the water layers and the organic extracts were analyzed by high performance liquid chromatography with radiodetection (HPLC/radiodetection) to quantify the test item as well as possible transformation products.

The exhaustive extracted sediment phases were air-dried, homogenized and combusted in an oxidizer. The evolved CO₂ was trapped in a scintillation cocktail and measured by LSC to determine the amounts of non-extractable residues (NERs). At the last sampling date, sediment aliquots were used to determine the amount of CO₂ trapped in the sediment as well as for a further characterization of the non-extractable residues.

RESULT AND DISCUSSION

Mass balance and Distribution of Radioactivity :

Table 8-175: Material balance and Biotransformation Angler See in % of AR

| Compound | Source | Mean | DAT | | | | | | | |
|---------------------------------|---------------|------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
| | | | 0 | 3 | 7 | 22 | 30 | 65 | 93 | 125 |
| Ethofumesate | Water Layer | Mean | 98.1 | 76.6 | 72.8 | 61.6 | 58.7 | 36.8 | 26.2 | 22.0 |
| | Sediment | Mean | 1.1 | 15.8 | 18.9 | 25.5 | 28.3 | 23.9 | 17.9 | 14.2 |
| | Entire System | Mean | 99.3 | 92.4 | 91.7 | 87.2 | 87.0 | 60.7 | 44.1 | 36.2 |
| NC 20645 (AE C639175) | Water Layer | Mean | n.d. | 1.4 | 1.7 | 2.5 | 1.1 | 4.8 | 2.8 | 3.7 |
| | Sediment | Mean | n.d. | 0.1 | 0.4 | n.d. | 2.6 | 1.4 | 0.7 | n.d. |
| | Entire System | Mean | n.d. | 1.5 | 2.1 | 2.5 | 3.7 | 6.2 | 3.5 | 3.7 |
| u2 | Water Layer | Mean | n.d. | n.d. | n.d. | n.d. | 0.8 | n.d. | n.d. | n.d. |
| | Sediment | Mean | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| | Entire System | Mean | n.d. | n.d. | n.d. | n.d. | 0.8 | n.d. | n.d. | n.d. |
| u3 | Water Layer | Mean | n.d. | n.d. | n.d. | n.d. | n.d. | 1.1 | 0.7 | n.d. |
| | Sediment | Mean | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| | Entire System | Mean | n.d. | n.d. | n.d. | n.d. | n.d. | 1.1 | 0.7 | n.d. |
| u4 | Water Layer | Mean | n.d. | n.d. | n.d. | n.d. | n.d. | 2.0 | 3.8 | 2.6 |
| | Sediment | Mean | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| | Entire System | Mean | n.d. | n.d. | n.d. | n.d. | n.d. | 2.0 | 3.8 | 2.6 |
| u5 | Water Layer | Mean | n.d. | n.d. | n.d. | n.d. | n.d. | 0.3 | n.d. | 1.8 |
| | Sediment | Mean | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| | Entire System | Mean | n.d. | n.d. | n.d. | n.d. | n.d. | 0.3 | n.d. | 1.8 |
| u6 | Water Layer | Mean | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 0.7 | 3.0 |
| | Sediment | Mean | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| | Entire System | Mean | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 0.7 | 3.0 |
| u7 | Water Layer | Mean | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 0.9 | 0.7 |
| | Sediment | Mean | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| | Entire System | Mean | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 0.9 | 0.7 |
| u8 | Water Layer | Mean | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 2.8 |
| | Sediment | Mean | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| | Entire System | Mean | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 2.8 |
| Total Extractable Residues * | Water Layer | Mean | 98.1 | 78.0 | 74.5 | 64.2 | 60.5 | 45.1 | 35.1 | 36.6 |
| | Sediment | Mean | 1.1 | 15.8 | 19.3 | 25.5 | 30.9 | 25.3 | 18.6 | 14.2 |
| | Entire System | Mean | 99.3 | 93.7 | 93.7 | 89.7 | 91.5 | 70.3 | 53.7 | 50.8 |
| ¹⁴ CO ₂ # | | Mean | n.a. | 0.1 | 0.1 | 0.1 | 0.3 | 2.8 | 8.5 | 15.3 |
| Organic Volatiles # | | Mean | n.a. | < 0.1 | < 0.1 | < 0.1 | < 0.1 | 0.1 | < 0.1 | < 0.1 |
| Non-Extractable Residues # | | Mean | 0.2 | 1.6 | 2.1 | 5.3 | 4.9 | 21.4 | 32.8 | 43.2 |
| Total Recovery * | | Mean | 99.4 | 95.4 | 95.9 | 95.1 | 96.7 | 94.7 | 94.9 | 109.3 |

n.d.: not detected, n.a.: not analyzed, DAT: days after treatment, SD: standard deviation

* Difference to Material Balance values due to rounding errors as well as clean up and chromatographic losses

Values taken from Material Balance Tables

Table 8-176: Material balance and Biotransformation Hönniger Weiher in % of AR

| Compound | Source | Mean SD | DAT | | | | | | | |
|--------------------------|---------------|------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
| | | | 0 | 3 | 7 | 22 | 30 | 65 | 93 | 125 |
| Ethofumesate | Water Layer | Mean | 96.4 | 66.3 | 56.7 | 37.7 | 34.5 | 19.5 | 18.1 | 10.5 |
| | Sediment | Mean | 2.4 | 27.3 | 35.4 | 50.1 | 50.3 | 50.2 | 50.0 | 35.9 |
| | Entire System | Mean | 98.8 | 93.6 | 92.1 | 87.8 | 84.8 | 69.8 | 68.1 | 46.4 |
| NC 20645 (AE C639175) | Water Layer | Mean | n.d. | 1.1 | 1.4 | 1.9 | 0.5 | 8.6 | 10.3 | 13.8 |
| | Sediment | Mean | n.d. | n.d. | 0.5 | 0.3 | 3.8 | 3.3 | 4.4 | 5.1 |
| | Entire System | Mean | n.d. | 1.1 | 1.9 | 2.2 | 4.3 | 11.9 | 14.7 | 18.8 |
| u3 | Water Layer | Mean | n.d. | n.d. | n.d. | n.d. | n.d. | 0.5 | 0.6 | 0.5 |

| | | | | | | | | | | |
|--------------------------------------|---------------|------|------|-------|-------|-------|-------|------|-------|-------|
| | Sediment | Mean | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| | Entire System | Mean | n.d. | n.d. | n.d. | n.d. | n.d. | 0.5 | 0.6 | 0.5 |
| u4 | Water Layer | Mean | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 0.3 |
| | Sediment | Mean | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| | Entire System | Mean | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 0.3 |
| u5 | Water Layer | Mean | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 0.5 |
| | Sediment | Mean | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| | Entire System | Mean | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 0.5 |
| u6 | Water Layer | Mean | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 0.7 |
| | Sediment | Mean | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| | Entire System | Mean | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 0.7 |
| Total Extractable Residues * | Water Layer | Mean | 96.4 | 67.4 | 58.1 | 39.6 | 35.0 | 28.7 | 29.0 | 26.3 |
| | Sediment | Mean | 2.4 | 27.3 | 35.9 | 50.4 | 54.1 | 53.5 | 54.4 | 40.9 |
| | Entire System | Mean | 98.8 | 94.7 | 94.0 | 90.0 | 89.1 | 82.2 | 83.4 | 67.2 |
| ¹⁴CO₂ # | | Mean | n.a. | < 0.1 | < 0.1 | 0.1 | 0.2 | 0.9 | 1.9 | 5.3 |
| Organic Volatiles # | | Mean | n.a. | < 0.1 | < 0.1 | < 0.1 | < 0.1 | 0.1 | < 0.1 | < 0.1 |
| Non-Extractable Residues # | | Mean | 0.2 | 2.4 | 3.6 | 6.0 | 7.9 | 11.3 | 13.1 | 25.7 |
| Total Recovery * | | Mean | 99.0 | 97.1 | 97.6 | 96.1 | 97.2 | 94.5 | 98.3 | 98.1 |

n.d.: not detected, n.a.: not analyzed, DAT: days after treatment, SD: standard deviation

* Difference to Material Balance values due to rounding errors as well as clean up and chromatographic losses

Values taken from Material Balance Table

Non-extractable and Extractable Residues:

The amount of extractable residues decreased from 99.3% / 99.8% of AR at DAT-0 to 50.8% / 67.2% of AR at the end of incubation for test systems Angler See and Hönniger Weiher, respectively. The amount of non-extractable residues increased from 0.2% / 0.2% of AR to 43.2% / 25.7% under the same conditions.

Due to the high formation rate of non-extractable residues a supplementary test with sterilized water/sediment systems was performed. Under sterile conditions significantly less NERs were formed (3.2% and 6.9% for Anglersee and Hönniger Weiher, respectively) indicated that the formation of bound residues was primarily not a matter of strong adsorption or binding of ethofumesate. The binding of ethofumesate and its transformation products is due to metabolism and irreversible enzyme-mediated binding to sediment or incorporation into microbial processes.

Mineralization :

The maximum amount of ¹⁴-CO₂ was 15.3% and 5.3% in the water sediment system Anger Weiher and Hönniger Weiher, respectively.

Transformation of Test Material and Transformation Products :

The dissipation time (DT₅₀) of ethofumesate from the water layer (sum of degradation and translocation processes into the sediment) was calculated to be 42.9 days for the Anglersee test systems and 10.0 days for the Hönniger Weiher test systems.

The degradation half-lives (DT_{50}) of ethofumesate in the entire water/sediment systems were calculated to be 89.1 days for the Anglersee test systems and 139.3 days for the Hoenniger Weiher test systems, respectively.

The major metabolite appearing in the test systems was NC20645 (AE C639175, K⁺ salt of ethofumesate-carboxylic acid). It was identified by HPLC co-chromatography with the primary chromatographic method and a confirmation method using a non-radiolabeled reference item. This metabolite amounted to a maximum of 6.2% AR (DAT-65) in the entire Anglersee water/sediment systems and to a maximum of 18.8% AR (DAT-125) in the entire Hoenniger Weiher water/sediment systems.

The maximum amounts of a single minor radioactivity zone in the entire Anglersee and Hoenniger Weiher water/sediment systems were 3.8% and 0.7% AR, respectively. Due to the low amounts of the minor metabolites, identification procedures were not performed.

Ethofumesate is a racemate of two enantiomers. In order to demonstrate the same behavior of both enantiomers, water and sediment fractions from both test systems (DAT-125) were isolated by the standard non-chiral HPLC. These fractions were analyzed with a chiral HPLC method. The chromatograms obtained for Ethofumesate (DAT-125) and for pure solutions of the enantiomers demonstrated that the ratio of the two enantiomers in water and in sediment did not change during the time of incubation.

Conclusion:

Ethofumesate was moderately fast degraded in 2 different water / sediment systems. The main metabolite was NC 20645 (ethofumesate carboxylic acid). In addition some minor metabolites were detected in low amounts (max. 3.8%). The behavior of the enantiomers is the same in water and in sediment.

Comments RMS

The study is valid. The kinetic evaluation is carried out in Chapple (2013).

| | |
|---------------------|--|
| Reference: | Kinetic evaluation of the degradation of ethofumesate in an aerobic water-sediment system |
| Notifier: | Taskforce |
| Author(s), year: | Chapple, A.C.;2013 |
| Report/Doc. number: | EnSa-13-0250 / M-459125-01-1 |
| Guideline(s): | Not applicable |
| GLP: | No |
| Deviations: | |
| Validity: | Valid |
| Status: | New study |

The degradation and dissipation behavior of ethofumesate in water-sediment systems was investigated by kinetic evaluation of an aerobic laboratory water-sediment study conducted with ^{14}C -labelled ethofumesate ([phenyl-UL- ^{14}C]-AE B049913) in two different test systems: a sand from Anglersee, Germany, and a loamy-sand from Hoenniger Weiher, Germany (Stupp and Weuthen, 2013).

According to the recommendations of FOCUS (2006), (Level I) dissipation half-lives of ethofumesate in water and sediment were determined as well as the degradation DT_{50} for the total systems. An overview over the arithmetic DT_{50} values for use as inputs in environmental fate models is given in as well as for use in assessing persistence endpoints. A Level II degradation assessment was attempted but the high correlations between the various transformation factors so derived were sufficiently high as to render the analysis invalid. (It is, however, reported in detail.)

Generally, where the evaluations were done using SFO kinetics, the persistence endpoints are equal to those for modeling purposes. Only in the case of the dissipation from the water phase did ethofumesate show a non-SFO behavior and consequently both modeling and persistence endpoints were obtained using different kinetic models, according to FOCUS (2006).

Total system Angler See:

Table 8-177: DT_{50} values for ethofumesate and its metabolite and results of statistical evaluation of the model fits using SFO kinetic for total system Anglersee

| Substance | DT_{50} | DT_{90} | χ^2 test | t-test probability | Visual acceptability | |
|---------------------------------------|---------------------------------------|------------------|---------------|--------------------|----------------------|----------|
| | | | | | Curve | Residues |
| Ethofumesate | 89.0 | 295.5 | 4.2 | <0.001 | ++ | + |
| Ethofumesate-carboxylic acid NC 20645 | 18.7 | 62.2 | 18.1 | <0.001 | + | - |
| Other details: | M_0 99.49; Formation fraction 0.385 | | | | | |

Total system Hönniger Weiher:

Table 8-178: DT_{50} values for ethofumesate and its metabolite and results of statistical evaluation of the model fits using SFO kinetic for total system Hoenniger Weiher [NR: not reliable]

| Substance | DT_{50} | DT_{90} | χ^2 test | t-test probability | Visual acceptability | |
|---------------------------------------|--|---------------------|---------------|--------------------|----------------------|----------|
| | | | | | Curve | Residues |
| Ethofumesate | 141.2 | 468.9 | 3.4 | <0.001 | + | ++ |
| Ethofumesate-carboxylic acid NC 20645 | >1000 ^{NR} | >1000 ^{NR} | 9.9 | 0.5 | ++ | + |
| Other details: | M_0 97.06; Formation fraction 0.416 ^{NR} Not Reliable | | | | | |

RESULT AND DISCUSSION

DT₅₀ values for ethofumesate in the entire system ranged from 89.0 to 141.2 days, with an arithmetic mean of 115.1 days.

The following figures and tables show the results of the kinetic evaluation carried out by the notifier.

Figure 8-100: Kinetic evaluation of the water/sediment study Anglersee (Ethofumesate, SFO, total system)

```
# -----
# Chi2 error estimation
# -----
          EthTot      AECTot      All
Chi2Err% :      4.243      18.094      6.218
Kinetic model :      SFO      SFO

# -----
# Parameter estimation
# -----

Degrees of Freedom : 27
Parameter      Estimate      Lower CI      Upper CI      St.Dev      Prob > t
M(0) EthTot    :      9.949e+01      9.615e+01      102.835      1.706e+00      < 2e-16
k   EthTot    :      7.791e-03      6.895e-03      0.009      4.571e-04      2.81e-16
k   AECTot    :      3.704e-02      1.977e-02      0.054      8.814e-03      0.000129
FF   EthTot -> AECTot :      0.3854      8.117e-02

# -----
# DT50 and DT90 values
# -----
          EthTot      AECTot
DT50 :      88.970      18.712
DT90 :      295.55      62.160
Kinetic model :      SFO      SFO
```

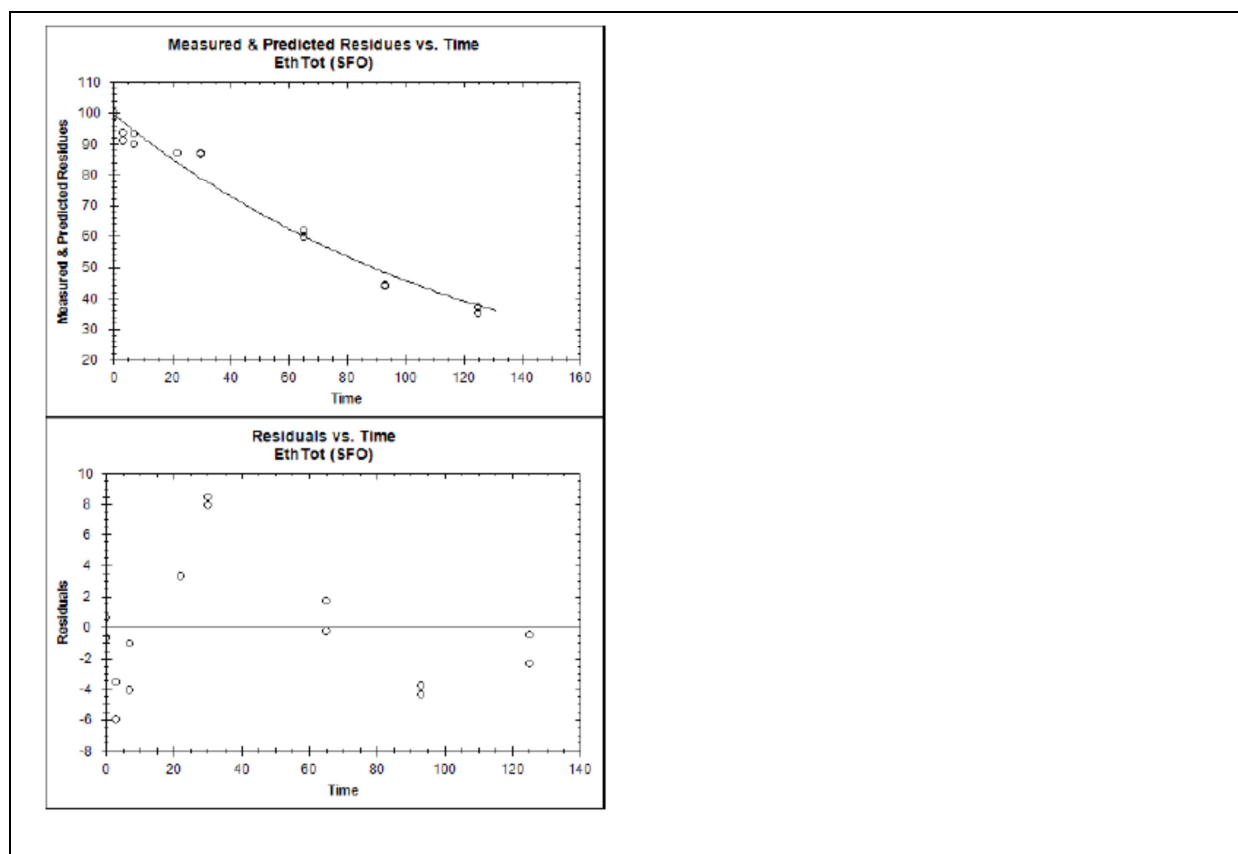


Figure 8-101: Kinetic evaluation of the water/sediment study Anglersee (Ethofumesate, SFO, water phase)

```

# -----
# Chi2 error estimation
# -----
          EthWat      All
Chi2Err% :      7.988      7.988
Kinetic model :      SFO

# -----
# Parameter estimation
# -----

Degrees of Freedom : 14
Parameter      Estimate      Lower CI      Upper CI      St.Dev      Prob > t
M(0) EthWat    :  85.804021    80.758805     90.849      2.574137     4.86e-15
k      EthWat    :   0.012778     0.010595      0.015      0.001114     8.32e-09

# -----
# DT50 and DT90 values
# -----
          EthWat
DT50 :      54.247
DT90 :     180.20
Kinetic model :      SFO

```

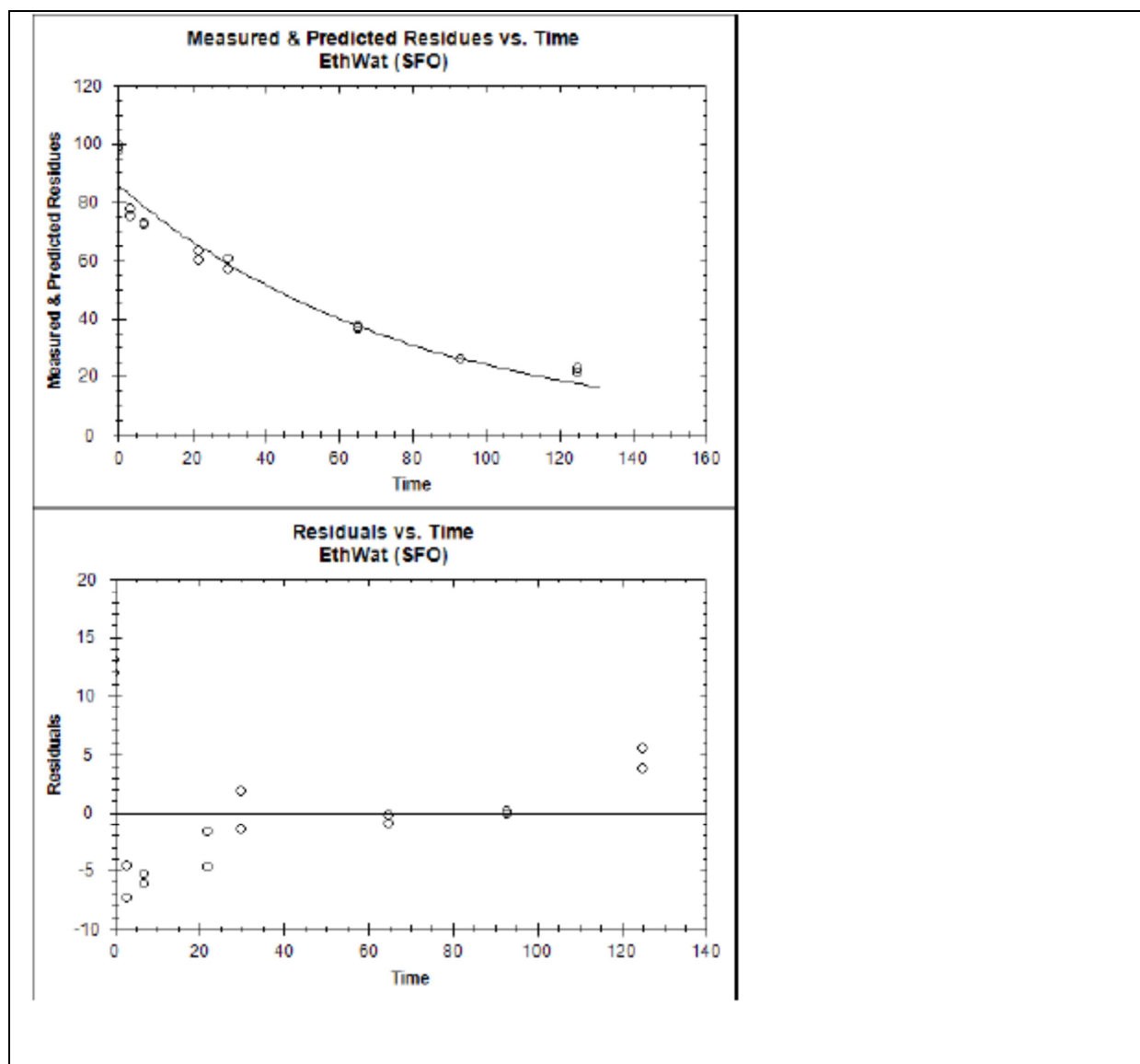


Figure 8-102: Kinetic evaluation of the water/sediment study Anglersee (Ethofumesate, DFOP, water phase)

```
# -----
# Chi2 error estimation
# -----
                EthWat      All
Chi2Err% :      2.264      2.264
Kinetic model :      DFOP

# -----
# Parameter estimation
# -----

Degrees of Freedom : 12
Parameter      Estimate      Lower CI      Upper CI      St.Dev      Prob > t
M(0) EthWat :    9.838e+01    9.888e+01    101.120    1.413e+00    < 2e-16
k1 EthWat :    1.833e+00    -1.362e+01    17.286    7.884e+00    0.41
k2 EthWat :    1.118e-02    1.032e-02    0.012    4.175e-04    2.34e-12
g EthWat :    1.955e-01    1.607e-01    0.230    1.773e-02    6.17e-08

# -----
# DT50 and DT90 values
# -----
                EthWat
DT50 :      42.668
DT90 :      187.05
Kinetic model :      DFOP
```

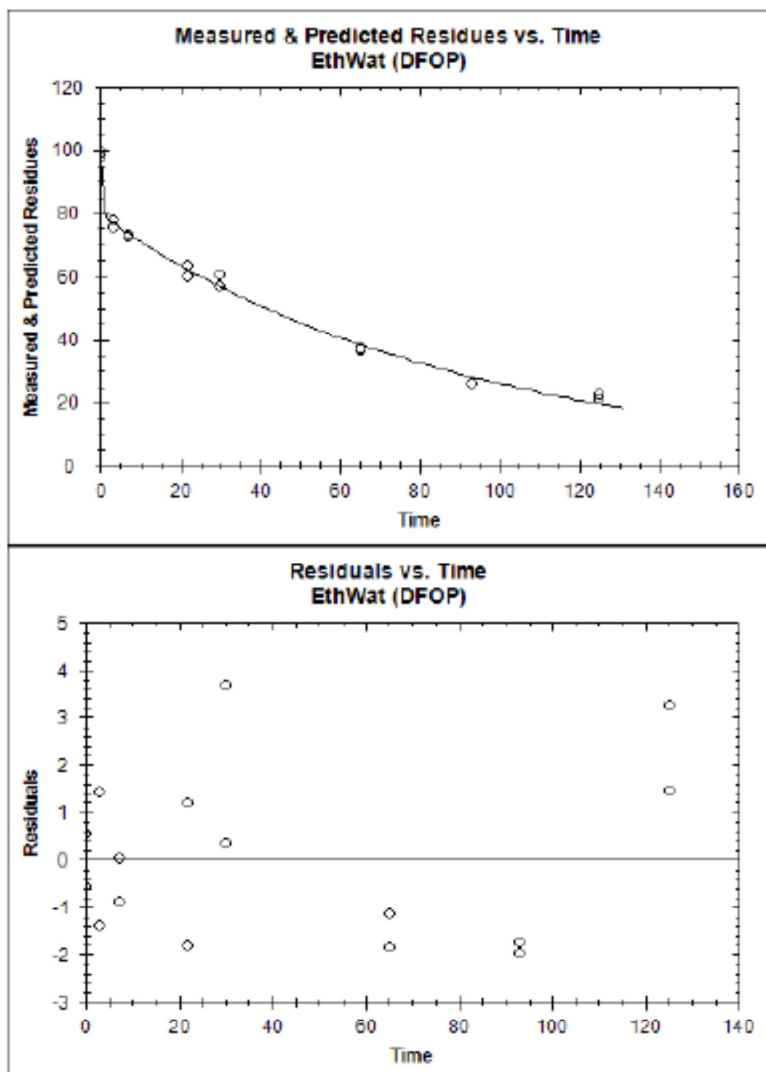



Figure 8-103: Kinetic evaluation of the water/sediment study Anglersee (NC20645, SFO, total system)

```

# -----
# Chi2 error estimation
# -----
                AECWat      All
Chi2Err% :      15.98      15.98
Kinetic model :      SFO

# -----
# Parameter estimation
# -----

Degrees of Freedom : 4
Parameter      Estimate      Lower CI      Upper CI      St.Dev      Prob > t
M(0) AECWat    :      6.156924    0.623981     11.690     2.822982     0.0473
k   AECWat    :      0.005310    -0.004539     0.015     0.005025     0.1751

# -----
# DT50 and DT90 values
# -----
                AECWat
DT50 :      130.54
DT90 :      433.65
Kinetic model :      SFO

```

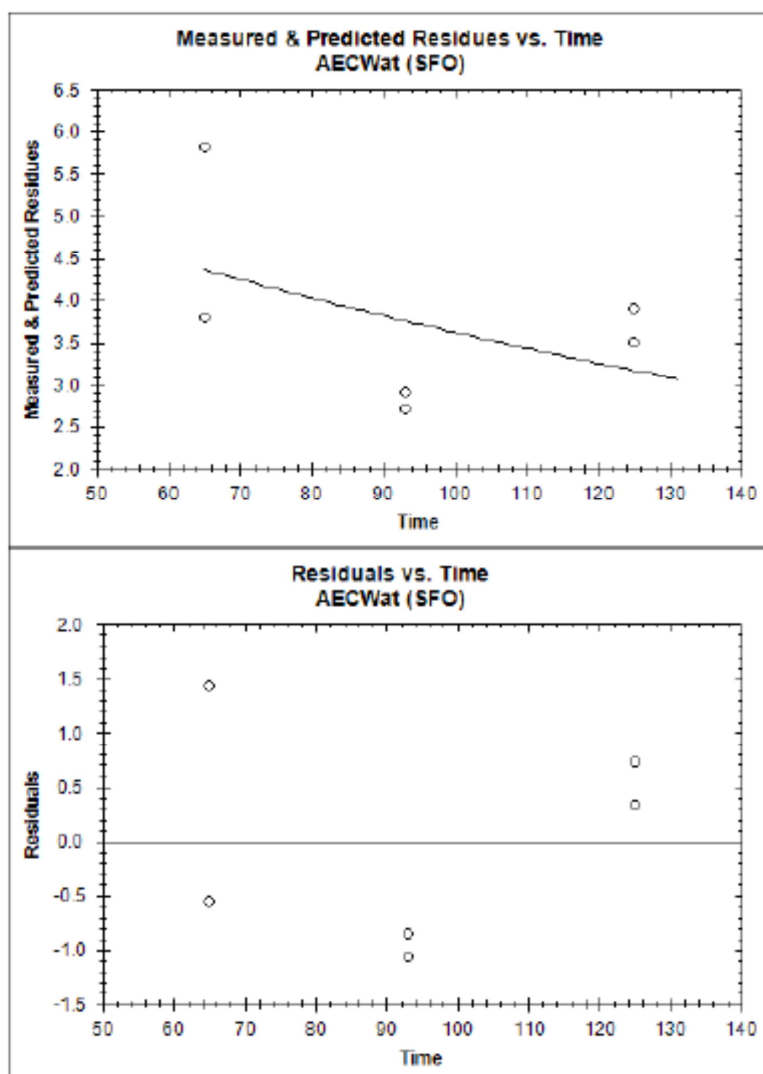


Figure 8-104: Kinetic evaluation of the water/sediment study Anglersee (Ethofumesate, SFO, sediment)

```

# -----
# Chi2 error estimation
# -----
#
#           Chi2Err% :      EthSed      All
#           Kinetic model :      SFO
#
# -----
# Parameter estimation
# -----
#
# Degrees of Freedom : 6
#
# Parameter      Estimate      Lower CI      Upper CI      St.Dev      Prob > t
# M(0) EthSed      :      3.586e+01      3.270e+01      39.030      1.616e+00      2.74e-07
# k      EthSed      :      7.206e-03      5.935e-03      0.008      6.486e-04      1.58e-05
#
# -----
# DT50 and DT90 values
# -----
#
#           EthSed
#           DT50 :      96.190
#           DT90 :      319.54

```

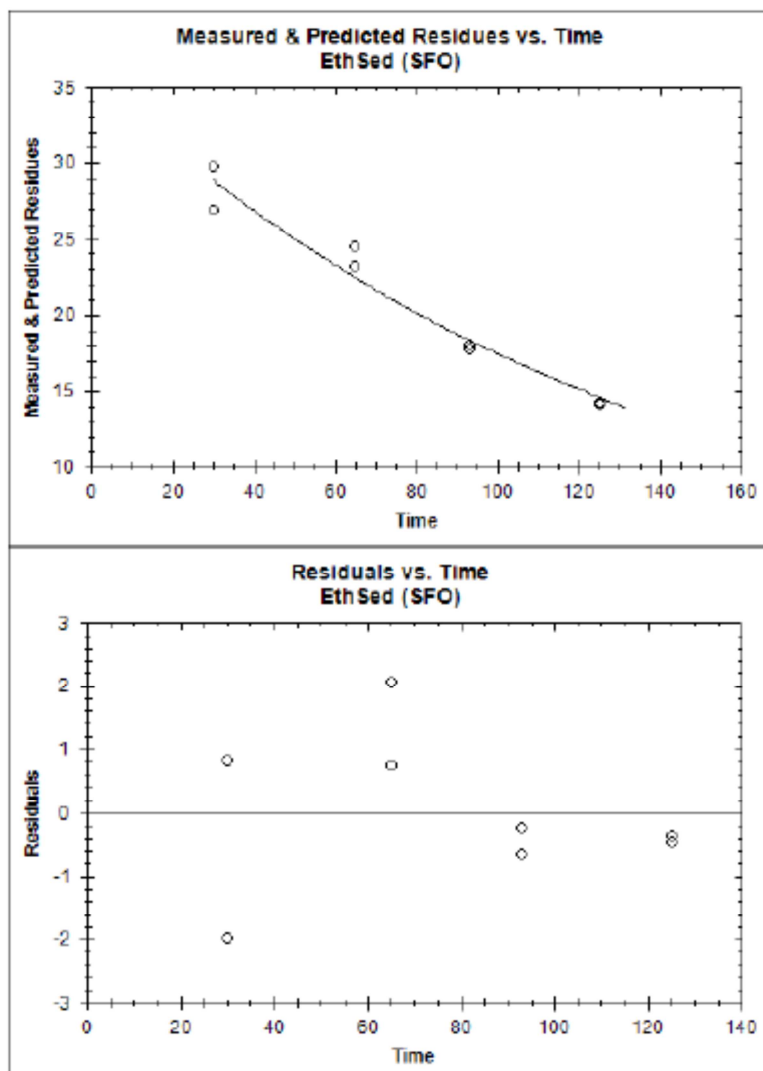


Figure 8-105: Kinetic evaluation of the water/sediment study Anglersee (NC20645, SFO, sediment)

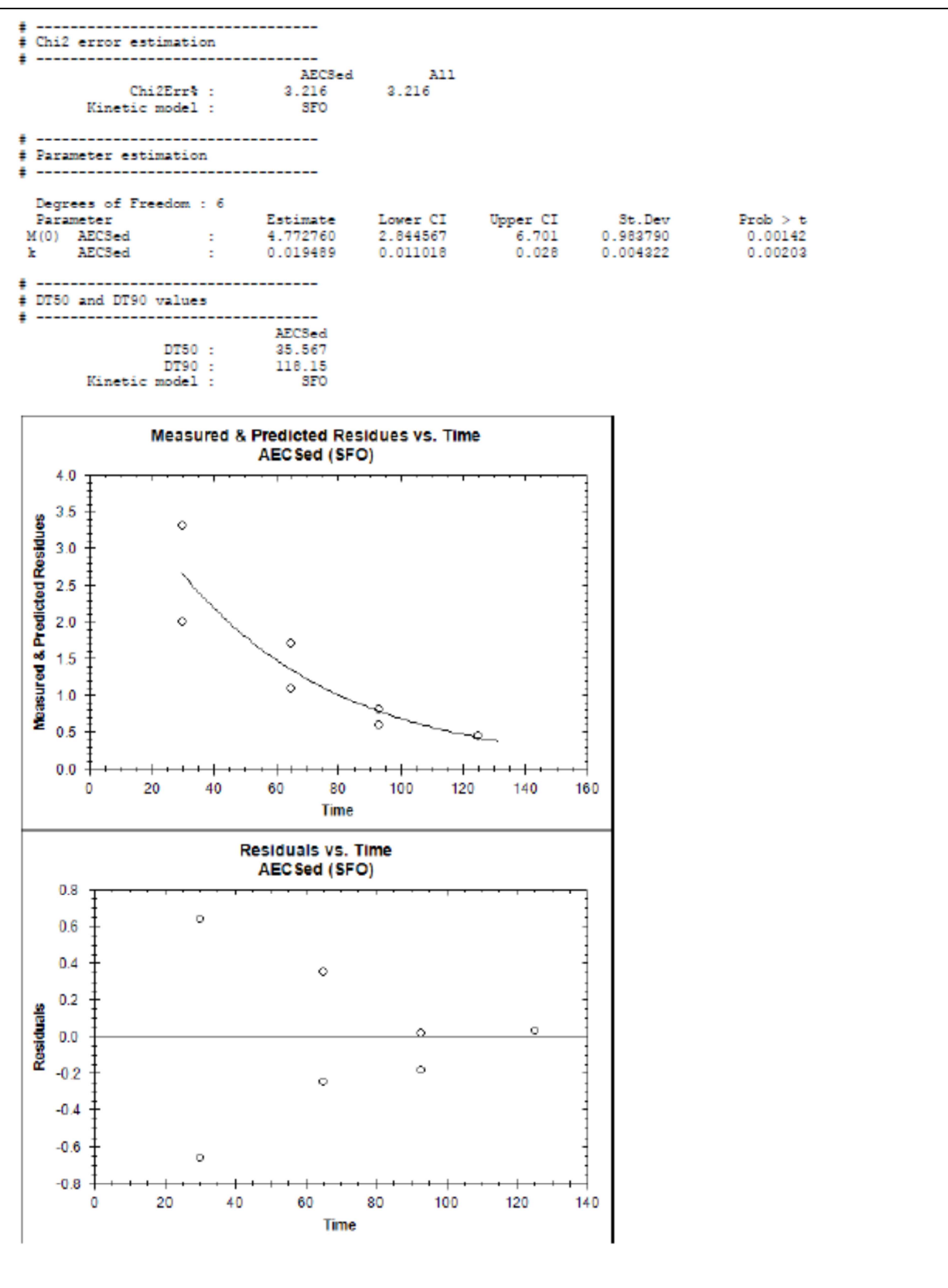


Figure 8-106: Kinetic evaluation of the water/sediment study Hönniger Weiher (Ethofumesate, SFO, total system)

```
# -----
# Chi2 error estimation
# -----
          EthTot    AECTot    All
Chi2Err% :      3.408      9.862      4.872
Kinetic model :      SFO      SFO

# -----
# Parameter estimation
# -----

Degrees of Freedom : 28
Parameter      Estimate    Lower CI    Upper CI    St.Dev    Prob > t
M(0) EthTot    : 9.706e+01    9.365e+01    100.456    1.735e+00    < 2e-16
k EthTot      : 4.911e-03    4.133e-03    0.006      3.967e-04    3.56e-13
k AECTot      : 2.191e-03    -4.337e-03    0.004      2.213e-03    0.5
FF EthTot -> AECTot : 0.4162    6.385e-02

# -----
# DT50 and DT90 values
# -----
          EthTot    AECTot
DT50 :      141.15    316390193
DT90 :      468.89    1051025471
Kinetic model :      SFO      SFO
```

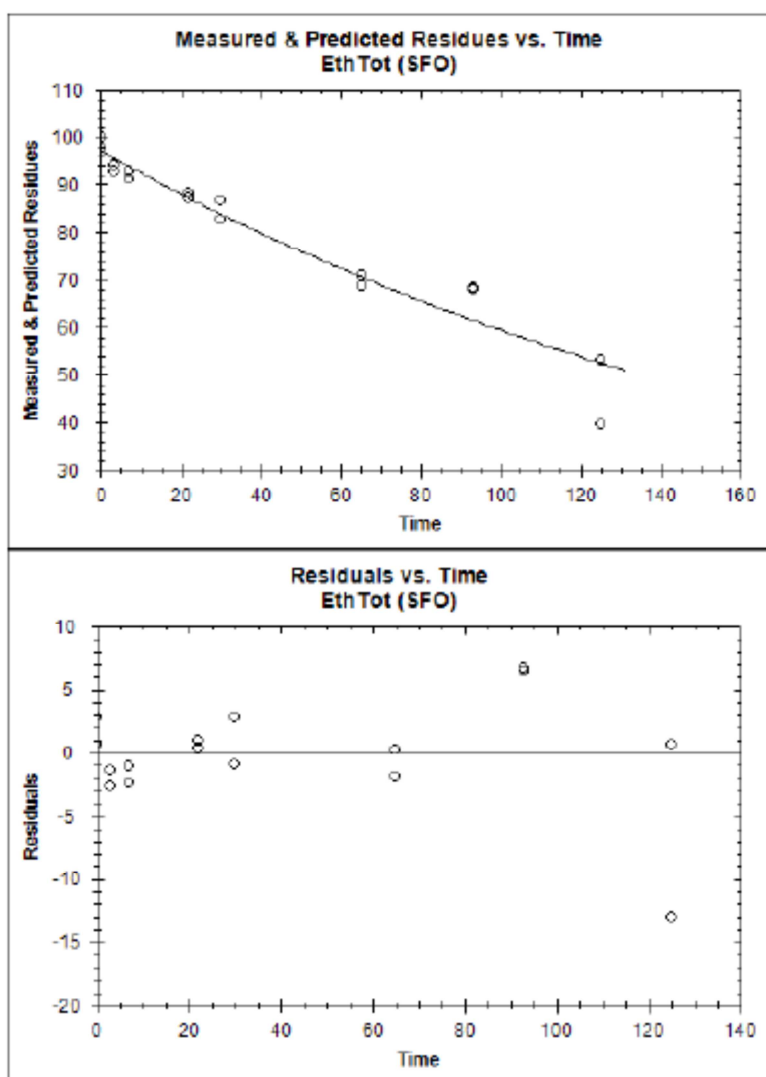


Figure 8-107: Kinetic evaluation of the water/sediment study Hönniger Weiher (Ethofumesate, SFO, water phase)

```

# -----
# Chi2 error estimation
# -----
          EthWat      All
Chi2Err% :      17.46      17.46
Kinetic model :      SFO

# -----
# Parameter estimation
# -----

Degrees of Freedom : 14
Parameter      Estimate      Lower CI      Upper CI      St.Dev      Prob > t
M(0) EthWat    :      79.488717      70.082049      88.895      4.799409      6.81e-11
k      EthWat    :      0.026139      0.017704      0.035      0.004304      1.43e-05

# -----
# DT50 and DT90 values
# -----
          EthWat
DT50 :      26.518
DT90 :      88.090
Kinetic model :      SFO

```

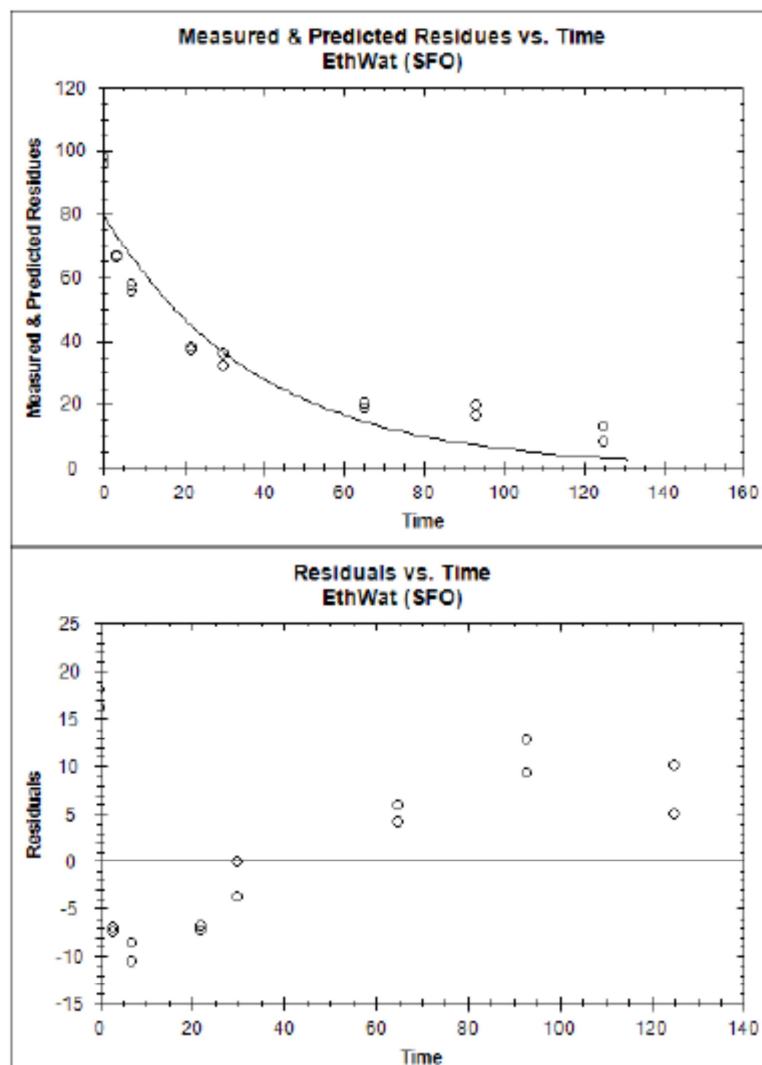


Figure 8-108: Kinetic evaluation of the water/sediment study Hönniger Weiher (Ethofumesate, DFOP, water phase)

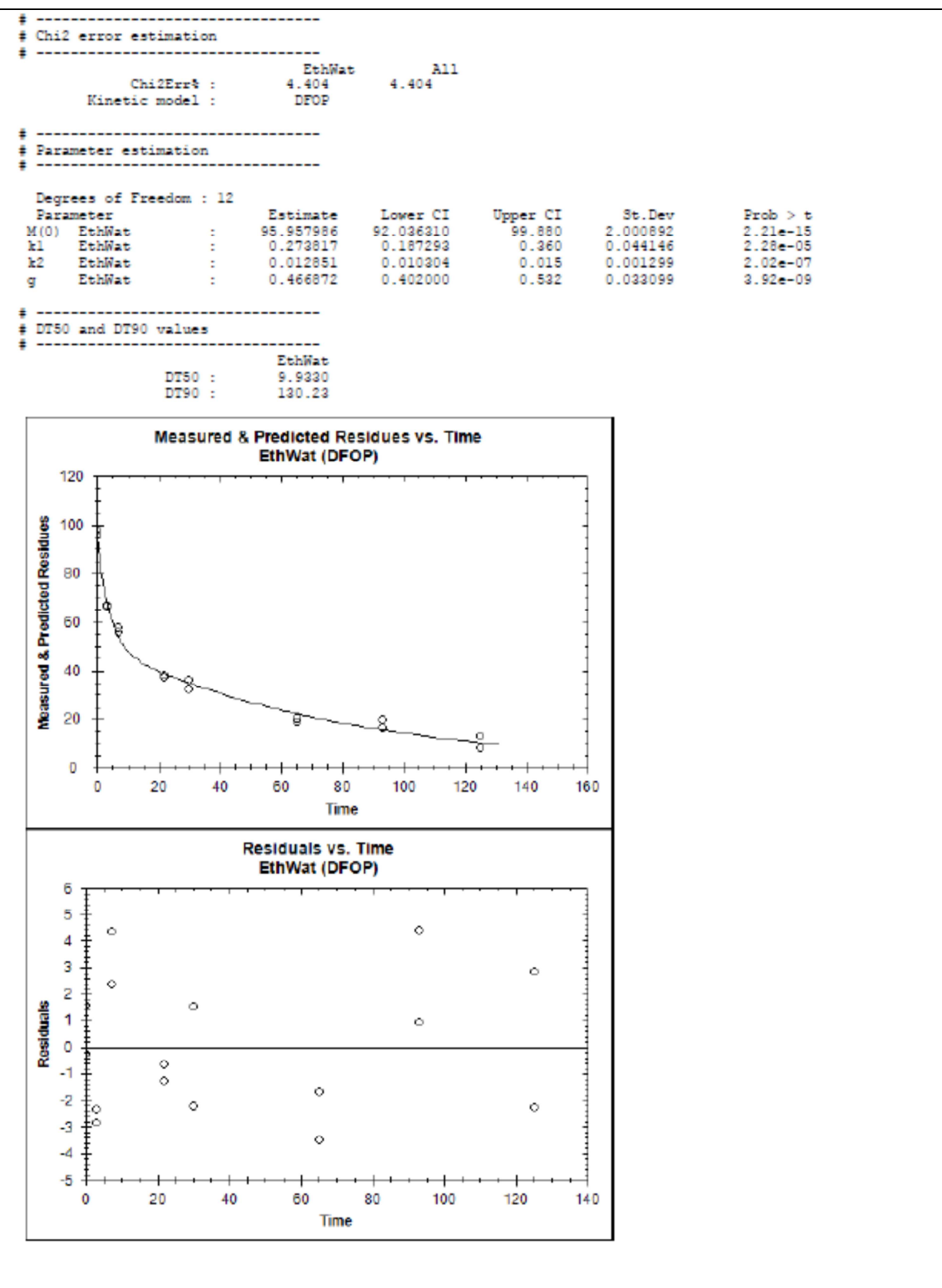


Figure 8-109: Kinetic evaluation of the water/sediment study Hönniger Weiher (Ethofumesate, SFO, sediment)

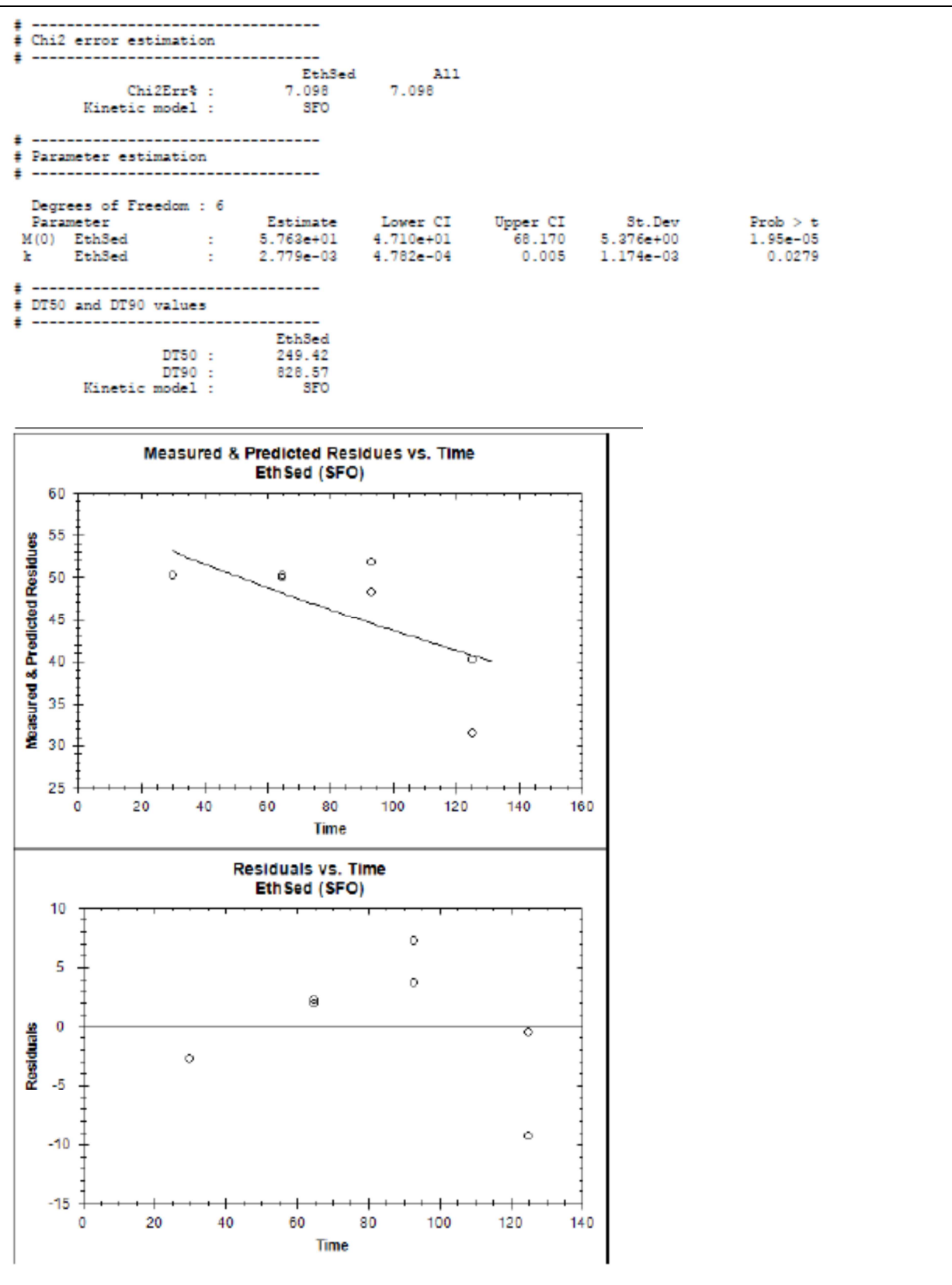
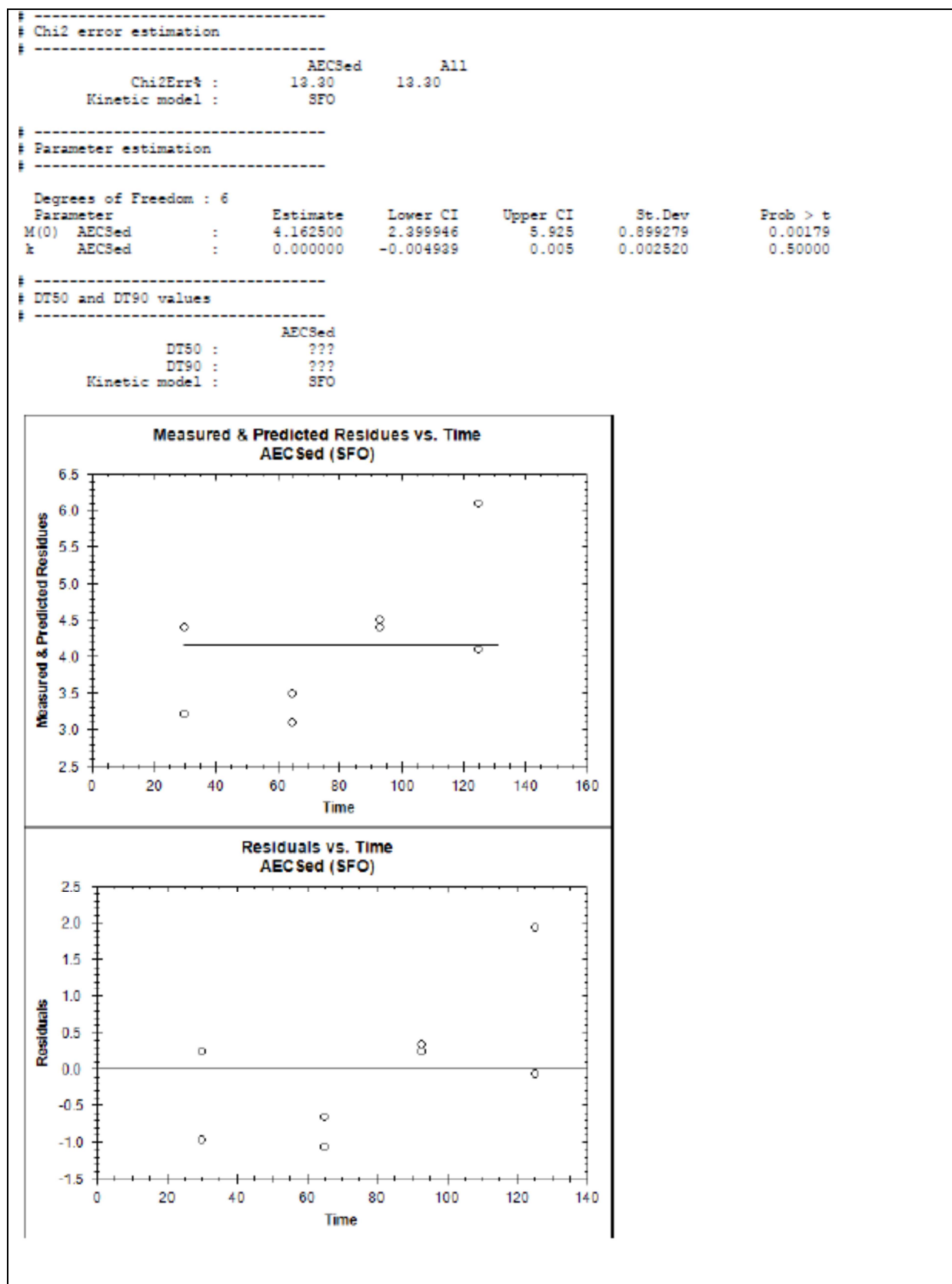


Figure 8-110: Kinetic evaluation of the water/sediment study Hönniger Weiher (NC20645, SFO, sediment)



Comments RMS

The study is valid.

The relevant endpoints are:

| | whole sys. | | water phase | | sediment | | |
|-------------|--------------|------------------|---------------|------------------|---------------|------------------|---------------|
| | DegT50 /DT90 | Chi ² | DissT50 /DT90 | Chi ² | DissT50 /DT90 | Chi ² | Kinetic model |
| | (d) | (%) | (d) | (%) | (d) | (%) | |
| Anglersee | 89 / 296 | 4.2 | 54 / 180 | 8.0 | 96 / 320 | 3.2 | SFO |
| Hönniger W. | 141 / 469 | 3.4 | 9.9 / 130 | 4.4 | 1000 | - | SFO |

| | |
|---------------------|--|
| Reference: | Kinetic evaluation of the degradation of ethofumesate in an aerobic water/sediment system |
| Notifier: | Taskforce |
| Author(s), year: | Schmitt, W.;2008 |
| Report/Doc. number: | MEF-08/247 / M-301623-01-1 |
| Guideline(s): | Not applicable |
| GLP: | No |
| Deviations: | |
| Validity: | Valid |
| Status: | New study |

EXECUTIVE SUMMARY

The degradation and dissipation kinetics of [¹⁴C]-ethofumesate in aquatic systems was investigated by evaluating respective experimental data from three different water/sediment systems. These include a river water and loamy sand sediment (Rhine River) system and a pond water and clay loam sediment (Anwiler Teich) system, [Kellner G., 1995] as well as a pond system with sandy sediment (Hubertus-see) [Celorio, J., 1984].

The evaluation followed the recommendations of the FOCUS working group on degradation kinetics [FOCUS, 2006] and considered modeling endpoints. It includes an analysis of the total system degradation and single phase dissipation by analyzing the decline curves.

Table 8-179: SFO degradation parameters for the total system.

| System | DT ₅₀ [days] | DT ₉₀ [days] |
|---|----------------------------|----------------------------|
| Hubertussee (Celorio, J., 1984, M-155553-01-1) | 162 | 538 |
| Rhine River (Kellner, G., 1995, M-161568-01-1) | 103 | 342 |

| | | |
|--|-----|-----|
| Anwiler Teich (Kellner, G., 1995, <u>M-161568-01-1</u>) | 164 | 543 |
|--|-----|-----|

Table 8-180: SFO dissipation parameters for ethofumesate in the water phase

| System | DT ₅₀ [days] | DT ₉₀ [days] |
|---------------|----------------------------|----------------------------|
| Hubertussee | 31.2 | 104 |
| Rhine River | 34.8* | 116 |
| Anwiler Teich | 56.8* | 189 |

*derived from biphasic model

Table 8-181: SFO Dissipation parameters for ethofumesate in the sediment phase

| System | DT ₅₀ [days] | DT ₉₀ [days] |
|---------------|----------------------------|----------------------------|
| Rhine River | 174 | 578 |
| Anwiler Teich | 279 | 928 |

RESULT AND DISCUSSION

DT₅₀ values for ethofumesate in the entire system ranged from 103 to 164 days, with a geometric mean of 140 days.

The following figures and tables show the results of the kinetic evaluation carried out by the notifier.

Figure 8-111: Kinetic evaluation of the water/sediment study Rhine River (Ethofumesate, SFO, total system)

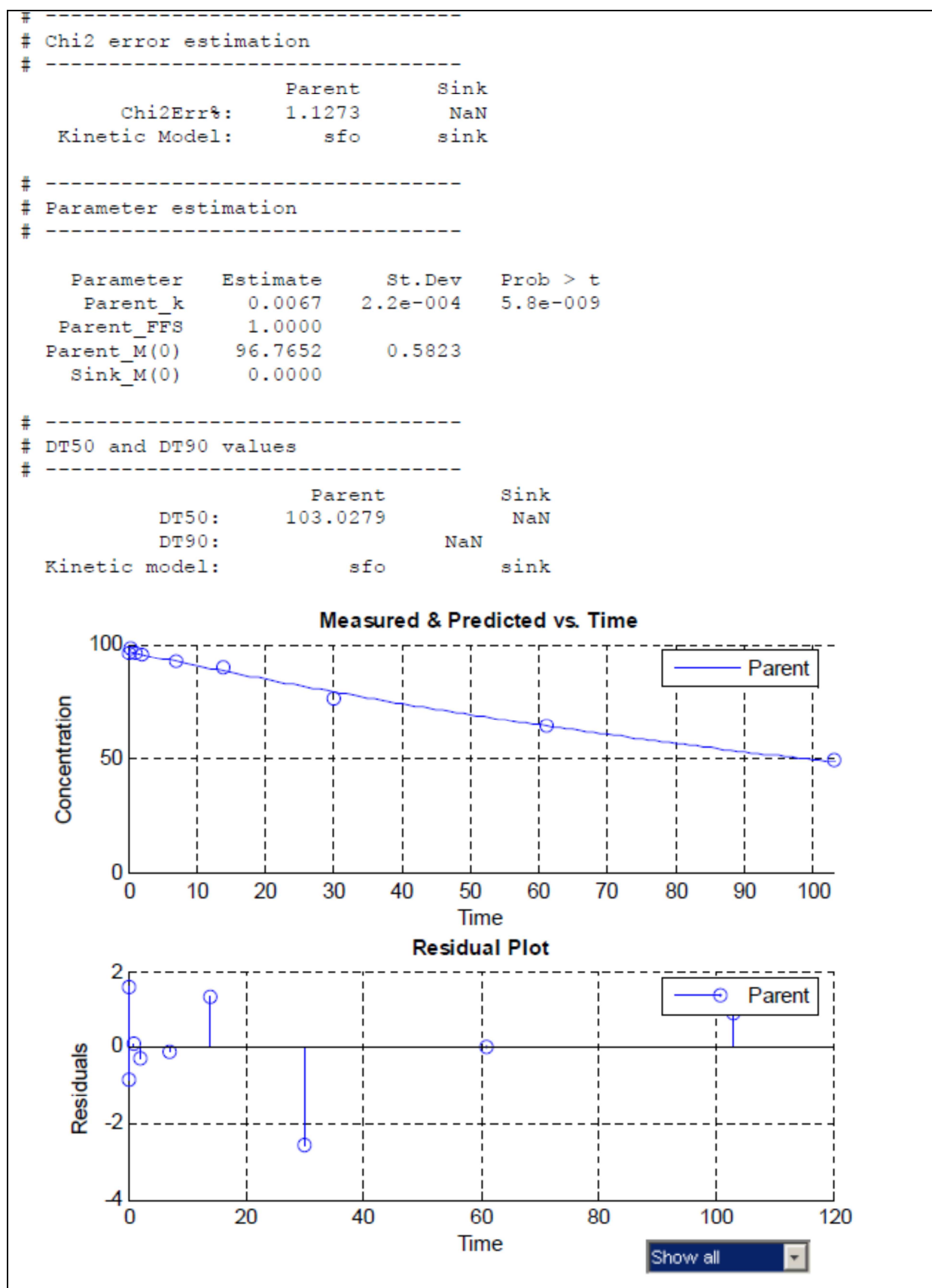


Figure 8-112: Kinetic evaluation of the water/sediment study Rhine River (Ethofumesate, SFO, water phase)

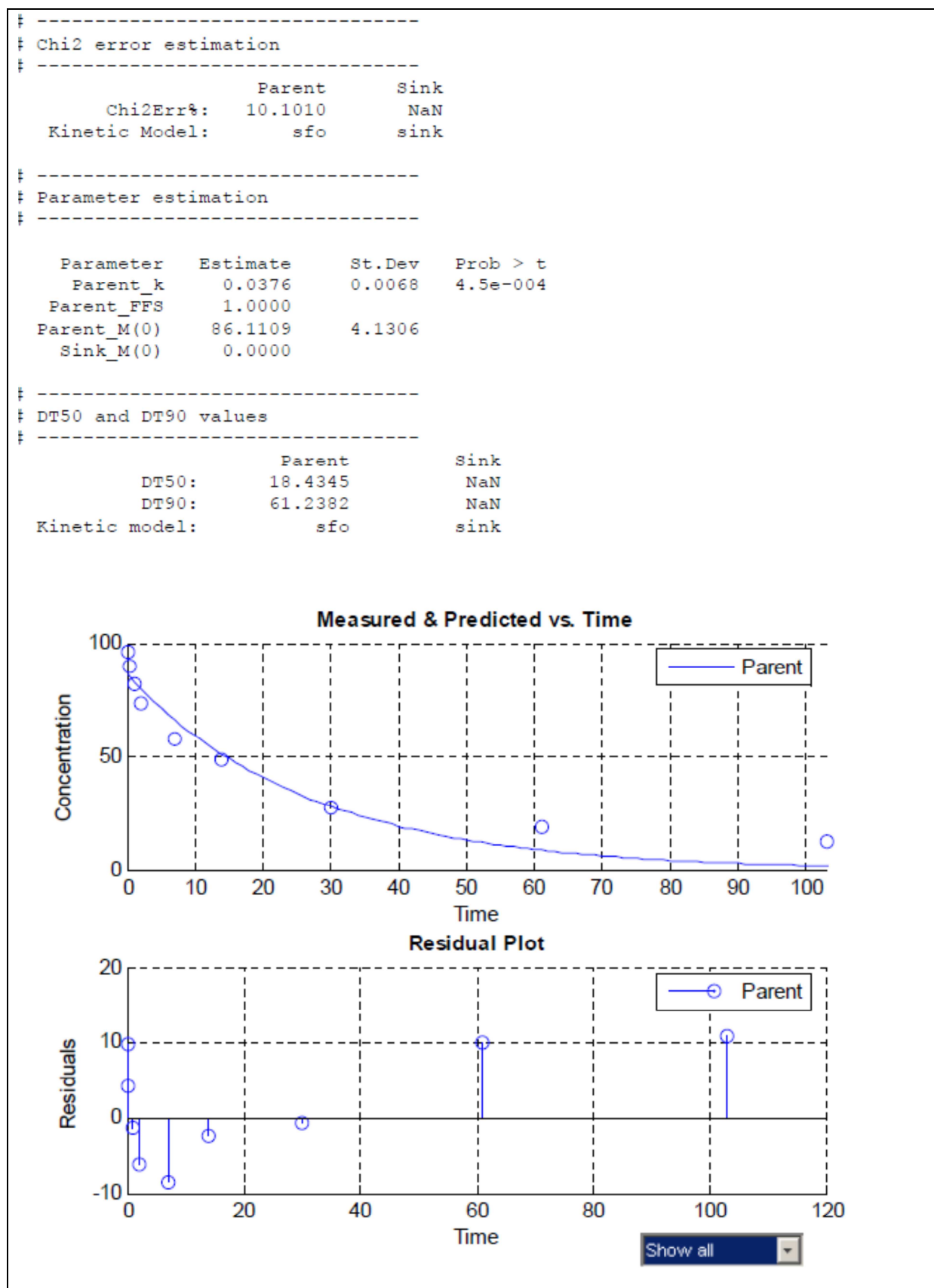


Figure 8-113: Kinetic evaluation of the water/sediment study Rhine River (Ethofumesate, DFOP, water phase)

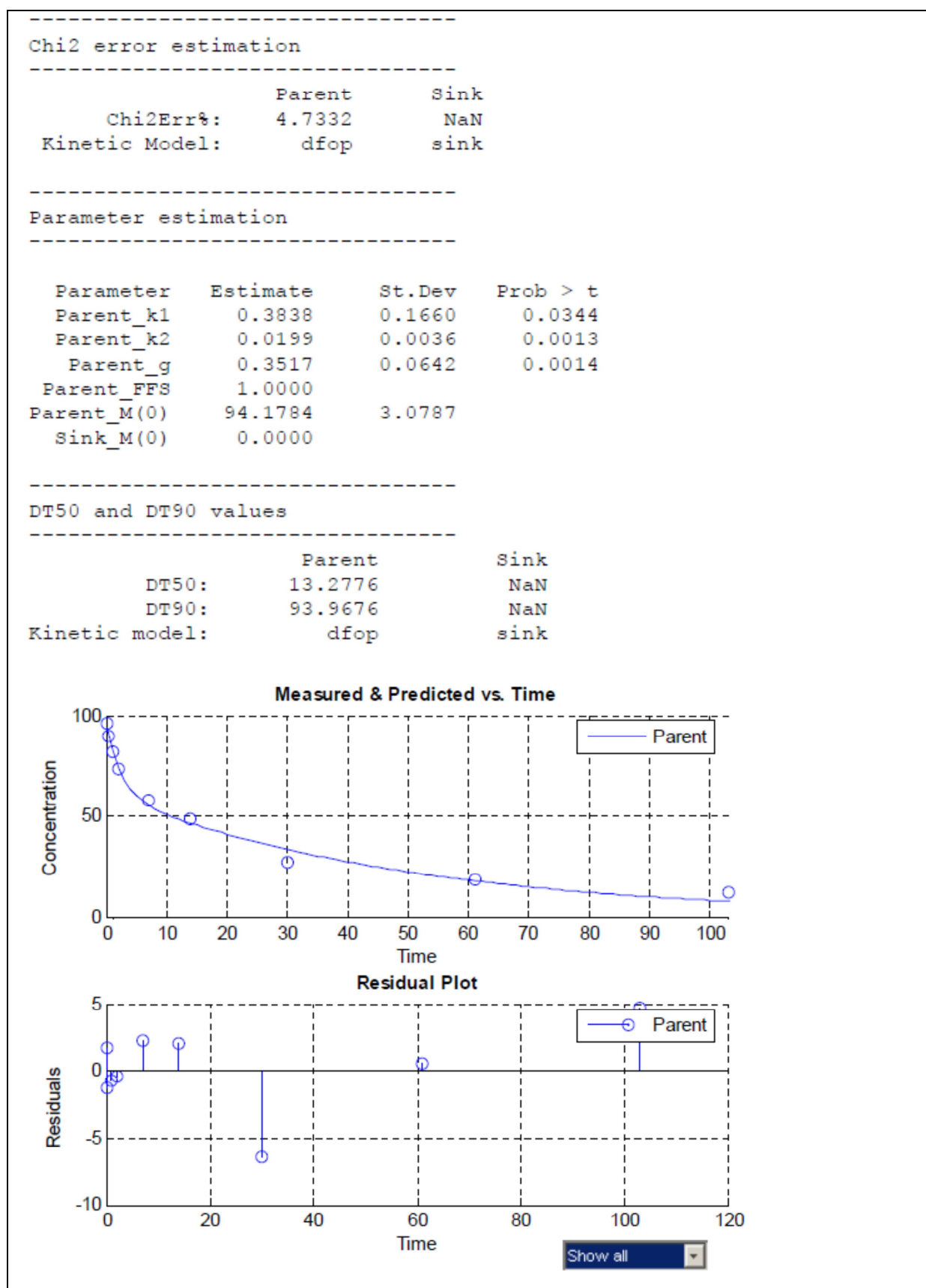


Figure 8-114: Kinetic evaluation of the water/sediment study Rhine River (Ethofumesate, SFO, sediment)

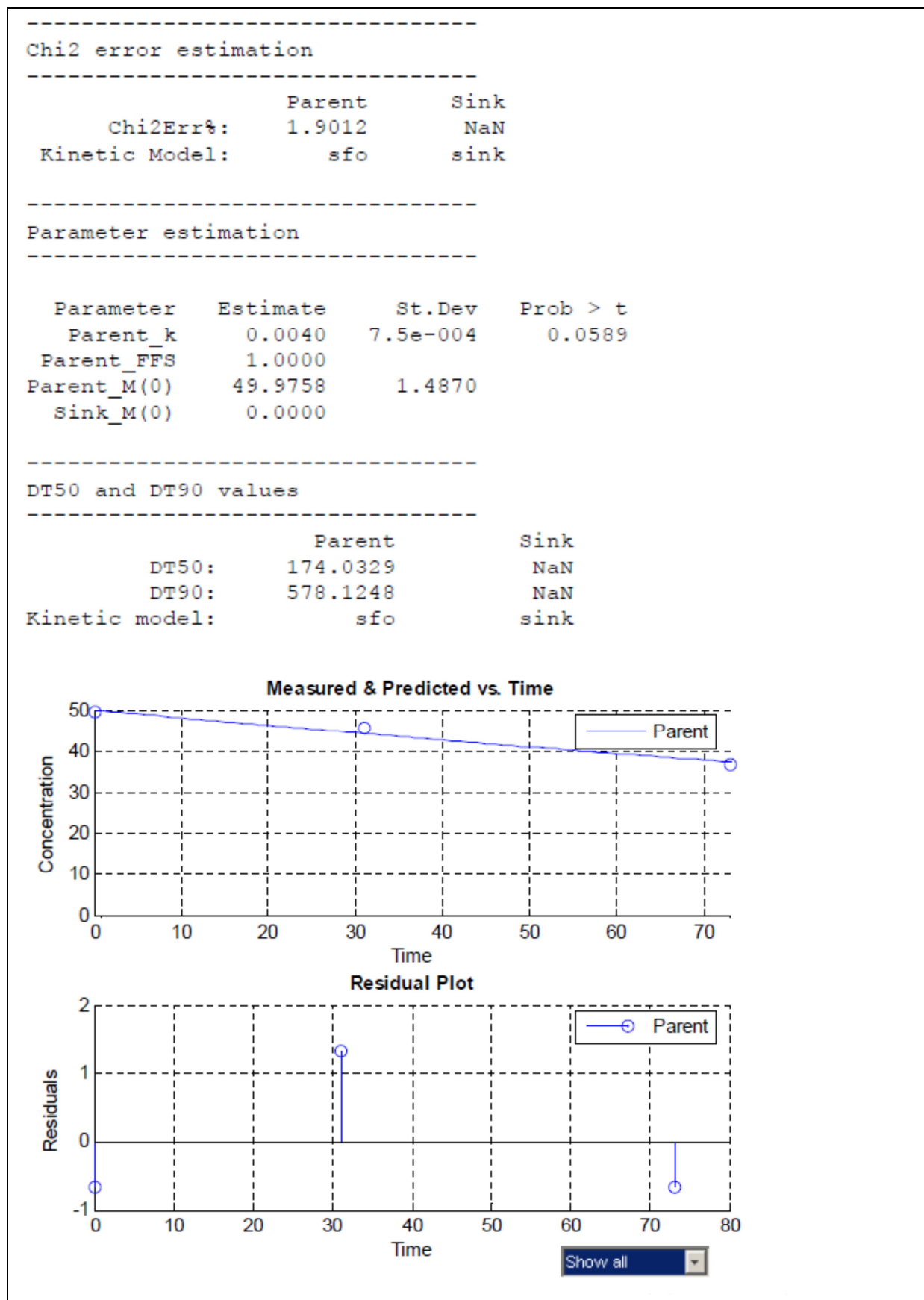


Figure 8-115: Kinetic evaluation of the water/sediment study Anwiler Teich (Ethofumesate, SFO, total system)

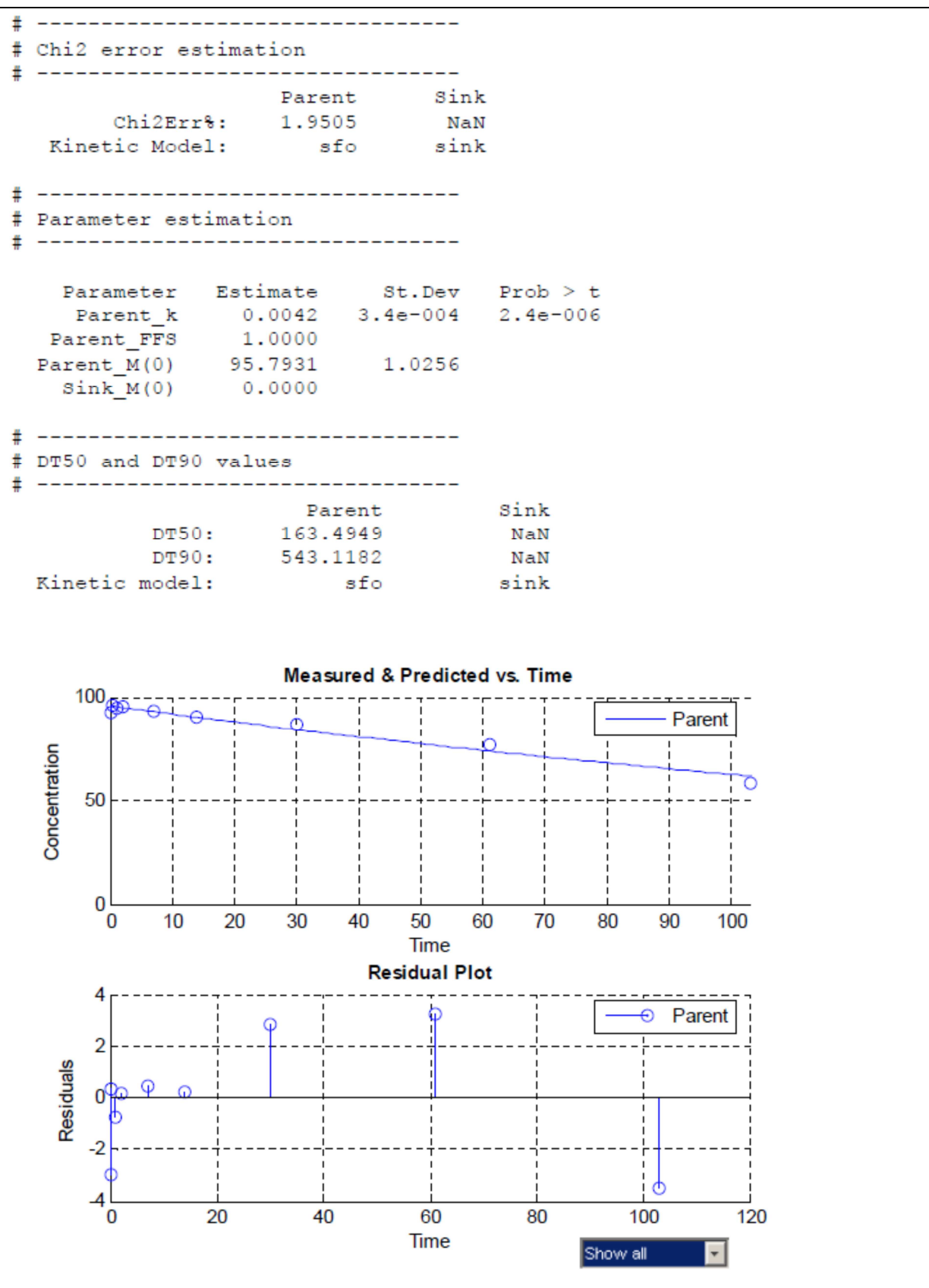


Figure 8-116: Kinetic evaluation of the water/sediment study Anwiler Teich (Ethofumesate, SFO, water phase)

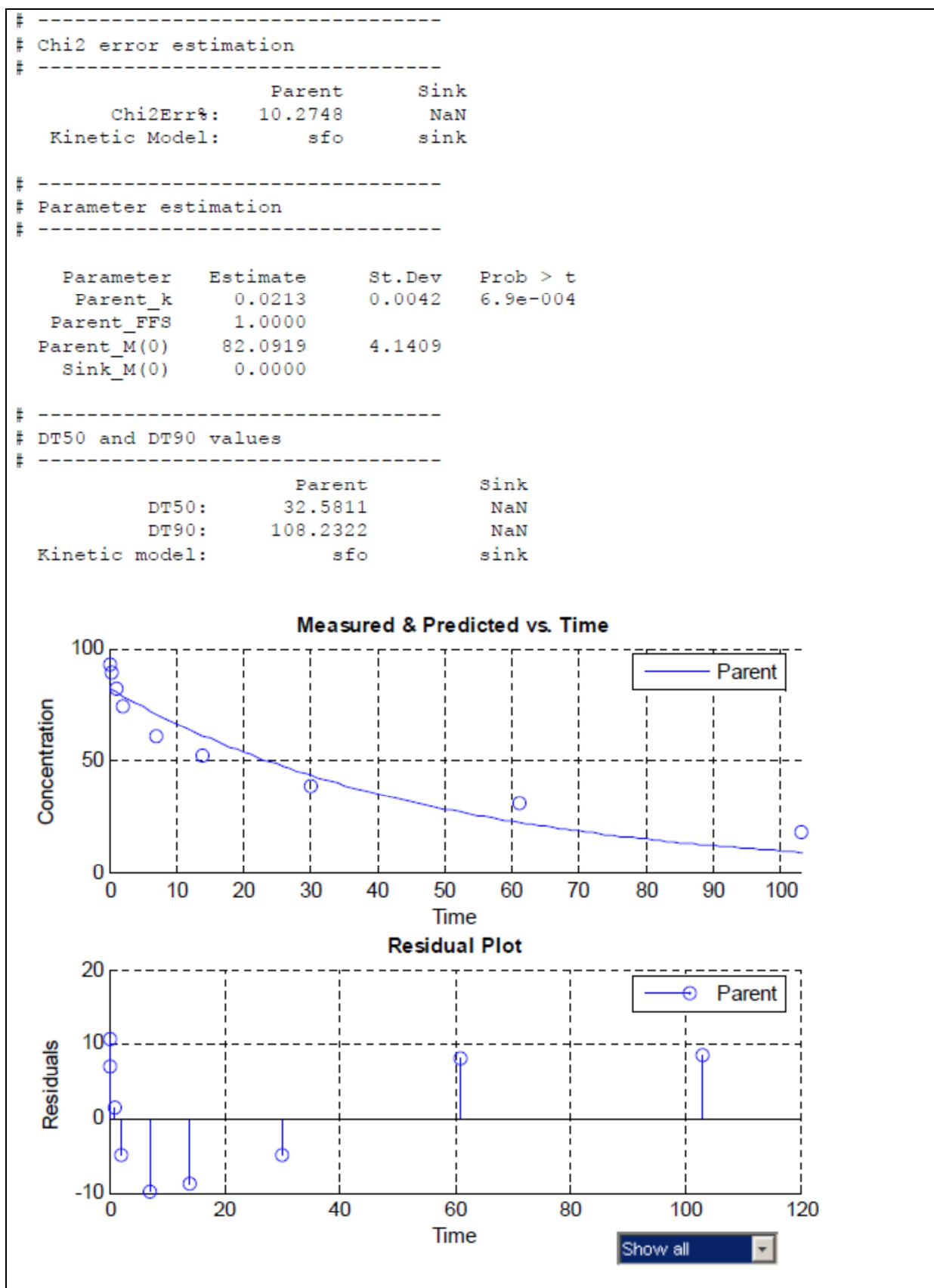


Figure 8-117: Kinetic evaluation of the water/sediment study Anwiler Teich (Ethofumesate, DFOP, water phase)

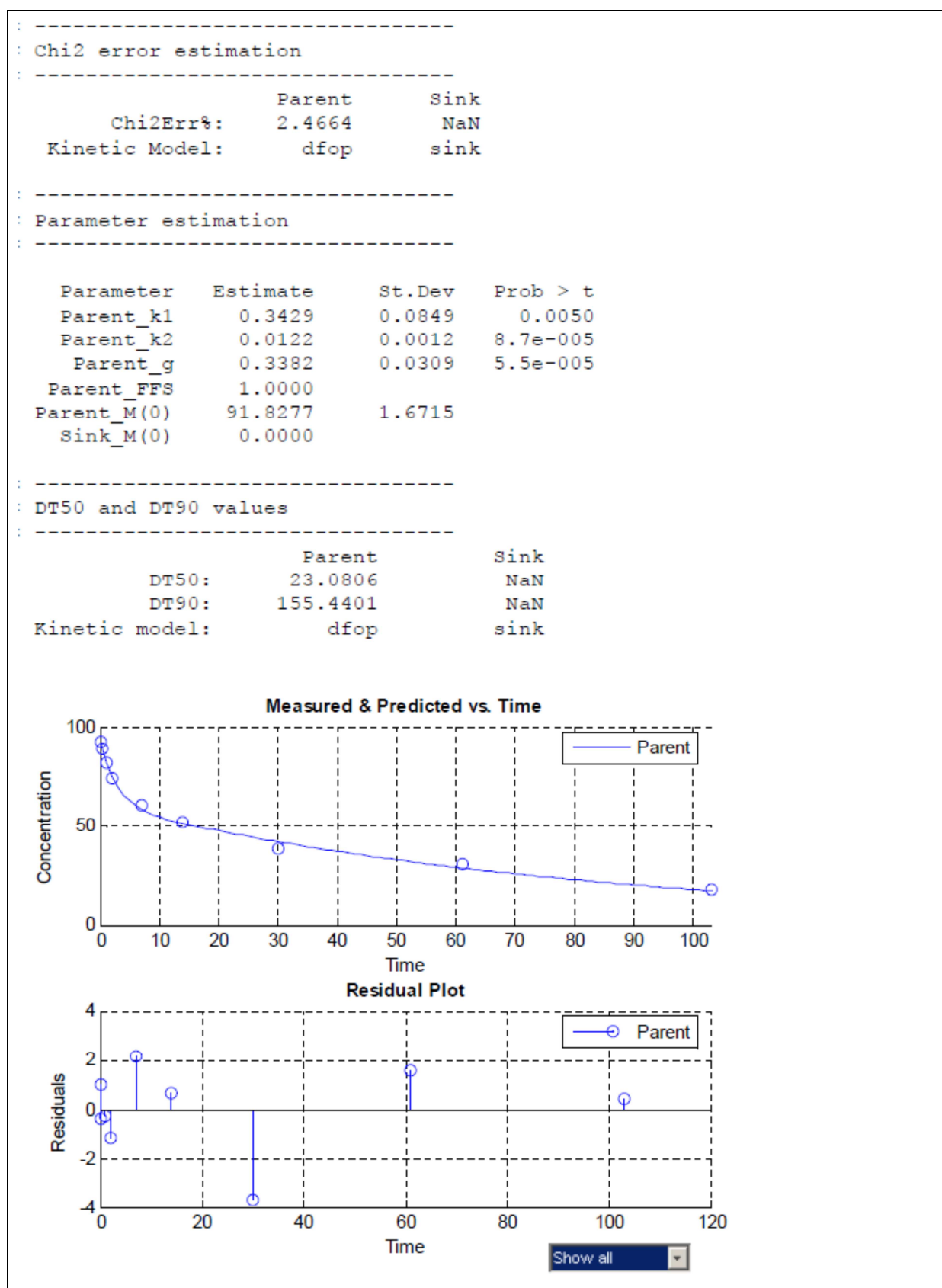


Figure 8-118: Kinetic evaluation of the water/sediment study Anwiler Teich (Ethofumesate, SFO, sediment)

| | | | |
|-----------------------|----------|----------|----------|
| ----- | | | |
| Chi2 error estimation | | | |
| ----- | | | |
| | Parent | Sink | |
| Chi2Err%: | 1.4861 | NaN | |
| Kinetic Model: | sfo | sink | |
| ----- | | | |
| Parameter estimation | | | |
| ----- | | | |
| Parameter | Estimate | St.Dev | Prob > t |
| Parent_k | 0.0025 | 5.7e-004 | 0.0722 |
| Parent_FFS | 1.0000 | | |
| Parent_M(0) | 49.2732 | 1.1895 | |
| Sink_M(0) | 0.0000 | | |
| ----- | | | |
| DT50 and DT90 values | | | |
| ----- | | | |
| | Parent | Sink | |
| DT50: | 279.2496 | NaN | |
| DT90: | 927.6472 | NaN | |
| Kinetic model: | sfo | sink | |

Comments RMS

The study is valid. Results from the experiment Hubertussee were not further considered since the respective study (Celorio, 1984) was considered not valid.

Whereas the notifier calculated the water compartment half-lives from the slow phase degradation rate (DFOP kinetic model), the RMS thinks that the actual DT50 is more appropriate in this case.

The relevant endpoints are:

| whole sys. | water phase | | sediment | | | | Kinetic model |
|---------------|--------------|------|---------------|------|---------------|------|---------------|
| | DegT50 /DT90 | Chi² | DissT50 /DT90 | Chi² | DissT50 /DT90 | Chi² | |
| | (d) | (%) | (d) | (%) | (d) | (%) | |
| Rhine River | 103 / 342 | 1.1 | 13 / 94 | 4.7 | 174 / 578 | 3.2 | SFO |
| Anwiler Teich | 141 / 469 | 3.4 | 9.9 / 130 | 4.4 | 1000 | - | SFO |

| | |
|---------------------|--|
| Reference: | Degradation and Metabolism of Ethofumesate in two Water/Sediment Systems under Aerobic Conditions – Laboratory Test |
| Notifier: | UPL |
| Author(s), year: | Heintze, A. (2003) |
| Report/Doc. number: | 20011407/01-CUWS |
| Guideline(s): | BBA Guideline, part IV, 5-1 (1990) and SETAC recommendations (1995). |
| GLP: | Yes |
| Deviations: | |
| Validity: | Valid |
| Status: | New study |

I. MATERIALS AND METHODS

A. MATERIALS

1. **Test Material:** [¹⁴C U-ring]Ethofumesate

Batch No.: 00BDR495/2/1

Radiochemical Purity: 99.3%

Specific activity: 1.72 GBq/mmol (46.4 mCi/mmol)

CAS No.: 26225-79-6
2. **Test material:** Ethofumesate

Batch No.: #1997/1

CAS No.: 26225-79-6

Purity: 98.59%
3. **Test material (reference):**

EDB (2-ethoxy-2,3-dihydro-3,3-dimethylbenzofuran-5-ol)

HDBM (2,3-dihydro-2-hydroxy-3,3-dimethyl-benzofuran-5-yl methanesulphonate, =NC 8493)

HDS (2-(2-hydroxy-5-methanesulphonyloxyphenyl)-2-methylpropionic acid, = NC 20645)

Ethofumesate-2-keto ([2,3-dihydro-3,3-dimethyl-2-oxo-benzofuran-5-yl methanesulphonate)

4. Water/Sediment:

Two test systems were used, pond and creek sampled from different locations. The test system was characterised and acclimated at 20°C under aerobic conditions in the dark over a period of 44 days. The water sediment systems were sieved through a 2 mm mesh and water was filtered through a 0.2 mm sieve, the sediment was sieved through a 2.00 mm sieve.

Table 8-182: Characterization of water and sediment samples

| Parameter | Pond (silty loam) | | | Creek (sand) | | |
|---------------------------------------|---------------------------------------|----------------|----------------|---------------------------------------|----------------|----------------|
| | Before start / Beginning of the study | After 140 days | After 232 days | Before start / Beginning of the study | After 140 days | After 232 days |
| Water | | | | | | |
| Total P [mg/L] | 0.06 / < 0.02 | 0.38 | 0.075 | < 0.02 | 0.58 | 0.18 |
| Ca/Mg/Na/K [mg/L] | 68/30/9.3/2.3 ^a | | | 44/21/10/3.3 ^a | | |
| Total N [mg/L] | < 1 / < 1 | < 1 | < 1 | 3.6 / < 1 | < 1 | < 1 |
| Total organic carbon [mg/L] | 11.7 / 103 | 6.7 | 8.8 | 2.3 / 97 | 4.2 | 10 |
| Temperature [°C] | 16.8 ^a | n.d. | n.d. | 6.0 ^a | n.d. | n.d. |
| pH | 7.92 ^a | n.d. | n.d. | 8.24 ^a | n.d. | n.d. |
| Oxygen [mg/L] | 10.4 ^a | n.d. | n.d. | 10.5 ^a | n.d. | n.d. |
| Redox potential [mV] | + 135 ^a | n.d. | n.d. | + 141 ^a | n.d. | n.d. |
| Sediment | | | | | | |
| Total P [mg/L] | 470 ^a | n.d. | n.d. | 69.5 ^a | n.d. | n.d. |
| Total N [mg/L] | 715 ^a | n.d. | n.d. | 112 ^a | n.d. | n.d. |
| pH | 7.8 ^a | n.d. | n.d. | 7.5 ^a | n.d. | n.d. |
| Total organic carbon [%] | 1.14 ^a | n.d. | n.d. | 0.14 ^a | n.d. | n.d. |
| Sand/silt/clay [%] | 21.9/60.9/17.2 ^a | n.d. | n.d. | 88.9/6.9/4.1 ^a | n.d. | n.d. |
| Cation exchange capacity [mval/100 g] | 22.9 ^a | n.d. | n.d. | 4.27 ^a | n.d. | n.d. |
| Redox potential [mV] | - 150 ^a | n.d. | n.d. | + 566 ^a | n.d. | n.d. |
| Microbial biomass [µg C/g dry matter] | 832 ± 345 | 1819 | 2373 | < 10 ± 0 | 454 | 433 |

^a determined at the time of sampling

n.d. not determined

B. STUDY DESIGN**1. Experimental conditions**

The study was performed with a closed glass flow system using 1000 mL all-glass metabolism flasks (≈ 10.1 cm inner diameter) containing about 500 ± 100 mL water and 300 ± 100 g sediment. The height of the water column was about 6 cm and sediment was about 2.5 cm thick (bulk density of 1.5 g/cm³). The system was aerated by

shaking with CO₂-free, moistened air. The organic volatiles in the flask were trapped. 6 flasks were not treated and served as control and were used to determine the biomass. The samples were incubated at 20 ± 2°C protected from light for incubation periods up to 232 days.

Each test system was treated with 249 µg Ethofumesate/80 cm², equivalent to 1.556 kg/ha.

2. Sampling

The organic volatiles were trapped with Tenax volatile trap. The ¹⁴CO₂ was trapped by sodium hydroxide solution.

Duplicate samples were collected at sampling intervals 0, 6, 24, 48 hours and 7, 14, 29, 61, 103, 121 and 230 days after treatment.

2. Description of analytical procedures

The water was separated from the sediment by pour-out. The organic volatiles were extracted from Tenax trap with 15 ML acetone and radioactivity in the extracts was determined by LSC of an aliquot. The sodium hydroxide trapped CO₂ was determined by LSC.

After pour out of the water phase, the sediment was mixed by stirring and shaking and 100 mL acetonitrile/water (1/1, v/v) was added to the aliquots of about 100 g w.w. and amount of acetic acid sufficient to get an pH below 5.0 was added to the extracts. The incubation flasks were closed with a carbon dioxide trap and shaken overnight. The dispersed sediment was transferred to a 200 mL glass centrifuge tube and centrifuged for 10 minutes at 2600 rpm. The extraction was repeated twice and the radioactivity after each extraction step and in the combined extracts was determined by LSC of an aliquot. The sediment was afterwards extracted minimum two times with 80 mL pure acetone and the radioactivity after each extraction step and in the combined extracts was determined by LSC of an aliquot.

Partitioning of the extractables was characterised by TLC. The fractions were co-chromatographed with the reference compounds.

After the final extraction the sediment was dried and the total amount of non-extractable radioactive residues in sediment was determined by combustion and LSC.

After pour out of water from the incubation flasks the radioactivity in the water was determined by LSC. The water phase was added with 10% of its volume of acetonitrile and radioactivity was determined by LSC. An aliquot of around 100 mL was transferred to a 300 mL Erlenmeyer flask, acidified with acetic acid to reach a pH below 5.0 and closed with a carbon dioxide trap. The assemble was shaken overnight and the amount of radioactivity in the carbon dioxide trap was determined. Afterwards the remaining non-volatile radioactivity in the aqueous phase was determined by LSC on an aliquot.

Partitioning of the dissolved radioactivity was characterised by two TLC systems. The fractions were co-chromatographed with the reference compounds.

II. RESULTS AND DISCUSSION

A. MASS BALANCE

The mean recovery from the pond water/sediment system during the whole study was 98.2% AR (91.4% - 113.1%) and the mean recovery from creek water/sediment system during the whole study was 100.6% AR (79.3% - 115.9)

B. FINDINGS

In the pond system the CO₂ trapped from air increased to 4.2% AR after 230 days. In the sediment radioactivity increased from 1.5% AR immediately after the treatment to 68.7% AR after 230 days. In the water phase the radioactivity decreased from 96.2% AR on day 0 to 28.1% AR after 230 days. The extractable residues increased from 1.4% AR (0 days) to approx. 43.9% AR after 61 days and decreased to 26.4% AR after 230 days. The un-extractables reached 41.9% AR at the end of the study. No organic volatiles could be found throughout the incubation period. Total mineralisation to carbon dioxide was 6.1% AR after 230 days.

The metabolite HDS increased to maximum rates of 10.6% AR after 103 days and 10.7% after 230 days. Other metabolites were below 5% AR at all sampling dates.

In the creek system the CO₂ trapped from air increased to 4.6% AR after 230 days. In the sediment radioactivity increased from 1.7% AR immediately after the treatment to 35.3% AR after 230 days. In the water phase the radioactivity decreased from 105.8% AR (0 days) to 44.7% AR after 230 days. The extractable residues increased from 1.6% AR (0 days) to approx. 26.6% AR after 29 days and decreased to 15.5% AR after 230 days. The un-extractables reached 19.4% AR at the end of the study. No organic volatiles could be found throughout the incubation period. Total mineralisation to carbon dioxide was 9.1% AR after 230 days.

The metabolite HDS increased to maximum rates of 7.5% AR after 61 days and was not detected in the system after 230 days. Other metabolites were below 5% AR at all sampling dates.

Table 8-183: Distribution of radioactivity in the pond and creek water/sediment system in % of AR

| Time | CO ₂ trapped directly | Water | | | Sediment | | | | Sum |
|---------------------|----------------------------------|----------------------|------------------|-----------------|----------------------|---------|-----------------|------|-------|
| | | Total after sampling | SNV ^a | CO ₂ | Total after sampling | Extract | CO ₂ | NER | |
| [d] | [%] | [%] | [%] | [%] | [%] | [%] | [%] | [%] | [%] |
| Pond System | | | | | | | | | |
| 0 | 0.0 | 96.2 | 96.1 | 0.1 | 1.5 | 1.4 | 0.0 | 0.1 | 97.7 |
| 0.25 | 0.0 | 94.9 | 94.8 | 0.1 | 1.7 | 1.5 | 0.0 | 0.2 | 96.6 |
| 1 | 0.0 | 92.0 | 91.9 | 0.1 | 3.1 | 2.8 | 0.0 | 0.4 | 95.2 |
| 2 | 0.0 | 99.3 | 99.1 | 0.2 | 7.2 | 6.5 | 0.0 | 0.6 | 106.5 |
| 7 | 0.0 | 70.9 | 70.7 | 0.2 | 26.7 | 24.2 | 0.0 | 2.4 | 97.5 |
| 14 | 0.0 | 61.9 | 61.6 | 0.3 | 34.8 | 32.3 | 0.0 | 2.5 | 96.7 |
| 29 | 0.0 | 53.5 | 53.3 | 0.2 | 41.5 | 39.4 | 0.0 | 2.1 | 95.1 |
| 61 | 0.6 | 48.2 | 47.8 | 0.4 | 49.5 | 43.9 | 0.1 | 5.5 | 98.3 |
| 103 | 1.3 | 41.9 | 41.2 | 0.6 | 53.1 | 40.7 | 0.1 | 12.4 | 96.4 |
| 121 | 1.1 | 42.8 | 41.4 | 1.5 | 53.3 | 38.8 | 0.4 | 14.1 | 97.3 |
| 203 | 4.2 | 28.1 | 26.7 | 1.4 | 68.7 | 26.4 | 0.5 | 41.9 | 101.1 |
| Creek System | | | | | | | | | |
| 0 | 0.0 | 105.8 | 105.7 | 0.1 | 1.7 | 1.6 | 0.0 | 0.1 | 107.5 |
| 0.25 | 0.0 | 109.8 | 109.7 | 0.1 | 2.2 | 2.0 | 0.0 | 0.1 | 111.9 |
| 1 | 0.0 | 100.1 | 100.0 | 0.1 | 2.8 | 2.5 | 0.0 | 0.2 | 102.8 |
| 2 | 0.0 | 98.4 | 98.2 | 0.2 | 6.1 | 5.8 | 0.0 | 0.3 | 104.5 |
| 7 | 0.0 | 84.5 | 84.3 | 0.2 | 17.6 | 16.9 | 0.0 | 0.6 | 102.1 |
| 14 | 0.1 | 80.7 | 80.4 | 0.2 | 21.9 | 21.2 | 0.0 | 0.7 | 102.7 |
| 29 | 0.3 | 72.1 | 72.0 | 0.1 | 27.3 | 26.6 | 0.0 | 0.7 | 99.7 |
| 61 | 1.0 | 67.4 | 66.7 | 0.6 | 29.5 | 24.6 | 0.0 | 4.9 | 97.9 |
| 103 | 1.1 | 63.8 | 62.6 | 1.2 | 30.8 | 22.3 | 0.2 | 8.3 | 95.7 |
| 121 | 1.0 | 64.8 | 60.9 | 3.8 | 31.2 | 21.7 | 0.4 | 9.0 | 96.9 |
| 203 | 4.6 | 44.7 | 40.6 | 4.2 | 35.3 | 15.5 | 0.4 | 19.4 | 84.6 |

a soluble but not volatile after acid treatment

Table 8-184: Characterisation of the radioactivity in the water phase of the creek system in % of applied radioactivity

| Time (d) | Ethofumesate (%) | Keto-Ethofumesate (%) | EDB (%) | HDBM (%) | HDS (%) |
|----------|------------------|-----------------------|---------|----------|---------|
| 0 | 105 | 0 | 4.7 | 0 | 0 |
| 0 | 97.7 | 0 | 4 | 0 | 0 |
| 0.25 | 100.6 | 0 | 4.8 | 0.8 | 0 |
| 0.25 | 108.7 | 0 | 3.9 | 0.6 | 0 |
| 1 | 94 | 0 | 3.8 | 0 | 0 |
| 1 | 97.7 | 0 | 3.1 | 1.6 | 0 |

| | | | | | |
|-----|------|---|-----|-----|-----|
| 2 | 95.6 | 0 | 2.8 | 1.2 | 0.8 |
| 2 | 91.4 | 0 | 2.3 | 1 | 1.2 |
| 7 | 78.9 | 0 | 5.1 | 0 | 0 |
| 7 | 80.6 | 0 | 0 | 0 | 4.1 |
| 14 | 75.4 | 0 | 0 | 0 | 3.7 |
| 14 | 77.9 | 0 | 0 | 0 | 3.8 |
| 29 | 66.7 | 0 | 1.8 | 0 | 3.1 |
| 29 | 66.8 | 0 | 1.5 | 0 | 3.9 |
| 61 | 54.3 | 0 | 0 | 0 | 9.7 |
| 61 | 64.2 | 0 | 0 | 0 | 5.2 |
| 103 | 62.3 | 0 | 0 | 0 | 4.2 |
| 103 | 52.4 | 0 | 0 | 0 | 6.3 |
| 121 | 60.3 | 0 | 0 | 0 | 8.8 |
| 121 | 50.2 | 0 | 0 | 0 | 2.6 |
| 230 | 44.7 | 0 | 0 | 0 | 0 |
| 230 | 36.5 | 0 | 0 | 0 | 0 |

Table 8-185: Characterisation of the radioactivity in the sediment of the creek system in % of applied radioactivity

| Time (d) | Ethofumesate (%) | Keto-Ethofumesate (%) | EDB (%) | HDBM (%) | HDS (%) |
|----------|------------------|-----------------------|---------|----------|---------|
| 0 | 1.2 | 0 | 0 | 0 | 0 |
| 0 | 2 | 0 | 0 | 0 | 0 |
| 0.25 | 1.7 | 0 | 0 | 0 | 0 |
| 0.25 | 2.4 | 0 | 0 | 0 | 0 |
| 1 | 3 | 0 | 0 | 0 | 0 |
| 1 | 2.1 | 0 | 0 | 0 | 0 |
| 2 | 5.6 | 0 | 0 | 0 | 0 |
| 2 | 6 | 0 | 0 | 0 | 0 |
| 7 | 16.9 | 0 | 0 | 0 | 0 |
| 7 | 16.9 | 0 | 0 | 0 | 0 |
| 14 | 22.6 | 0 | 0 | 0 | 0 |
| 14 | 19.7 | 0 | 0 | 0 | 0 |
| 29 | 25.7 | 0 | 0 | 0 | 0 |
| 29 | 27.5 | 0 | 0 | 0 | 0 |
| 61 | 26.3 | 0 | 0.8 | 0 | 0 |
| 61 | 21.6 | 0 | 0.5 | 0 | 0 |
| 103 | 23.2 | 0 | 0 | 0 | 0 |
| 103 | 21.4 | 0 | 0 | 0 | 0 |
| 121 | 23.2 | 0 | 0 | 0 | 0 |
| 121 | 20.3 | 0 | 0 | 0 | 0 |
| 230 | 15.7 | 0 | 0 | 0 | 0 |
| 230 | 15.4 | 0 | 0 | 0 | 0 |

Table 8-186: Characterisation of the radioactivity in the water phase of the pond system in % of applied radioactivity

| Time (d) | Ethofumesate (%) | Keto-Ethofumesate (%) | EDB (%) | HDBM (%) | HDS (%) |
|----------|------------------|-----------------------|---------|----------|---------|
| 0 | 96.9 | 0 | 2.2 | 0 | 0 |
| 0 | 88.5 | 0 | 4.6 | 0 | 0 |
| 0.25 | 88.6 | 0 | 2.5 | 0 | 0 |
| 0.25 | 93.3 | 0 | 4 | 1.2 | 0 |
| 1 | 91.7 | 0 | 2.5 | 1.1 | 0 |
| 1 | 83.3 | 0 | 3 | 2.1 | 0 |
| 2 | 89.9 | 0 | 2 | 0.7 | 0.3 |
| 2 | 101.3 | 0 | 2.3 | 1.1 | 0.6 |
| 7 | 68.8 | 0 | 0 | 0 | 2.4 |
| 7 | 65.9 | 0 | 0 | 0 | 4.2 |
| 14 | 58.1 | 0 | 0 | 0 | 3.2 |
| 14 | 57.3 | 0 | 0 | 0 | 4.6 |
| 29 | 50.3 | 0 | 0 | 0 | 3 |
| 29 | 48.1 | 0 | 0 | 4.6 | 0 |
| 61 | 43.3 | 0 | 0 | 0 | 5.6 |
| 61 | 41.5 | 0 | 0 | 0 | 5.2 |
| 103 | 30.8 | 0 | 0 | 0 | 9.3 |
| 103 | 33.7 | 0 | 0 | 0 | 8.7 |
| 121 | 35.5 | 0 | 0 | 1.1 | 5.2 |
| 121 | 34.9 | 0 | 0 | 0.4 | 5.6 |
| 230 | 15 | 0 | 1.1 | 2.1 | 8.6 |
| 230 | 11.6 | 0 | 0.8 | 1.3 | 12.8 |

Table 8-187: Characterisation of the radioactivity in the sediment of the pond system in % of applied radioactivity

| Time (d) | Ethofumesate (%) | Keto-Ethofumesate (%) | EDB (%) | HDBM (%) | HDS (%) |
|----------|------------------|-----------------------|---------|----------|---------|
| 0 | 1.5 | 0 | 0 | 0 | 0 |
| 0 | 1.3 | 0 | 0 | 0 | 0 |
| 0.25 | 1.4 | 0 | 0 | 0 | 0 |
| 0.25 | 1.6 | 0 | 0 | 0 | 0 |
| 1 | 3 | 0 | 0 | 0 | 0 |
| 1 | 2.5 | 0 | 0 | 0 | 0 |
| 2 | 6.2 | 0 | 0 | 0 | 0 |
| 2 | 6.9 | 0 | 0 | 0 | 0 |
| 7 | 22.8 | 0 | 0.7 | 0 | 0 |
| 7 | 24.4 | 0 | 0.6 | 0 | 0 |
| 14 | 31.8 | 0 | 0 | 0 | 0 |
| 14 | 32.7 | 0 | 0 | 0 | 0 |
| 29 | 39.4 | 0 | 0 | 0 | 0 |
| 29 | - | - | - | - | - |
| 61 | 40.9 | 0 | 1.4 | 0 | 0 |
| 61 | 43.6 | 0 | 2 | 0 | 0 |

| | | | | | |
|-----|------|---|-----|-----|-----|
| 103 | 38.6 | 0 | 0 | 1.2 | 1 |
| 103 | 38.3 | 0 | 0 | 0 | 2.2 |
| 121 | 35.3 | 0 | 0 | 1 | 0.8 |
| 121 | 38.9 | 0 | 1.6 | 0 | 0 |
| 230 | 25.2 | 0 | 2.4 | 0 | 0 |
| 230 | 22 | 0 | 3.2 | 0 | 0 |

Table 8-188: Sums of Ethofumesate and its metabolites in water and sediment of the pond and creek system in % AR

| Time [d] | 0 | 0.25 | 1 | 2 | 7 | 14 | 29 | 61 | 103 | 121 | 230 |
|---------------------|-------|-------|------|-------|------|------|------|------|------|------|------|
| Pond System | | | | | | | | | | | |
| Ethofumesate | 94.1 | 92.5 | 90.3 | 102.2 | 91.0 | 90.0 | 89.7 | 84.7 | 70.7 | 72.3 | 36.9 |
| Keto-Ethofumesate | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| EDB | 3.4 | 3.3 | 2.8 | 2.2 | 0.7 | 0.0 | 0.0 | 1.7 | 0.0 | 0.8 | 3.8 |
| HDBM | 0.0 | 0.6 | 1.6 | 0.9 | 0.0 | 0.0 | 0.0 | 0.0 | 0.6 | 1.3 | 1.7 |
| HDS | 0.0 | 0.0 | 0.0 | 0.5 | 3.3 | 3.9 | 3.0 | 5.4 | 10.6 | 5.8 | 10.7 |
| Creek System | | | | | | | | | | | |
| Ethofumesate | 103.0 | 106.7 | 98.4 | 99.3 | 96.7 | 97.8 | 93.4 | 83.2 | 79.7 | 77.0 | 56.2 |
| Keto-Ethofumesate | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| EDB | 4.4 | 4.4 | 3.5 | 2.6 | 2.6 | 0.2 | 1.7 | 0.7 | 0.0 | 0.0 | 0.0 |
| HDBM | 0.0 | 0.7 | 0.8 | 1.1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| HDS | 0.0 | 0.0 | 0.0 | 1.0 | 2.1 | 3.8 | 3.5 | 7.5 | 5.3 | 5.7 | 0.0 |

The half-lives of Ethofumesate in water/sediment system were 188 days (1st order) in pond system and 275 days (1st order) in creek system. The DT₉₀ values were not calculated.

Table 8-189: Degradation parameters of Ethofumesate in water/sediment systems

| System | Phase | Kinetics | Confidence limits (95%) [days] | DT ₅₀ [days] |
|--------|--------------|----------------------------|-----------------------------------|----------------------------|
| Pond | Water phase | 1 st order | 76.0 - 97.9 | 86.9 |
| | | Sqrt 1 st order | 28.1 – 42.4 | 34.9 |
| | Whole system | 1 st order | 175 - 200 | 188 |
| | | Linear | 191 - 210 | 201 |
| Creek | Water phase | 1 st order | 163 - 199 | 181 |
| | | Sqrt 1 st order | 121 - 153 | 136 |
| | Whole system | 1 st order | 264 - 286 | 275 |
| | | Linear | 243 - 264 | 253 |

III. CONCLUSION

The half-lives of Ethofumesate in water/sediment system were 188 days (1st order) in pond system and 275 days (1st order) in creek system. One metabolite, HDS (= NC 20645), was found in the water/sediment systems above 5% for two succeeding sampling point (creek system) or above 10% (pond system).

Comments RMS

Although the study was conducted according to the BBA Guideline, part IV, 5-1 (1990) and SETAC recommendations (1995), the study was in accordance with the relevant OECD 308 guideline. Significant details on the analytical method are missing, such as LOQ and LOD. This has also consequences for the subsequent kinetic evaluation. After first detect concentrations below LOD should be set to ½ LOD. Although the impact on the endpoints might be limited, clarification regarding analytical methods (LOD, LOQ) has to be provided.

The study is acceptable.

| | |
|----------------------------|---|
| Reference: | Calculations of the environmental fate endpoints in water/sediment systems for Ethofumesate according to recommendations of the FOCUS working group on degradation kinetics |
| Notifier: | UPL |
| Author(s), year: | Stangelj, A.; 2014 |
| Report/Doc. number: | 210790-CA-07020203-01 |
| Guideline(s): | Not applicable |
| GLP: | No |
| Deviations: | |
| Validity: | Valid |
| Status: | New study |

A kinetic analysis of the Heintze 2003 study was performed according to recommendations of the FOCUS workgroup on degradation kinetics (2006) and is reported in Stangelj (2014). The results of this analysis support the degradation as reported in the Heintze 2003 study. The analysis is submitted under KCA 7.2.2.3/02 and shortly summarised below.

Water/sediment degradation rates derived from experimental values obtained in a laboratory study with ^{14}C -Ethofumesate (Heintze, 2003) were calculated according to recommendations of the FOCUS workgroup on degradation kinetics (2006 & 2011).

Degradation data of two water-sediment systems were used in calculations performed with the model software KinGUI version 2.0. Modelling was done using all data, no weighting and M0 (total amount at time 0) were not fixed for the parent. M0 of the metabolites were fixed to 0. Flows from parent to metabolites as well as from parent or metabolite, resp., to sink were considered for the simultaneous fittings.

The data were optimized and integrated according to standard recommendations and assuming SFO (single first order) kinetics and FOMC (first order multi compartment) kinetics for Ethofumesate and assuming single first order kinetics for the metabolite. The calculated output data (consisting of daily percentages of the nominally applied concentration) and residuals (differences between calculated concentrations and actual measured concentrations) were graphically fitted and visually assessed. Following an acceptable visual assessment, the deviations between observed and calculated values relative to the uncertainty of the measurements were assessed using the chi-square (χ^2) statistical test where the FOCUS trigger level of < 15% was applied. A test of the confidence of the calculated data returned after optimisation was performed using a t-test and employing the FOCUS trigger value for probability of < 0.05.

For Ethofumesate, the obtained results indicate that SFO was the model that clearly fits best for both water-sediment systems. In all cases the kinetic evaluation using SFO resulted in better curve fittings and lower χ^2 values. For FOMC the probabilities of the t-test indicated that the parameters α and β are not significantly different from zero. FOMC did also not provide better Chi^2 (χ^2) values than the SFO model.

For parent/metabolite combination (pond and creek system) the simultaneous fittings led to acceptable results. The resulting curve fittings and residual plots for parent and metabolite were visually acceptable considering the inherent scatter of degradation data. However, the Chi^2 (χ^2) value for the metabolite significantly exceeds the trigger of 15 which was considered to be acceptable due to the scatter of degradation data. Furthermore, only the values of pond system can be used for the metabolite, due to inadequate simultaneous fitting for the creek system as the Chi^2 for the metabolite fitting is above 40.

Table 8-190: Whole system modelling and persistence endpoints for Ethofumesate and metabolite based on data obtained in two water/sediment system (pond and creek) and considering FOCUS kinetics

| Substance | Kinetic model | degDT50 (d) | degDT90 (d) | Formation fraction | Plots visually acceptable | Chi2 | t-test | EF |
|--------------|---------------|-------------|-------------|--------------------|---------------------------|--------|--------|--------|
| Pond | | | | | | | | |
| Ethofumesate | SFO | 217.7 | 723.1 | n.a. | yes | 5.151 | <0.05 | 0.9888 |
| NC 20645 | SFO | 99.1 | 329.2 | 0.443 | yes | 32.445 | <0.05 | |
| Creek | | | | | | | | |
| Ethofumesate | SFO | 204.8 | 680.2 | n.a. | yes | 3.711 | <0.05 | 0.9903 |
| NC 20645 | SFO | 13.4 | 44.6 | 1 | yes | 40.056 | <0.05 | |

Table 8-191: Results of the kinetic evaluation for the active substance Ethofumesate (parent to sink)

| Water-sediment system | Kinetic model | degDT50 (d) | degDT90 (d) | Plots visually acceptable | Chi2 (trigger:15) | t-test (trigger:0.05) | EF |
|-----------------------|---------------|-------------|-------------|---------------------------|-------------------|-----------------------|--------|
| Pond | SFO | 217.3 | 722 | yes | 5.049 | <0.05 | 0.8864 |
| | FOMC | 217.5 | 728.2 | yes | 5.162 | a: 0.406 b: 0.406 | 0.886 |
| Creek | SFO | 208.6 | 692.9 | yes | 3.626 | <0.05 | 0.8985 |
| | FOMC | 208.7 | 696.6 | yes | 3.709 | a: 0.43 b: 0.43 | 0.8983 |

Comment RMS

The notifier has provided calculations for the whole system, however dissipation kinetics of ethofumesate in the water and sediment compartment were not calculated by the notifier. The RMS has performed a kinetic evaluation according to level-I (FOCUS, 2006).

The dissipation kinetics for metabolite NC20645 in the total system of the experiment “Pond” are acceptable. In the water phase, maximum occurrence was not reached at study end - no degradation kinetics could be derived. NC 20645 occurs only at two sampling dates in the sediment phase (<3% AR).

The dissipation kinetics for metabolite NC20645 in the total system of the experiment “Creek” showed a very large scatter and the fits are visually unacceptable. For the water compartment, acceptable fits were achieved. The metabolite was not detected in the sediment phase.

The endpoints are:

| | DissT ₅₀ /DissT ₉₀ | Chi ² | Kinetic model | DissT ₅₀ /DissT ₉₀ | Chi ² | Kinetic model |
|-------|--|------------------|---------------|--|------------------|---------------|
| | Water | | | sediment | | |
| Pond | 37 / 343 | 5.7 | DFOP | 258 / 857 | 6.6 | SFO |
| Creek | 141 / 804 | 2.4 | DFOP | 273 / 907 | 1.7 | SFO |

The calculations are shown in the figures below.

Figure 8-119: Dissipation kinetics of ethofumesate in the water compartment of the system “Pond” (SFO)

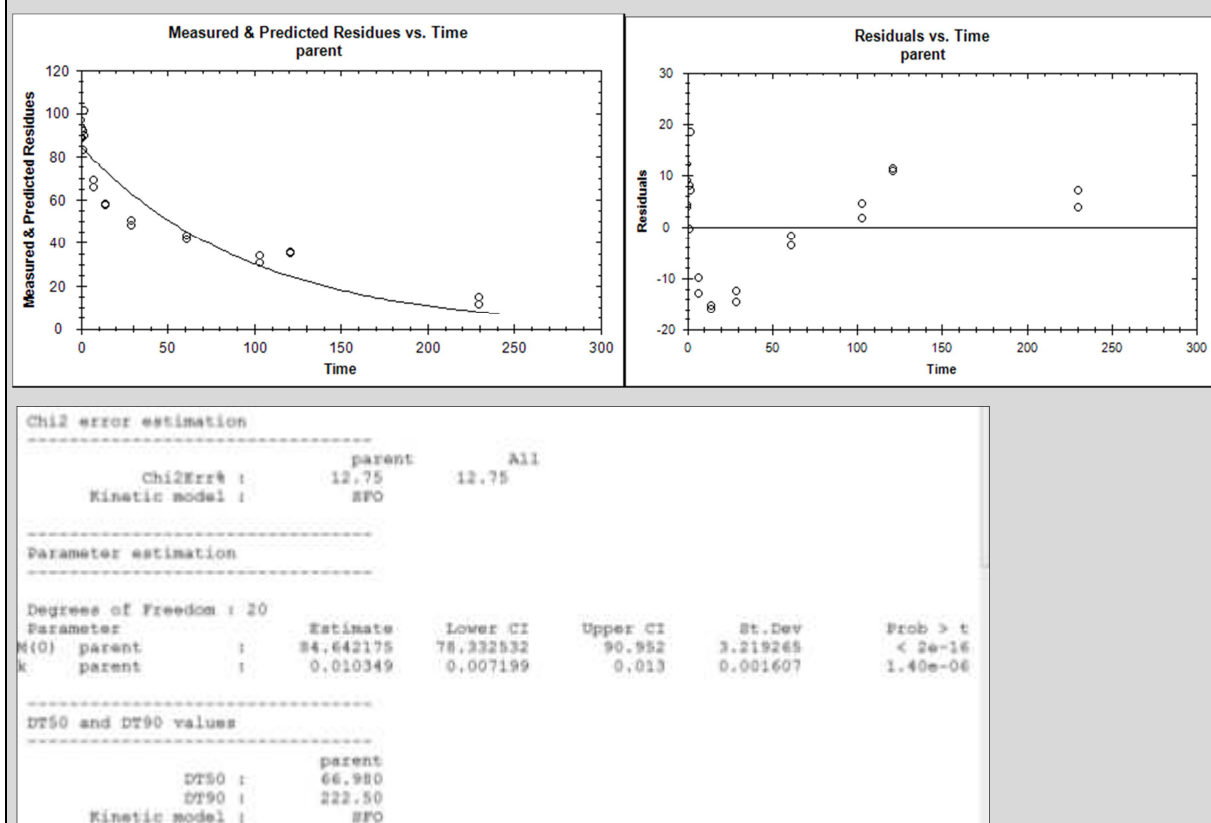


Figure 8-120: Dissipation kinetics of ethofumesate in the water compartment of the system “Pond” (DFOP)

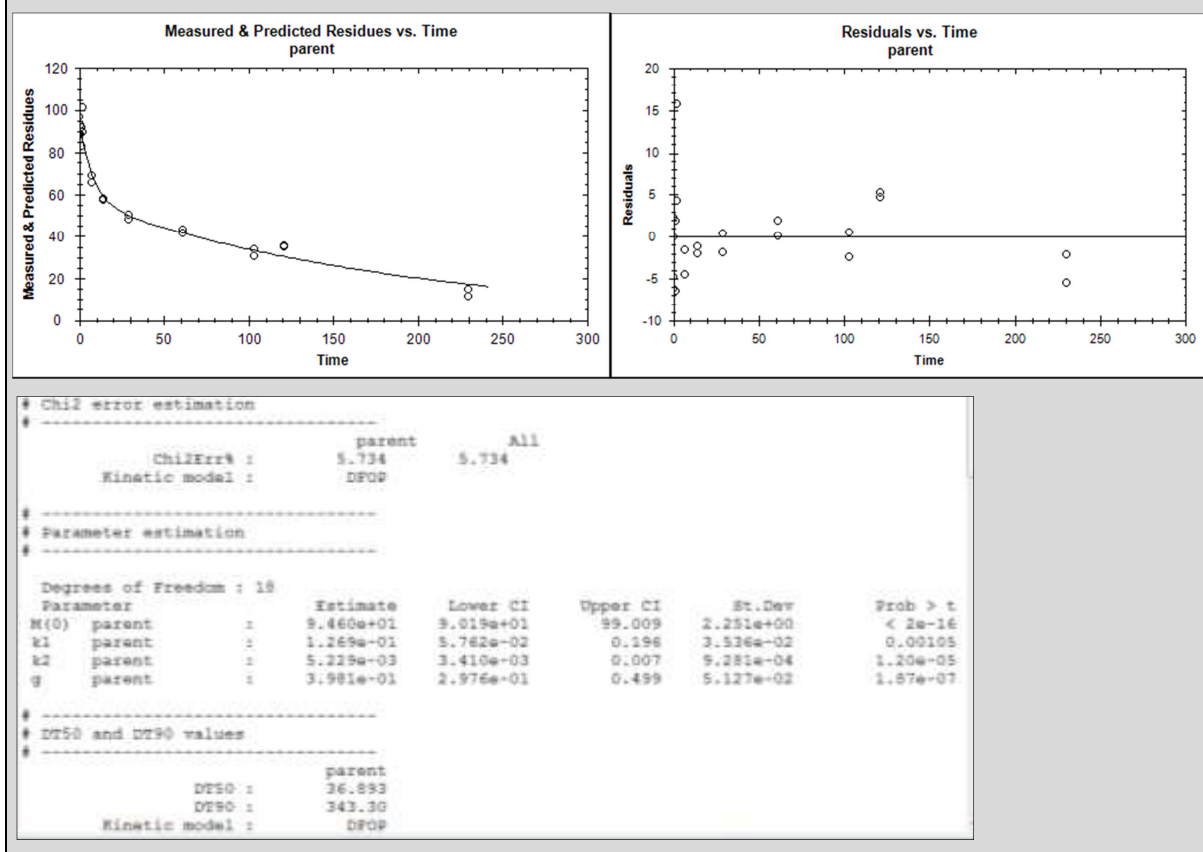


Figure 8-121: Dissipation kinetics of ethofumesate in the sediment compartment of the system “Pond” (SFO)

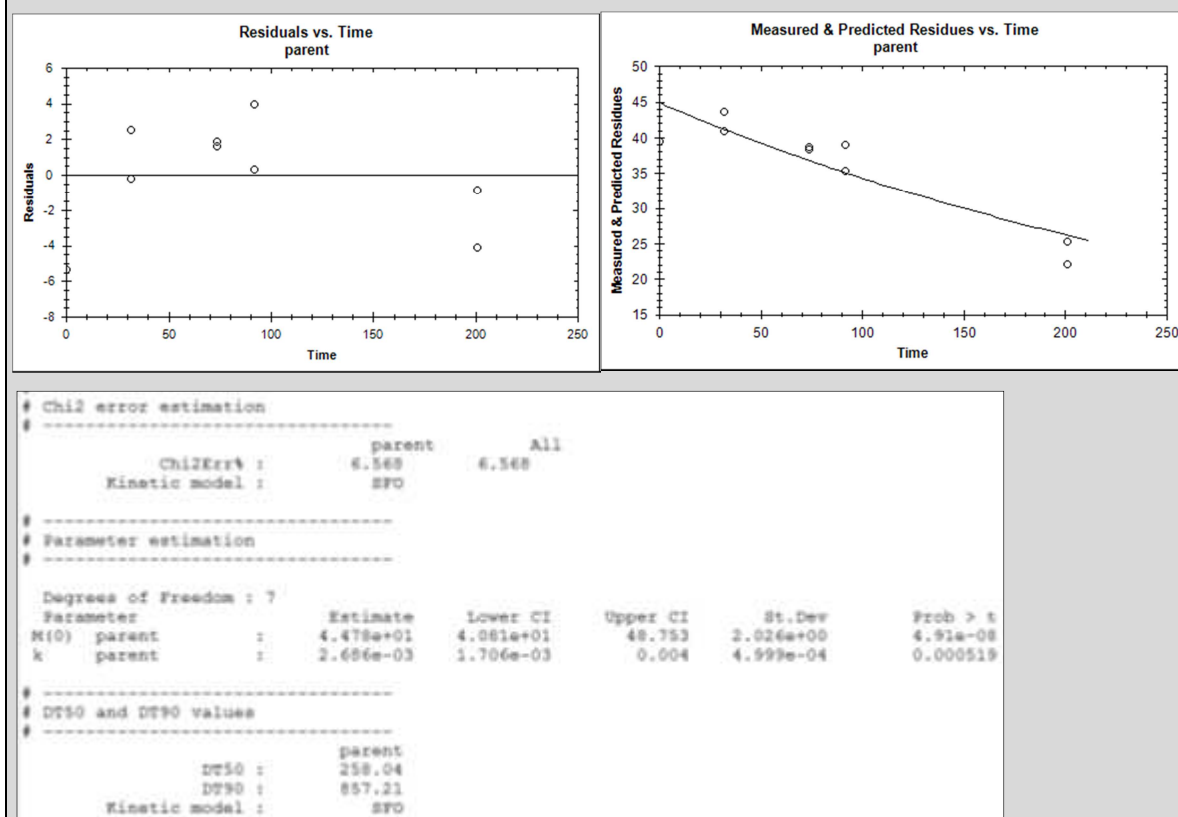


Figure 8-122: Dissipation kinetics of ethofumesate in the water compartment of the system “Creek” (SFO)

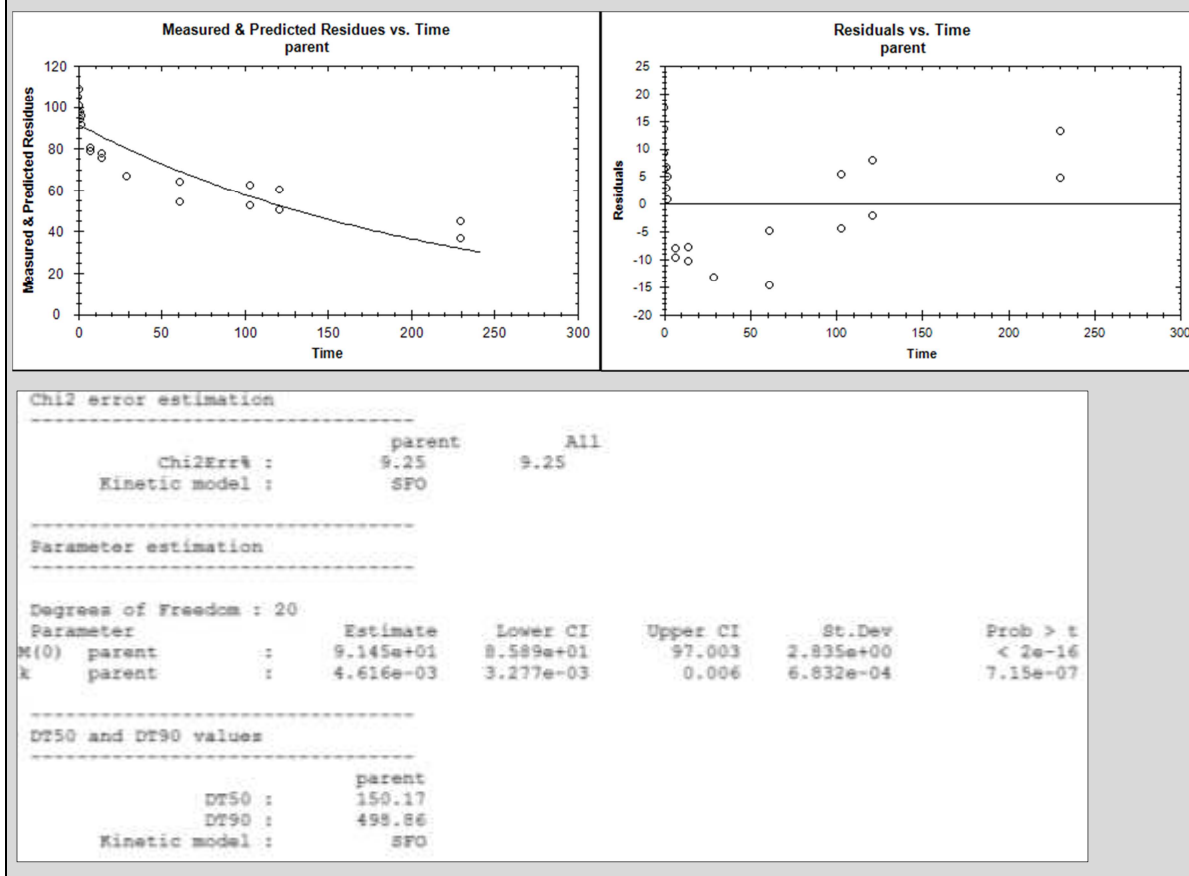


Figure 8-123: Dissipation kinetics of ethofumesate in the water compartment of the system “Creek” (DFOP)

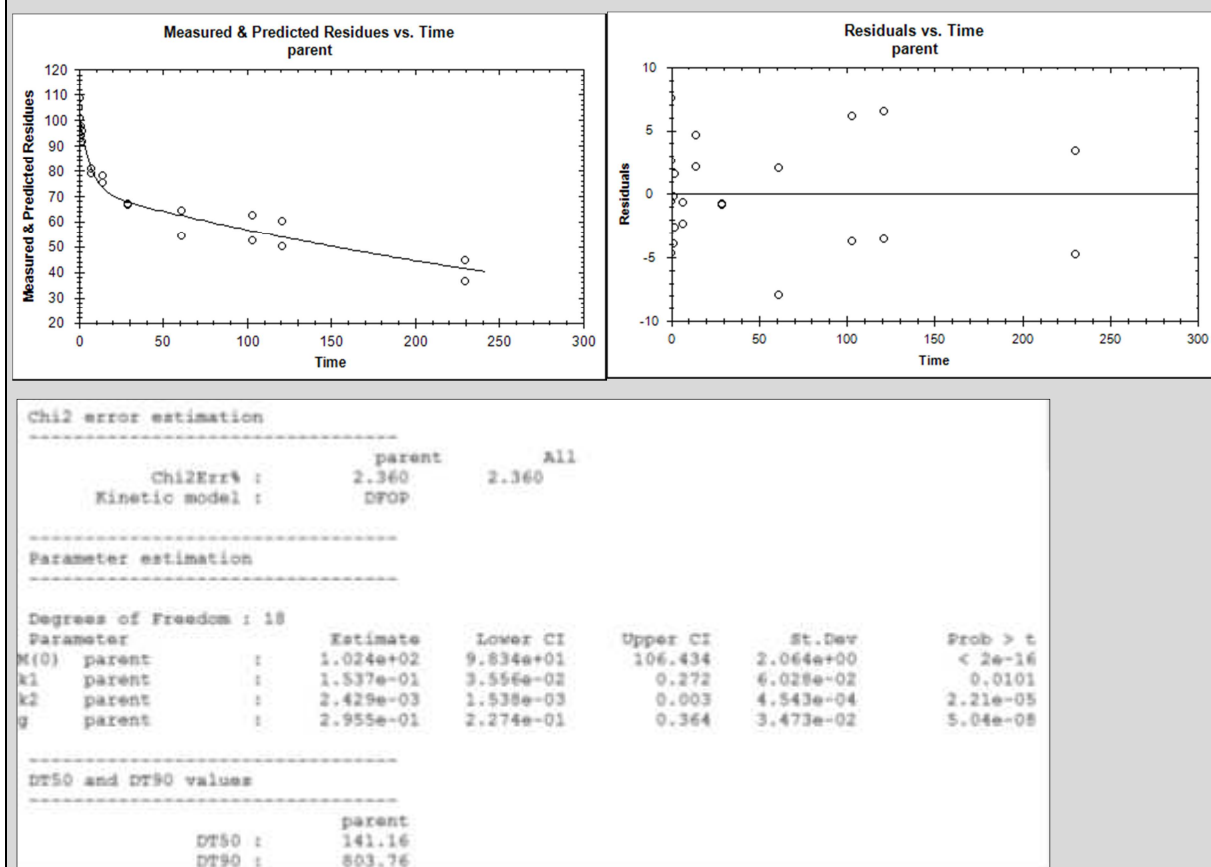
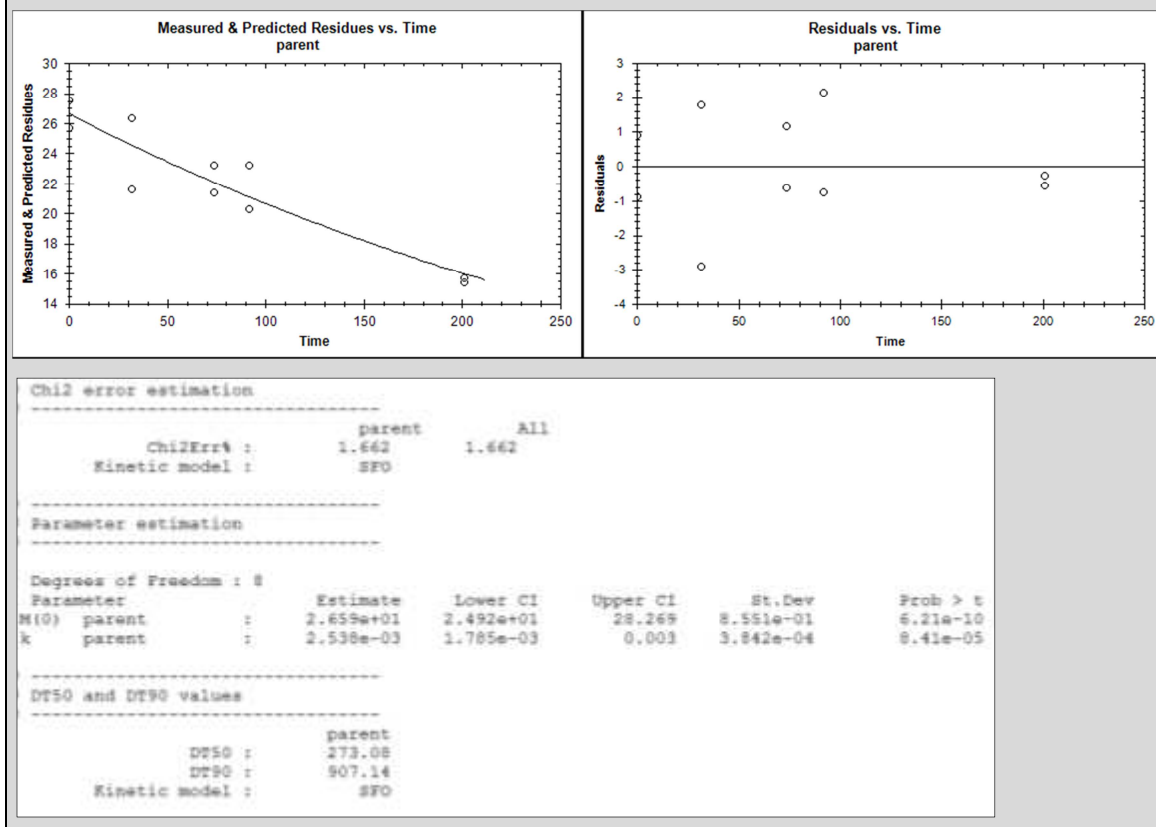


Figure 8-124: Dissipation kinetics of ethofumesate in the sediment compartment of the system “Creek” (SFO)



B.8.2.3.4. Irradiated water/sediment study

The behaviour of ethofumesate in water under light conditions and in water / sediment is adequately described. Therefore, the route and rate of degradation of ethofumesate in irradiated water/sediment systems were not separately studied.

B.8.2.4. Degradation in the saturated zone

The degradation of ethofumesate in the saturated zone was not studied.

B.8.2.5. Summary: fate and behaviour in water and sediment

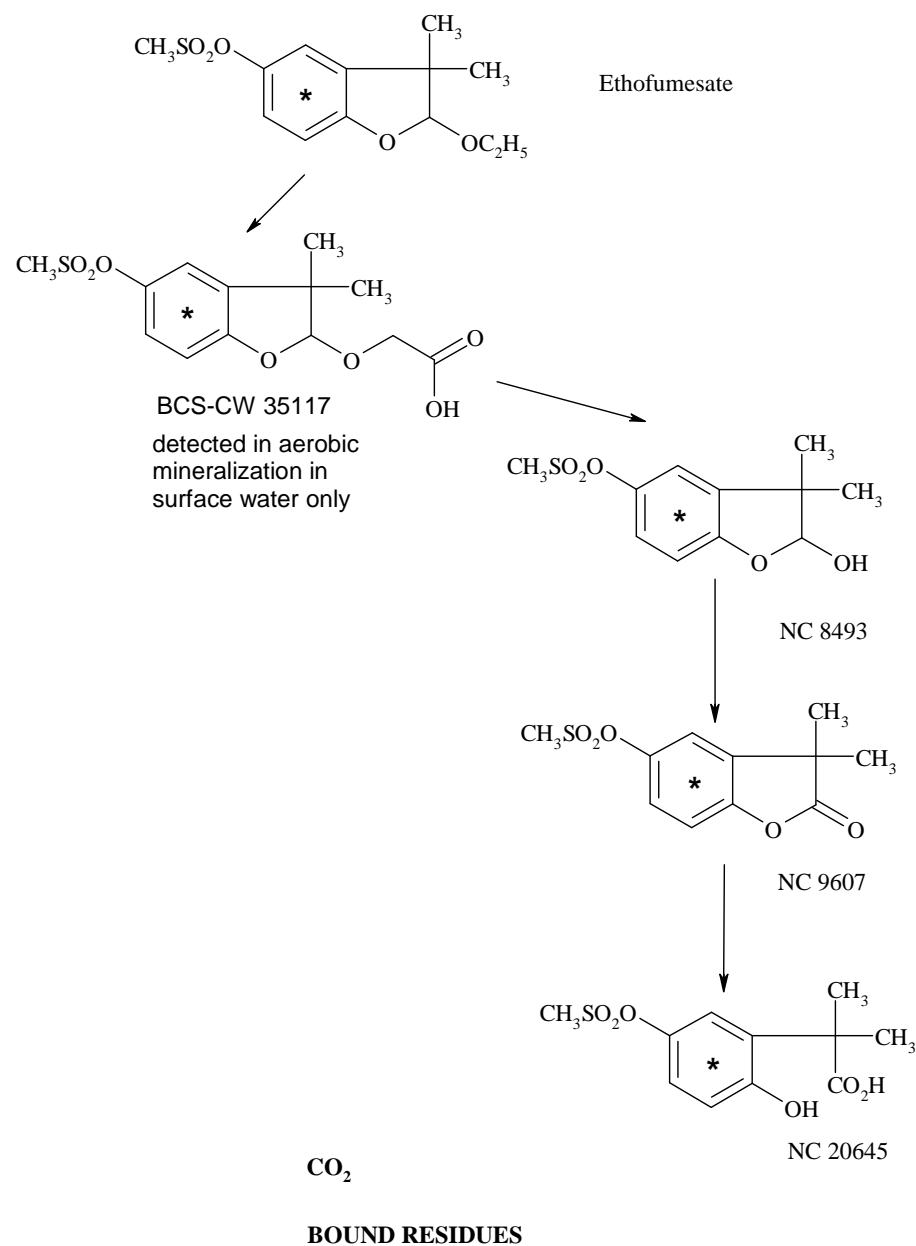
Ethofumesate is stable to hydrolysis at pH 4, pH 7 and pH 9. No major degradation products were observed.

In the first evaluation for approval, the photolytic degradation of ethofumesate was reported for a number of studies with variable results. Aqueous photolysis at pH 7 with filtered light from an Hg-arc lamp resulted in a DT₅₀ of 28-31 hours (3-5 fold intensity of natural sunlight) in irradiated solutions. However, due to 41% of unidentified radioactivity in this study and experimental deficiencies in other aqueous photolysis studies, new studies were conducted by both notifiers. In both new aqueous photolysis studies, a multitude of transformation products was formed; none of them exceeding 10% AR. A similar degradation pattern is observed in a study investigating the photolysis of ethofumesate in natural water, which was performed for registration in Japan and is an optional data requirement. The results mirrored the findings of the study on aqueous photolysis in buffered solution. A large number of unidentified photodegradates were formed, two of them above 5% AR.

Contrasting results were reported for the new aerobic mineralization studies in water. In the study by the notifier UPL, ethofumesate was found to be stable in natural surface water until day 62 of incubation and the mineralisation was marginal with a maximum of 1.1% (high-dose test) and 0.8% (low-dose test) at the end of the incubation period. The new study on aerobic mineralization in surface water submitted by the notifier Taskforce, however, showed that after a lag phase of 60 days a significant degradation of ethofumesate was observed: the remaining amounts of ethofumesate after 88 days were 58.3% AR and 79.3% AR in the low- (10 µg/L) and high-dose (100 µg/L) experiment, respectively. The main metabolite formed was NC 8493 (ethofumesate-2-hydroxy) with a maximum amount of 18.3% AR. The metabolite identified as BCS CW35117 (ethofumesate acetic acid) was formed at 13.4% AR and 2.4% AR in the low-dose and high-dose experiment, respectively.

Three dark water/sediment studies submitted for the previous evaluation were found to be not valid anymore, mainly due to experimental insufficiencies. For instance, in two of these studies only the pH of the water phase was reported whereas in one study only the sediment pH was determined. In addition, metabolites above 10% AR were not identified within these studies. Therefore, new water sediment studies were submitted by both notifiers. Mineralisation of the active substance ranged between 1.2 % AR and 15.3% AR after 103 and 125 days, respectively. Non-extractable residues in the sediment compartment ranged between 14.2 % AR and 43.2% AR at study end. Whole system half-lives ranged between 89 and 294 days (geomean 170 d; n = 8). In both new studies, NC20645 was identified as a major metabolite (max. occurrence in whole system 18.8% AR after 125 days). However, metabolite NC20645 did not reach the maximum occurrence at study end in two out of four water/sediment systems.

Figure 8-125: Degradation pathway of ethofumesate in water/sediment systems



B.8.3. FATE AND BEHAVIOUR IN AIR

B.8.3.1. Route and rate of degradation in air

| | |
|---------------------|--|
| Reference: | ESTIMATION OF THE PHOTOCHEMICAL- OXIDATIVE DEGRADATION OF ETHOFUMESATE (SCHERING CODE NO ZK 49 913) IN THE ATMOSPHERE |
| Notifier: | Taskforce |
| Author(s), year: | Brehm, M.; 1992 |
| Report/Doc. number: | A83382 / W 126/2 / M-155650-01-1 |
| Guideline(s): | None |
| GLP: | No |
| Deviations: | |
| Validity: | Valid |
| Status: | Previous evaluation in DAR for original approval / baseline dossier. |

Study summary based on previous draft assessment report

Materials and Methods

The photolysis of ethofumesate in air was determined according to the Atkinson method described in the OECD Draft Guidelines on Photochemical Oxidative Degradation in the Atmosphere (1991).

Results

The half-life for photooxidation of ethofumesate in air was calculated to 4.1 hours at 25°C, based on first order kinetics.

Comments RMS

The study is acceptable

| | |
|---------------------|---|
| Reference: | Ethofumesate - Predictive model calculation of the atmospheric oxidation behaviour (AOP) |
| Notifier: | Taskforce |
| Author(s), year: | Schneider, E.; 2002 |
| Report/Doc. number: | OFC00004956 / M-352110-01-1 |
| Guideline(s): | None |
| GLP: | No |
| Deviations: | |
| Validity: | Not valid |
| Status: | Previous evaluation in DAR for original approval / baseline dossier. |

Study summary based on previous draft assessment report

Materials and Methods

The photolytical half-life of ethofumesate in air was estimated to 2.1 hours using the "Atmospheric Oxidation Program, Version 1.5" (Meylan and Howard; Syracuse). AOPWIN estimates the rate constant for the atmospheric, gasphase reaction between photochemically produced hydroxyl radicals and organic chemicals.

The estimation methods used by AOPWIN are based upon structureactivity relationship (SAR) methods

Results

The half-life for photooxidation of ethofumesate in air was calculated to 2.1 hours.

Comments RMS

Key parameters, such as the assumed temperature, are missing. The study is not valid.

B.8.3.2. Transport via air

The vapour pressure of ethofumesate is 0.00065 Pa at 25°C indicating a moderate potential for volatilization from plant and soil. Since the compound is rapidly degraded in air ($DT_{50} = 4.1$ hours; Brehm, 1992), no further investigation of its transport in air is required. It is unlikely that the compound is transported in air over long distances or accumulates in air.

B.8.3.3. Local and global effects

There are no indications that the compound has local or global effects beyond those covered elsewhere in the draft review assessment report.

B.8.3.4. Summary: fate and behavior in air

The vapour pressure of ethofumesate is 0.00065 Pa at 25°C indicating a moderate potential for volatilization from plant and soil. Since the compound is rapidly degraded in air ($DT_{50} = 4.1$ hours), no further investigation of its transport in air is required. It is unlikely that the compound is transported in air over long distances or accumulates in air.

B.8.4. DEFINITION OF THE RESIDUE

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 | ethofumesate, NC 8493(ethofumesate-2-hydroxy), |
| Groundwater | ethofumesate, NC 8493(ethofumesate-2-hydroxy) NC 20645 (ethofumesate-carboxylic acid) |
| Surface Water | ethofumesate, NC 8493(ethofumesate-2-hydroxy) NC 20645 (ethofumesate-carboxylic acid) BCS-CW35117 (ethofumesate-acetic acid) |
| Sediment | ethofumesate, NC 20645 (ethofumesate-carboxylic acid) |
| Air | ethofumesate |

B.8.4.2. Definition of the residue for monitoring

The residue definition for monitoring is ethofumesate only for all compartments because all major degradation products are of no pesticidal nor toxicological nor ecotoxicological relevance.

B.8.5. MONITORING DATA CONCERNING FATE AND BEHAVIOUR OF THE ACTIVE SUBSTANCE, METABOLITES, DEGRADATION AND REACTION PRODUCTS

| | |
|---------------------|---|
| Reference: | Occurrence of 38 pesticides in various French surface and ground waters. |
| Notifier: | Taskforce |
| Author(s), year: | Legrand, M. F.; Costentin, E.; Bruchet, A.;1991 |
| Report/Doc. number: | A47899 / M-136600-01-1 |
| Guideline(s): | None |
| GLP: | No |
| Deviations: | |
| Validity: | Relevant. Not reliable. |
| Status: | Previous evaluation in DAR for original approval / baseline dossier. |

Study summary based on previous draft assessment report

A study including 38 pesticides, including ethofumesate, was carried out throughout France in 11 groundwater wells and on one site each in the River Seine and the River Marne. Each site was sampled 5 times over one year. The depths of the ground water wells were in the range 14-280 metres. Seven different multi-residue analytical techniques had to be used to cover all substances. The recovery for ethofumesate from tap water was, at 50 ppb = 83±% and at 200 ppb = 77±7%.

Results

Ethofumesate was recovered once in one well (depth 30 m) at a concentration of 0.050 µg/L.

Comments RMS

Rather than a survey, the study was mainly an analytical/methodological paper aimed to test different analytical methods. From this study, no conclusions on occurrence of ethofumesate in ground and surface water can be drawn since there was no information of the frequency and density of the use of pesticides in the areas around the sampling sites.

| | |
|---------------------|---|
| Reference: | Groundwater monitoring for ethofumesate in two sugar beet growing regions of Spain |
| Notifier: | Taskforce |
| Author(s), year: | Klaas, Ph.;2007 |
| Report/Doc. number: | IF-06/00624786 / M-294853-01-1 |
| Guideline(s): | None |
| GLP: | Yes |
| Deviations: | |
| Validity: | Relevant. Not reliable. |
| Status: | New study. |

EXECUTIVE SUMMARY

A groundwater monitoring study was conducted in two regions in Spain in order to determine levels of ethofumesate in groundwater.

The monitoring was conducted in the regions "Medina del Campo" and "Arévalo", both in Castile and León. They are part of a tableland in the centre of the Iberian Peninsular called "Meseta Central", that is at the same time the basin of the river Duero. The river basin is the most important production area of sugar beet in Spain.

Wells for groundwater sampling were selected by complying with realistic worst case conditions of the regions as well as avoiding contamination that did not derive from the normal agricultural use of ethofumesate.

Sampling was performed in two campaigns at the beginning and the end of the groundwater recharge period (September 2006 and February 2007). The monitoring included two wells in Arévalo. In Medina del Campo, one well was sampled in September 2006 and three wells were sampled in February 2007.

INFORMATION ON TEST METHOD:

Application:

Ethofumesate is a registered herbicidal active ingredient. Thus, the test items are commercial herbicidal products, which contain ethofumesate. Ethofumesate containing products are common herbicides in conventional sugar beet cultivation. Applications of ethofumesate on parcels in the surroundings of the selected monitoring wells were confirmed by the farmers.

The data concerning Ethofumesate applications were provided by the farmers (non-GLP).

Table 8-192: Region "Medina del Campo"

| Name | Parcel of the well | | | Distance to the next parcel on that ethofumesate was applied * [m] |
|------------|--|--|--------------|--|
| | Period of ethofumesate application | Amount of ethofumesate application [g ai / ha] | Surface [ha] | |
| Alaejos | 24.03.06 - 17.04.06 | 550 | 14 | 20 |
| Alaejos 91 | no data, ethofumesate applications on parcel of the well in 2005 confirmed by the farmer | | | |
| Val Verde | no data, ethofumesate applications in 2006 on nearby field confirmed by the farmer | | | |

* different from the one of the well

Table 8-193: Region "Arévalo"

| Name | Parcel of the well | | | Distance to the next parcel on that ethofumesate was applied * [m] |
|----------------|------------------------------------|--|--------------|--|
| | Period of ethofumesate application | Amount of ethofumesate application [g ai / ha] | Surface [ha] | |
| Aldeaseca | 29.04.06 - 01.06.06 | 400 | 5 | 70 |
| Fuentes de Año | 11.04.06 - 17.05.06 | 400 | 6 | 1000 |

* different from the one of the well

Test systems:

The test systems are the local groundwater bodies of the regions "Arévalo" and "Medina del Campo" in the autonomous community Castile and León. These regions are typical Spanish sugar beet cultivation areas and therefore selected by the Spanish authorities as representative test regions. The monitoring points are irrigation wells.

Analytical Method:

The groundwater specimen were analysed for ethofumesate at the Laboratorio de Análisis de Residuos de Plaguicidas, Castellón, Spain. Residues of ethofumesate were determined by using Liquid Chromatography coupled with tandem Mass Spectrometry (LC-MS/MS). The limit of quantitation (LOQ) of the method is 0.05 µg/L

RESULTS AND DISCUSSION

Groundwater samples were taken in September 2006 and February 2007. A total of three (first sampling period) and five (second sampling period) wells in the two regions Medina del Campo and Arévalo were monitored. Additional wells were investigated but did not meet the selection criteria for groundwater monitoring wells. This is because the wells in this area are used for irrigation. Their construction does not need to fulfill the strict criteria for wells used for drinking water abstraction or groundwater monitoring.

The two geographical areas Medina del Campo and Arévalo are typical and representative areas for sugar beet cultivation: Sugar beet was cultivated in the surroundings of all monitoring points in previous years and for some wells in the year of the first sampling (the second samples were taken before the vegetation period). The aquifer from which the samples were taken, the Detritic Tertiary of the Duero, is the main aquifer used in the region for withdrawal of drinking and irrigation water. The soils around the wells are coarse soils with a high sand and gravel content, and with a low content of organic matter. Thus, the monitoring was conducted at realistic worst case conditions.

A sufficient number of wells were sampled to representatively characterize ethofumesate levels of the groundwater aquifer.

The results of the residue analysis of the individual groundwater samples are summarized in the following tables.

Table 8-194: Analytic Results for the Region Medina del Campo

| Name | Sampling Date | Ethofumesate [µg/L] |
|------------|-------------------|------------------------|
| Alaejos | 28.09.2006 | < 0.05 |
| Alaejos | 21.02.2007 | < 0.05 |
| Alaejos 91 | 21.02.2007 | < 0.05 |
| Val Verde | 21.02.2007 | < 0.05 |

Table 8-195: Analytic Results for the Region Arévalo

| Name | Sampling Date | Ethofumesate [µg/L] |
|----------------|---------------|------------------------|
| Aldeaseca | 27.09.2006 | < 0.05 |
| Aldeaseca | 21.02.2007 | < 0.05 |
| Fuentes de Año | 27.09.2006 | < 0.05 |
| Fuentes de Año | 21.02.2007 | < 0.05 |

The groundwater samples of all wells included in the groundwater monitoring contained no residues of ethofumesate (LOQ = 0.05 µg/L).

Comments RMS

The monitoring report shows that ethofumesate did not occur at concentrations above 0.05 µg/L in 8 groundwater samples from 5 locations in the main Spanish sugar beet growing area. The study areas are well characterized. In order to be fully reliable for this risk assessment, a more comprehensive and representative sampling campaign is needed. The actual vulnerability of the sites should be set into context with the relevant FOCUS groundwater scenarios, hydraulic connectivity with the fields where ethofumesate was applied and the actual pesticide use (e.g. from farmer surveys) should be determined.

| | |
|---------------------|--|
| Reference: | Micro-rates of herbicides used in sugar beet crop -influence on herbicide residues level in roots and soil. |
| Notifier: | Taskforce |
| Author(s), year: | Domaradzki, K.; Wujek, B.; Kucharski, M.;200 |
| Report/Doc. number: | M-455974-01 |
| Guideline(s): | None |
| GLP: | No |
| Deviations: | |
| Validity: | Relevant, not reliable. |
| Status: | Scientific peer-reviewed literature |

Study summary

The aim was to evaluate the influence of low-rates application on herbicide residues in soil and roots of sugar beet. Chemical weed control was applied at recommended and reduced (50 and 66%) doses of 3 different herbicides, one of these containing inter alia the a.s. ethofumesate, and oil adjuvant applied 4 times at 7- to 10-day intervals starting at the onset of weed emergence. Samples of soil and sugar beet roots were taken at the day of lifting (depth 0-20 cm). Ethofumesate residues were analyzed using HPCL with UV-detection. In soil samples where recommended herbicide doses were applied, the residue of ethofumesate amounted up to 0.0085 mg/kg. In root samples, the residue amounted up to 0.0042 mg/kg. Application of a reduced dose (50%) leads to a significant decrease of residues to maximum 0.0061 mg/kg in soil and 0.0011 mg/kg in sugar beet roots. Where reduction amounted 66% of the application dose, the decreased of residue level was significantly lower than those obtained at the recommended dose with 0.0029 mg/kg in soil and 0.0006 mg/kg in roots. The values did not exceed EU acceptable limits.

Results

Maximum ethofumesate residues detected after the use of Betanal 274 OF (91 g phenmedipham/L, 71 g desmedipham/L and 112 g ethofumesate/L) in sugar beets were 0.0085 mg/kg in soil samples and 0.0042 mg/kg in sugar beet root samples.

Conclusion of the notifier:

The degradation behavior in the literature confirms the degradation in the above mentioned TFD studies. A simple back calculation indicates a DT50 for ethofumesate of about 40 days.

Comment RMS

Residues of ethofumesate in soil were determined only at two time-points. Therefore, no reliable degradation kinetics can be determined.

| | |
|---------------------|---|
| Reference: | Analysis of pesticides and metabolites in Spanish surface waters by isotope dilution gas chromatography/mass spectrometry with previous automated solid-phase extraction |
| Notifier: | Taskforce |
| Author(s), year: | Planas, C.; Puig, A.; Rivera, J.; Caixach, J.; 2006 |
| Report/Doc. number: | M-455857-01-1 |
| Guideline(s): | None |
| GLP: | No |
| Deviations: | |
| Validity: | Not relevant. |
| Status: | Scientific peer-reviewed literature |

Study summary

A method based on isotope dilution gas chromatography/mass spectrometry (GC/MS) with automated solid phase extraction (SPE) was used for the analysis of 32 pesticides and metabolites in surface waters. Uncertainties in pesticide determination in real samples were estimated using quality assurance/quality control data. For most pesticides, including ethofumesate, the expanded uncertainty was below 40%, according to the commonly established requirements for analytical results.

Ninetythree Spanish surface waters collected in June-July and September-November 2004 were analysed. Concentration and occurrence of pesticides were evaluated. Ethofumesate was only found during the summer period.

Results

Ethofumesate results for the summer period are shown in Table 7.5-5. Ethofumesate was detected in approximately 15% of the samples collected during the summer period.

Ethofumesate was not detected in any of the samples taken during the autumn period.

Table 8-196: Range and median concentrations (ng/L) of ethofumesate detected in the analysed samples from the summer period

| Compound | Maximum | Minimum | Median |
|--------------|---------|---------|--------|
| Ethofumesate | 21 | 2 | 4 |

The analytical method based on SPE with isotope dilution GC/MS was suitable for the analysis of ethofumesate in surface water samples. The expanded uncertainty measurement for ethofumesate was < 40%, according to the commonly established requirements for analytical measurements.

Concentrations of ethofumesate were between 2 and 21 ng/L in the summer period and were not detected in the autumn period, which was also a general finding for the rest of the pesticides and metabolites in this study.

Conclusion of the notifier:

The concentrations detected in surface water were low and within or below the expected range.

Comments RMS

The present study is a methodological study and – although well performed and reported – does not contribute to the risk assessment of ethofumesate. In order to be fully reliable from the environmental fate point of view, the actual vulnerability of the sampling sites should be assessed (e.g. set into context with the relevant FOCUS groundwater scenarios; hydraulic connectivity with the fields where ethofumesate was applied) and the actual pesticide use (e.g. from farmer surveys) remains unknown.

| | |
|---------------------|--|
| Reference: | Occurrence of pesticides and some of their degradation products in waters in a Spanish wine region |
| Notifier: | Taskforce |
| Author(s), year: | Herrero-Hernandez, E.; Andrades, M.; Alvarez-Martin, A.; Pose-Juan, E.; Rodriguez-Cruz, M.; Sanchez-Martin, M.;2013; |
| Report/Doc. number: | M-462662-01-1 |
| Guideline(s): | None |
| GLP: | No |
| Deviations: | |
| Validity: | Relevant. Not reliable. |
| Status: | Scientific peer-reviewed literature |

Study summary

A multi-residual analytical method based on solid phase extraction (SPE) followed by liquid chromatography–electrospray ionisation–mass spectrometry (LC–MS) was developed to monitor pesticides in natural waters. Fifty-eight compounds and some of their degradation products were surveyed to evaluate the quality of natural waters throughout the wine-growing region of La Rioja. The herbicide ethofumesate was among the most frequently detected compounds in water samples (present in 60-80% of the samples, depending on the study area), at concentrations < 0.1 µg/L with one exception. The overall maximum concentration detected was 0.133 µg/L.

1. Validity of the method:

The proposed methodology was validated for each of the compounds by studying the accuracy (average recovery) and precision (reproducibility and repeatability) at the level of concentration established by EU legislation and the limits of detection (LOD) and quantification (LOQ) of the complete method. The accuracy and precision of the proposed method was determined by recovery experiments and the relative standard deviations (RSD) of the signals or peak areas obtained for each analyte corresponding to five groundwater samples spiked with 0.1 µg/L for each analyte (Table 7.5-6).

Table 8-197: Analytical characteristics of the GC-MS method for ethofumesate after SPE with Oasis HLB cartridges

| Pesticide | SIM ion (m/z) | Recovery ^a (%) | RSD (%) | r ² (0.1-2.0 µg/L) ^b | LOD ^c (µg/L) | LOQ ^d (µg/L) |
|--------------|---------------|---------------------------|---------|--|-------------------------|-------------------------|
| Ethofumesate | 287.2 | 70 | 10 | 0.993 | 0.015 | 0.048 |

^a Calculated from the replicated analysis (n = 5) of spiked (0.1 µ/L) groundwater samples.

^b Linear calibration range.

^c Limit of detection.

^d Limit of concentration that can be quantified.

2. Analytical findings:

The analytical findings are shown in Table 7.5-7.

Table 8-198: Percentage of positive samples (or samples with some compound detected) with concentrations below and over 0.1 µg/L and average and maximum concentrations for the pesticides detected in the different areas of study

| Region (sampling points) | Positive samples (%) | | Concentration (µ/L) | |
|--------------------------|----------------------|---------|---------------------|------------------|
| | C < 0.1 | C > 0.1 | Average ± SD | C _{max} |
| Rioja Alavesa (n = 15) | 80 | 0 | 0.037 ± 0.014 | 0.067 |
| Rioja Alta (n = 34) | 79 | 0 | 0.032 ± 0.012 | 0.071 |
| Rioja Baja (n = 43) | 60 | 2 | 0.038 ± 0.022 | 0.133 |

Results

The herbicide ethofumesate was among the most frequently detected compounds in water samples (present in 60-80% of the samples, depending on the study area), at concentrations < 0.1 µg/L with one exception. The overall maximum concentration detected was 0.133 µg/L.

Conclusion of the notifier:

Samples from surface and groundwater were analysed without specification of the origin (surface or groundwater). The concentration of Ethofumesate was < 0.1 µg/L with one exception (max. 0.133 µg/L).

Comments RMS

The paper describes the development of a multiresidual analytical method. However, since the origin of the water samples is unknown, the study is not further considered.

| | |
|---------------------|--|
| Reference: | A comparison of predicted and measured levels of runoff-related pesticide concentrations in small lowland streams on a landscape level. |
| Notifier: | Taskforce |
| Author(s), year: | Berenzen, N.; Lentzen-Godding, A.; Probst, M.; Schulz, H.; Schulz, R.; Liess, M.;2005 |
| Report/Doc. number: | M-458560-01-1 |
| Guideline(s): | None |
| GLP: | No |
| Deviations: | |
| Validity: | Relevant, not reliable. |
| Status: | Scientific peer-reviewed literature |

Study summary

Simulation models are often used for the assessment of exposure to pesticides on a landscape level. The aim of the investigation was to compare the predicted concentrations of various pesticides provided by the extended SFIL (“simplified formula for indirect loadings caused by runoff”) model with measured concentrations obtained by event triggered sampling in the field. This validation should clarify the degree to which the model can predict in-stream pesticide concentrations on a landscape level for a routine assessment of pesticide exposure.

Measured ethofumesate concentrations in streams were between 0.05 and 13.7 µg/L and no ethofumesate was detected in 3 streams at all. The simulated concentrations calculated with the SILF model were between 0 and 10 µg/L.

As indicated by the close linear relationships between predicted and measured concentrations of the pesticides the model presented here provides a good prediction of the pesticide concentrations in small lowland streams during rain events resulting in surface water runoff.

Results summary

Measured ethofumesate concentrations in streams were between 0.05 and 13.7 µg/L and no ethofumesate was detected in 3 streams at all. The simulated concentrations calculated with the SFIL model were between 0 and 10 µg/L.

The model presented here provides a good prediction of the pesticide concentrations in small lowland streams during rain events resulting in surface water runoff.

Conclusion of the notifier:

The concentration in surface water were below or within the expected range.

Comment RMS

The applied method is not valid for regulatory purposes. Therefore the study cannot be considered reliable.

| | |
|---------------------|--|
| Reference: | Determination and aquatic risk assessment of pesticide residues in riparian drainage canals in northeastern Greece. |
| Notifier: | Taskforce |
| Author(s), year: | Papadopoulou-Mourkidou, E.; Vassiliou, G.; Vryzas, Z.; Alexoudis, C.; Galanis, K.;2011 |
| Report/Doc. number: | M-458635-01-1 |
| Guideline(s): | None |
| GLP: | No |
| Deviations: | |
| Validity: | Relevant, not reliable. |
| Status: | Scientific peer-reviewed literature |

Study summary

Monitoring data is presented for pesticide loading in the drainage canals of two transboundary rivers of northeastern Greece near the Greek/Bulgarian/Turkish borders during 1999 and 2008. An aquatic risk assessment was based on the measured concentrations (median and extreme residue levels) and ecotoxicological endpoints of three trophic levels, algae, aquatic invertebrates and fish derived from the EU review process. The Risk Quotients (RQ = residue level / lowest ecotoxicological endpoint) shows that ethofumesate poses no risk to aquatic organisms neither at median nor at extreme concentrations.

Results

Ethofumesate was found at low concentrations ranging around a median of 0.0936 µg/L (extreme residue level of 0.336 µg/L) during the monitoring period from 1999 through 2008. In these years, totally 12 herbicides, 14 insecticides and 7 fungicides were measured at highest median concentrations of up to 0.286 µg/L for atrazine (highest extreme residue level of 9.8 µg/L for cypermethrin).

In addition, an environmental risk assessment was conducted on the detected pesticides based on ecotoxicological endpoints from the FOOTPRINT PPDB database. It contains endpoints for algae, aquatic invertebrates and fishes originally collected from information sources produced for the EU review processes.

Ethofumesate risk assessment was conducted with a toxicity level to aquatic invertebrates of 320 µg/L and an assessment factor of 10 resulting in a safe risk quotient (RQ) well below the trigger of 1 ($RQ_{\text{median}} = 0.003$ and $RQ_{\text{median}} = 0.01$).

Conclusion of the notifier:

Ethofumesate was detected in drainage canals in low concentration (max. 0.336 µg/L).

Comments RMS

In order to be fully reliable from the environmental fate point of view, the actual vulnerability of the sampling sites should be assessed (e.g. set into context with the relevant FOCUS groundwater scenarios; hydraulic connectivity with the fields where ethofumesate was applied) and the actual pesticide use (e.g. from farmer surveys) remains unknown.

| | |
|---------------------|---|
| Reference: | Assessing Exposure to Transformation Products of Soil-Applied Organic Contaminants in Surface Water: Comparison of Model Predictions and Field Data. |
| Notifier: | Taskforce |
| Author(s), year: | Kern, S.; Singer, H.; Hollender, J.; Schwarzenbach, R.; Fenner, K.; 2011 |
| Report/Doc. number: | M-459500-01-1 |
| Guideline(s): | None |
| GLP: | No |
| Deviations: | |
| Validity: | Relevant, not reliable. |
| Status: | Scientific peer-reviewed literature |

Study summary

A dynamic two-box multispecies model with the compartments soil and air was used to calculate the relative surface water exposure potential of transformation products and their parent compounds. The used analysing method was solid-phase extraction coupled with the liquid chromatography mass spectrometry (SPE-LC-MS/MS).

The surface water sampling procedure detected the transformation product of ethofumesate, ethofumesate-2-keto, in no measured samples. The parent compound was measured at concentrations between 68 (harvesting period), 116 (post-application period) and 790 ng/L (application period) in the river La Petite Glâne in Switzerland. The estimated application rate of ethofumesate was 490 kg (no amount of area for this application value given).

Results

1. Analytical findings:

Concentrations for ethofumesate and ethofumesate-2-keto are shown in Table 7.5-9 and Table 7.5-10.

Table 8-199: Measured concentrations for ethofumesate in the river La Petite Glâne from spring to autumn 2008. Median, minimal and maximal concentrations during three periods as indicated. Values below limit of quantification are indicated as <LOQ.

| | Application period (May-June) n=9 | | | Post-application period (July) n=8 | | | Harvesting period (August-October) n=3 | | |
|--------------|--------------------------------------|------------------------|------------------------|---------------------------------------|------------------------|------------------------|---|------------------------|------------------------|
| | median conc. (ng/L) | min conc. (ng/L) | max conc. (ng/L) | median conc. (ng/L) | min conc. (ng/L) | max conc. (ng/L) | median conc. (ng/L) | min conc. (ng/L) | max conc. (ng/L) |
| Ethofumesate | 790 | 199 | 1680 | 116 | 69 | 296 | 68 | <10 | 73 |

Table 8-200: Estimated Concentrations of ethofumesate-2-keto during Application, Post-Application, and Harvesting Period and the Number of Samples in Which These TPs Were Detected Using LC-HR-MS/MSa

| Transformation product | Estimated concentration (ng/L) | | | |
|---------------------------|--------------------------------|--------------------------------|----------------------|-----------------------------|
| | Application period | Post- application period | Harvesting period | No. detection in samples |
| Ethofumesate-2-keto | 2.3 | 0.5 | 0.3 | 0 |

The surface water sampling procedure detected the transformation product of ethofumesate, ethofumesate-2-keto, in no measured samples. The parent compound was measured at concentrations between 68 (harvesting period), 116 (post-application period) and 790 ng/L (application period) in the river La Petite Glâne in Switzerland. The estimated application rate of Ethofumesate was 490 g/ha.

Conclusion of the notifier:

The concentrations in surface water were below or within the expected range.

Comments RMS

The study provides useful insights into ethofumesate concentrations in surface waters. However, the number of samples is limited. Moreover, the vulnerability of the sites is not addressed.

| | |
|---------------------|---|
| Reference: | Occurrence and Toxicity of 331 Organic Pollutants in Large Rivers of North Germany over a Decade (1994 to 2004). |
| Notifier: | Taskforce |
| Author(s), year: | Schafer, R.; Von Der Ohe, P.; Kuhne, R.; Schuurmann, G.; Liess, M.;2011 |
| Report/Doc. number: | M-458649-01-1 |
| Guideline(s): | None |
| GLP: | No |
| Deviations: | |
| Validity: | Relevant, reliable. |
| Status: | Scientific peer-reviewed literature |

Study summary

Concentrations of 331 organic compounds were measured in the four largest rivers of north Germany and potential risk for aquatic fauna was investigated using experimental and predicted acute toxicity data for *Pseudokirchneriella subcapitata*, *Daphnia magna* and *Pimephales promelas*.

Results

The maximum measured ethofumesate concentration was 0.025 µg/L and below the LOQ (0.05 µg/L). As a general approach, this concentration was compared to the toxicity of the respective substance to daphnids, algae and fish. Ethofumesate effect concentrations reported for this purpose were 14 mg/L for *D. magna* (48h-EC₅₀), 3.9 mg/L for *P. subcapitata* (48h to 96h-EC₅₀) and 38.663 mg/L for *P. promelas* (96h-LC₅₀).

Conclusion of the notifier:

The concentrations in surface water were below or within the expected range.

Comments RMS

The maximum measured ethofumesate concentration in surface water was 0.025 µg/L and below the LOQ (0.05 µg/L). However, the study does not affect the current risk assessment.

| | |
|---------------------|--|
| Reference: | Current-use pesticides in stream water and suspended particles following runoff: exposure, effects, and mitigation requirements |
| Notifier: | Taskforce |
| Author(s), year: | Bereswill, R.; Streloke, M.; Schulz, R.;2013 |
| Report/Doc. number: | M-462597-02-1 |
| Guideline(s): | None |
| GLP: | No |
| Deviations: | |
| Validity: | Relevant. Not reliable. |
| Status: | Scientific peer-reviewed literature |

Study summary

The main objectives of the present study were to characterize pesticide exposure in stream water and suspended particles under current conventional agricultural farming practices following rainfall-related, edge-of-field runoff events and to detect pesticide effects on the macroinvertebrate community. Average and maximum concentrations of ethofumesate detected in stream water were $3.6 \pm 6.0 \mu\text{g L}^{-1}$ and $21 \mu\text{g L}^{-1}$ as well as $17 \pm 18 \mu\text{g kg}^{-1} \text{ dw}$ and $51 \mu\text{g kg}^{-1} \text{ dw}$ in suspended particles, respectively. Generally, invertebrate fauna was dominated by pesticide-tolerant species, suggesting a high pesticide exposure at almost all sites

Results

1. Pesticide monitoring:

In total, there were 41 detections of 9 active ingredients in the water-phase samples and 80 detections in the suspended particle samples. Most frequently detected in the water phase was the herbicide ethofumesate (87% of samples). Observed toxicity in stream water was attributed predominantly to other compounds while ethofumesate accounted for 0.1% of the total toxicity observed. Suspended particle samples contained, on average, a mix of 4 ± 2 different active ingredients. Ethofumesate was found in at least 25% of the suspended particle samples.

The analytical results for ethofumesate are given in Table 7.5-12.

Table 8-201: Average and maximum concentrations of ethofumesate detected in-stream water and suspended particles. Concentrations are given rounded to two significant digits (n = number of samples; SD = Standard Deviation).

| In-stream water phase (n = 15) | | | In-stream suspended particles (n = 20) | | |
|--------------------------------|---|--|--|---|--|
| Number of detections | Average concentration \pm SD ($\mu\text{g L}^{-1}$) | Maximum concentration ($\mu\text{g L}^{-1}$) | Number of detections | Average concentration \pm SD ($\mu\text{g kg}^{-1} \text{ dw}$) | Maximum concentration ($\mu\text{g kg}^{-1} \text{ dw}$) |
| 13 | 3.6 ± 6.0 | 21 | 12 | 17 ± 18 | 51 |

Ethofumesate was the most frequently detected compound in the water phase (87% of samples, maximum concentration of 21 µg L⁻¹). It was found in at least 25% of the suspended particle samples with a maximum concentration of 51 µg kg⁻¹ dw.

Conclusion of the notifier:

The concentrations in surface water were below or within the expected range.

Comment RMS

Ethofumesate was detected in 13 out of 15 surface water samples with a maximum concentration of 21 µg/L. The study is well conducted. However, the number of samples is small and the vulnerability of the study sites – from a regulatory point of view – is unknown.

| | |
|---------------------|---|
| Reference: | Macroinvertebrate community structure in agricultural streams: impact of runoff-related pesticide contamination. |
| Notifier: | Taskforce |
| Author(s), year: | Berenzen, N.; Kumke, T.; Schulz, H.; Schulz, R.;2004 |
| Report/Doc. number: | M-458568-01-1 |
| Guideline(s): | None |
| GLP: | No |
| Deviations: | |
| Validity: | Not relevant. |
| Status: | Scientific peer-reviewed literature |

Study summary

Ethofumesate residues during rainfall-induced surface runoff events were measured in 6 German headwater streams. No ethofumesate residues were detected at streams 1 and 6. At stream 2, only one of the three runoff events resulted in the presence of the a.i. in the region of the detection threshold (0.05 µg/L). At streams 3, 4 and 5, ethofumesate residues were detected after each of the 3 runoff events with maximum concentrations of 1.0, 3.0 and 1.2 µg a.i./L, respectively.

The toxicity of ethofumesate and other detected pesticides in these streams was compared to the 48h-LC₅₀ values for *Daphnia magna*, derived from the US EPA database AQUIRE (LC₅₀ = 13,500 µg ethofumesate/L).

Results

1. Analytical findings:

A total of 10 different active substances were detected in stream water samples taken following investigated runoff events. Ethofumesate was detected at four sampling sites: At streams 3, 4 and 5, ethofumesate residues were detected after each of the three runoff events with maximum concentrations of 1.0, 3.0 and 1.2 µg/L, respectively. At stream 2, only one of the three runoff events resulted in the presence of the a.s. in a

concentration close to detection limit (i.e. 0.05 µg/L). At streams 1 and 6, none of the three water samples per stream contained ethofumesate residues. The results regarding ethofumesate are summarized below (Table 7.5-13).

Table 8-202: Analytical findings concerning ethofumesate at investigated streams

| | Stream 1 | Stream 2 | Stream 3 | Stream 4 | Stream 5 | Stream 6 |
|---|----------|----------|----------|----------|----------|----------|
| Maximum ethofumesate concentration [µg/L] | n.d. | 0.05 | 1.0 | 3.0 | 1.2 | n.d. |
| Investigated runoff events | 3 | 3 | 3 | 3 | 3 | 3 |
| Samples with residues | 0 | 1 | 3 | 3 | 3 | 0 |

n.d.: not detectable.

2. Biological findings:

The toxicity of pesticide mixtures contained in a water sample was assessed by calculating a sum parameter based on toxic units (TU_{sum}). For this calculation acute *Daphnia magna* endpoints from secondary sources were used i.e. derived from US EPA database (endpoint used for ethofumesate was 13500 µg/L). A shift within the community structure of each stream as a result of pesticide entries was not observed within the monitoring period (April to June). However, the community composition of three contaminated stream sites (maximal TU_{sum} between 0.02 and 0.22, corresponding to total pesticide concentrations between 0.02 × and 0.22 × acute toxicity to *Daphnia magna*) was clearly distinct from control sites (TU_{sum} < 0.00001): at contaminated streams lower densities of *Plecoptera*, *Ephemeroptera*, *Trichoptera* and *Diptera* were observed. A specific statement with respect to toxicity of detected ethofumesate concentrations was not made.

Conclusion of the notifier:

The concentration in surface water were below or within the expected range.

Comments RMS

Ethofumesate was detected at 4 out of 5 surface water sampling sites with a maximum concentration of 3 µg/L. The study is well conducted. However, the number of samples is small and the vulnerability of the study sites – from a regulatory point of view – is unknown. Moreover, the study is rather a targeted run-off study than a long term monitoring study.

| | |
|---------------------|--|
| Reference: | Analyzing effects of pesticides on invertebrate communities in streams. |
| Notifier: | Taskforce |
| Author(s), year: | Liess, M.; Von Der Ohe, P.;2005 |
| Report/Doc. number: | M-458575-01-1 |
| Guideline(s): | None |
| GLP: | No |
| Deviations: | |
| Validity: | Relevant, not reliable. |
| Status: | Scientific peer-reviewed literature |

Study summary

Ethofumesate residues were measured together with various other pesticides in 20 stream sites near Braunschweig, Germany. An automated active sampler that measured conductivity and water level in the stream continuously was used for sampling as well as two passive samplers, each a 1-L bottle mounted in the stream. During the investigation period (1.8 years per site), pesticides (including ethofumesate) were detected at 125 runoff events at 18 of the 20 sites. The mean measured concentration of ethofumesate for all stream sites was reported to be $8.66 \pm 23.35 \mu\text{g/L}$. The highest measured concentration was $129 \mu\text{g/L}$.

Results

During the investigation period (1.8 years per site), pesticides (including ethofumesate) were detected in 125 runoff events at 18 of the 20 sites. The mean measured concentration of ethofumesate was reported to be $8.66 \pm 23.35 \mu\text{g/L}$. The highest measured concentration was $129 \mu\text{g/L}$, which resulted in a logTU of -2.02.

Conclusion of the notifier:

The mean observed concentration is in line with predicted estimates. The highest measured concentration of $129 \mu\text{g/L}$ looks like an outlier (rough estimate of outlier significance ± 3 times standard deviation). However, without original data this can not be demonstrated accurately.

Also from publically available historical weather data for Braunschweig, it does not appear to have rained for the 10 days prior to and including the 14th June 1999. Therefore, this peak event could also be a point source (e.g. tank washing), poor application practice (overspray of a stretch of stream), or a major drift event.

Comments RMS

The RMS agrees with the notifier that the mean observed concentration is in line with the predicted estimates and that the highest measured concentrations could come from a point source. The study is well conducted.

| | |
|---------------------|---|
| Reference: | Pesticides and degradation products in groundwaters from a vineyard region: Optimization of a multiresidue method based on SPE and GC-MS |
| Notifier: | Taskforce |
| Author(s), year: | Herrero-Hernandez, E.; Pose-Juan, E.; Alvarez-Martin, A.; Andrades, M.; Rodriguez-Cruz, M.; Sanchez-Martin, M.;2012 |
| Report/Doc. number: | M-462594-01-1 |
| Guideline(s): | None |
| GLP: | No |
| Deviations: | |
| Validity: | Relevant, not reliable. |
| Status: | Scientific peer-reviewed literature |

Study summary

A reliable multiresidue method based on solid phase extraction was developed using GC–MS to determine and quantify 34 pesticides and some of their degradation products in groundwater in a vineyard region of La Rioja (northern Spain). Limit of detection (LOD) and limit of quantification (LOQ) of ethofumesate were 0.010 and 0.028 µg/L, respectively. It was detected in 88% of all tested samples at concentrations between 0.015 and 0.028 µg/L.

Results

Ethofumesate was detected in 88% of the 25 groundwater samples from the La Rioja region (Spain). Concentrations were between 0.015 and 0.028 µg/L. The LOQ was 0.028 µg/L.

Conclusion of the notifier:

None of the analyzed groundwater samples exceeded 0.1 µg/L.

Comment RMS

Ethofumesate was detected in 22 out of 25 groundwater water samples from the Rioja region in Spain. None of the samples exceeded the parametric drinking water threshold of 0.1 µg/L. The study is well conducted. However, the number of samples is small and the vulnerability of the study sites – from a regulatory point of view – is unknown.

| | |
|---------------------|---|
| Reference: | Exposure assessment of pesticides in a shallow groundwater of the Tagus vulnerable zone (Portugal): a multivariate statistical approach (JCA). |
| Notifier: | Taskforce |
| Author(s), year: | Silva, E.; Cerejeira, M.; Ribeiro, L.; Mendes, M.;2012 |
| Report/Doc. number: | M-458651-01-1 |
| Guideline(s): | None |
| GLP: | No |
| Deviations: | |
| Validity: | Relevant, not reliable. |
| Status: | Scientific peer-reviewed literature |

Study summary

This study aims to correlate groundwater exposure to pesticides in the Tagus vulnerable zone of Portugal using laboratory studies and modelling.

Groundwater samples were taken from wells over a 2 year period and analysed for the presence of 12 pesticides, including ethofumesate. The maximum detected ethofumesate concentration in groundwater samples collected at the Tagus vulnerable zone from 2004 to 2006 was 1.8 µg/L.

Joint Correspondence Analysis (JCA) was employed to analyse the field data and this lead to the conclusion that the concentrations of pesticides in groundwater were higher during Autumn and Spring, following patterns in agricultural practices

Results

The maximum detected ethofumesate concentration in groundwater samples collected at the Tagus vulnerable zone from 2004 to 2006 was 1.8 µg/L. JCA concluded that in general, pesticides were found more in spring and autumn sampling periods rather than in summer campaigns for almost all the wells. The geographic and seasonal distribution of pesticide occurrence follows patterns in agricultural land and pesticide use with additional influences by natural factors and management practices.

Conclusion of the notifier:

In the present study 11 of the 20 investigated pesticides were detected in groundwater. This demonstrates the specific conditions given by the local situation. Under these vulnerable soil conditions Ethofumesate exceeded the 0.1 µg/L trigger in some cases.

The value of 1.8 µg/L is more than an order of magnitude higher than the next highest value found in literature and more than two orders of magnitude higher than modelling results. Therefore, this result has to be scrutinized carefully as it is likely to be a consequence of point source contamination or other extraordinary circumstances.

Comment RMS

The study shows that under very vulnerable conditions, ethofumesate is found in groundwater samples. In order to be fully reliable, the vulnerability of the sites should be set into relation to European sugar beet scenarios.

| | |
|---------------------|---|
| Reference: | Assessing the Quality of Freshwaters in a Protected Area within the Tagus River Basin District (Central Portugal). |
| Notifier: | Taskforce |
| Author(s), year: | Silva, E.; Pereira, A.; Estalagem, S.; Moreira-Santos, M.; Ribeiro, R.; Cerejeira, M.; 2013 |
| Report/Doc. number: | M-462658-01-1 |
| Guideline(s): | None |
| GLP: | No |
| Deviations: | |
| Validity: | Relevant, not reliable. |
| Status: | Scientific peer-reviewed literature |

Study summary

Water-sediment quality was assessed in an agricultural zone of a protected area within the Tagus River basin district (central Portugal) combining chemical analysis (groundwater from wells with 20 – 50 m depth, surface water, June to August 2008) to 20 pesticide compounds and whole toxicity testing using the bacterium *Vibrio fischeri*, the algae *Pseudokirchneriella subcapitata*, the crustacean *Daphnia magna*, and the midge *Chironomus riparius*. Ethofumesate was detected at the two points of the Alverca do Campo embankment with an overall maximum concentration of 0.16 µg L⁻¹. Most severe adverse effects were noted on the growth of *P. subcapitata* and lethality of *D. magna* in non-diluted water samples.

Results

Some pesticides were detected in groundwater, but Ethofumesate was not listed. It is therefore concluded, that Ethofumesate was not detected in groundwater.

Conclusion of the notifier:

Ethofumesate was not detected in groundwater.

Comments RMS

Ethofumesate was detected in surface water samples at concentrations up to 0.16 µg/L but not in groundwater samples. In order to be fully reliable, the vulnerability of the sites should be set into relation to European sugar beet scenarios.

| | |
|---------------------|---|
| Reference: | Multiresidues of herbicides in surface water and groundwater on cultivated terrain of Lower Silesia. |
| Notifier: | Taskforce |
| Author(s), year: | Kucharski, M.; Wysocki, A.; Wujek, B.; Sadowski, J.;2012 |
| Report/Doc. number: | M-459329-01-1 |
| Guideline(s): | None |
| GLP: | No |
| Deviations: | |
| Validity: | Relevant, not reliable. |
| Status: | Scientific peer-reviewed literature |

Study summary

Monitoring of potential pollutants in surface and ground waters was performed in 2004-2008 in Silesia, Poland. Samples were collected each year from the same at two basic times: spring (when herbicides were being applied in spring) and autumn (when herbicides were being applied in autumn). Samples were collected randomly during heavy rainfall or in order to measure residues of a specific herbicide. The measurement of residues in the samples was performed by gas chromatography using an electron capture detector and high-performance liquid chromatography with a UV detector.

Residues from 21 herbicide active substances were found. The highest environmental concentration of ethofumesate measured in surface water samples was 0.50 µg/L. In groundwater samples a maximum of 0.06 µg/L was detected.

Results

Herbicide concentrations in water samples were measured via gas chromatography and high-performance liquid chromatography. The highest environmental concentration of ethofumesate measured in surface water samples was 0.50 µg/L and 0.06 µg/L in groundwater samples (time period for sampling: 2004-2008).

Conclusion of the notifier:

None of the analyzed groundwater samples exceeded 0.1 µg/L.

Comments RMS

The highest environmental concentration of ethofumesate measured in surface water samples was 0.50 µg/L and 0.06 µg/L in groundwater samples (time period for sampling: 2004-2008). In order to be fully reliable, the vulnerability of the sites should be set into relation to European sugar beet scenarios.

| | |
|---------------------|---|
| Reference: | Occurrence of currently used pesticides in ambient air of Centre Region (France). |
| Notifier: | Taskforce |
| Author(s), year: | Yusa, V.; Petrique, O.; Colin, P.; Mellouki, A.; Pastor, A.; Coscolla, C.; Yahyaoui, A.; 2012 |
| Report/Doc. number: | M-458632-01-1 |
| Guideline(s): | None |
| GLP: | No |
| Deviations: | |
| Validity: | Relevant, not reliable. |
| Status: | Scientific peer-reviewed literature |

Study summary

Ambient air samples were collected, from 2006 to 2008 at three rural and two urban sites in Centre Region (France) and analyzed for 56 currently used pesticides. The majority of the CUPs showed a seasonal trend, with most of the detections and the highest concentrations occurring during the spring and early summer.

Results

During the study period 2006-2008, ethofumesate was exclusively detected at one rural site (Oysonville) which is intensively used for agriculture (maize, wheat, soybean, barley, sunflowers). The concentration ranged between 0.54-1.16 ng/m³ (SD: 0.92 ± 0.25 ng/m³; n = 262).

Conclusion of the notifier:

Ethofumesate was detected in air in very low concentrations.

Comments RMS

The study clearly shows that in an area of intensive agriculture, ethofumesate could be detected in ambient air and concentrations ranged between 0.54-1.16 ng/m³. From the study report it is unclear how representative such a site is for regulatory purposes.

| | |
|---------------------|--|
| Reference: | Temporal variations of concentrations of currently used pesticides in the atmosphere of Strasbourg, France. |
| Notifier: | Taskforce |
| Author(s), year: | Schummer, C.; Mothiron, E.; Appenzeller, B.; Rizet, A.; Wennig, R.; Millet, M.;2010 |
| Report/Doc. number: | M-457521-01-1 |
| Guideline(s): | None |
| GLP: | No |
| Deviations: | |
| Validity: | Relevant, not reliable. |
| Status: | Scientific peer-reviewed literature |

Study summary

Atmospheric samples have been collected in Strasbourg between April 18 and May 29, 2007 and were analyzed for 71 current-use pesticides, of which 38 were detected. Significant correlations to temperature were observed for ethofumesate. No evidence was given that the correlation is caused by ongoing treatment on agricultural fields.

The very same measurements were again published in another article with slight inconsistency in the sampling methods (flow rate in sampler)

Results

Herbicides are in general less abundant in air than fungicides or insecticides. Concentration peaks are presumably attributed to pre-emergence use early in the season. Ethofumesate was among the detected herbicides but concentrations were low compared to the other detected pesticides. Ethofumesate concentrations are significantly correlated to temperature but it cannot be concluded that this is caused by vaporizations from surfaces since no evidence for on-going treatments were given.

Conclusion of the notifier:

Ethofumesate was detected in air in very low concentrations.

Comments RMS

The study clearly shows that in an area of intensive agriculture, ethofumesate could be detected in ambient air and concentrations ranged between 0.07-1.13 ng/m³. In addition, concentrations of ethofumesate correlated with temperature. The RMS agrees with the notifier that without exact knowledge of the application times, no reliable conclusions on potential vaporization can be drawn. From the study report it is unclear how representative such a site is for regulatory purposes.

B.8.5.1. Summary monitoring data

The monitoring for the presence of ethofumesate in groundwater following the use on sugar beet has been requested by the Spanish Registration Authorities. The notifier Taskforce carried out a monitoring study in the regions "Medina del Campo" and "Arévalo", both in Castile and León. They are part of a tableland in the centre of the Iberian Peninsula called "Meseta Central", that is at the same time the basin of the river Duero. The river basin is the most important production area of sugar beet in Spain. The concentrations of ethofumesate in the eight groundwater samples from five locations were all below 0.05 µg/L. However, in order to be more convincing and conclusive, a more comprehensive and representative sampling campaign would have been needed. The actual vulnerability of the sites should have been set into context with the relevant FOCUS groundwater scenarios, hydraulic connectivity with the fields where ethofumesate was applied and the actual pesticide use (e.g. from farmer surveys) should have been determined.

Several scientific papers on surface and groundwater monitoring were retrieved and submitted by the notifier Taskforce. In a comprehensive and fully reliable study on the occurrence of 331 organic pollutants in rivers from North Germany, between 1994 and 2004 ethofumesate was never detected above the LOQ.

In a study from Spain, water samples from ninety two sampling points (13 surface and 79 ground water) were analysed. Ethofumesate was present in 60-80% of the samples at concentrations < 0.1 µg/L (mean about 0.032 – 0.038 µg/L) with one exception (0.133 µg/L). However, it is unknown whether the maximum concentration is from a groundwater or surface water sample.

Ethofumesate concentrations in air samples from rural and urban areas were investigated in a French monitoring study. Ethofumesate was detected in 2% of the ambient air samples and concentrations ranged between 0.54 and 1.16 ng/m³. In a study investigating the temporal variations of currently used pesticides in Strasbourg (France), Ethofumesate was found at concentrations ranging between 0.07 and 1.13 ng/L. However, without exact knowledge of the application times, no reliable conclusions on potential vaporization of ethofumesate can be drawn. From the study report it is unclear how representative such a site is for regulatory purposes.

B.8.6. REFERENCES RELIED ON

| Data Point | Author(s) | Year | Title Company Report No. Source (where different from company) GLP or GEP status 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 /03 | Waring, A. R. | 1992 | [14C]-ETHOFUMESATE: AEROBIC METABOLISM IN TWO SOILS AT TWO MOISTURE CONTENTS Hazleton UK; Bayer CropScience, Report No.: A83385, Report includes Trial Nos.: 194/58 89B Edition Number: M-155653-01-1 Date: 1992-07-22 GLP/GEP: yes, unpublished ...also filed: KCA 7.1.2.1.1 /06 | N | N | | Bayer CropScience | In DAR (1998) |
| KCA 7.1.1.1 /06 | Menke, U.; Telscher, M. | 2008 | [Phenyl-UL-14C]ethofumesate (AE B049913): Time - dependent sorption in soils Bayer CropScience, Report No.: MEF-08/514, Edition Number: M-313317-01-1 Date: 2008-12-16 GLP/GEP: yes, unpublished ...also filed: KCA 7.1.2.1.1 /13 ...also filed: KCA 7.1.3.2 /01 | N | Y | New data requirement | Task Force Ethofumesate | Submitted for the purpose of renewal (2014) |
| KCA 7.1.1.1 /01 | McLaughlin, S.P. | 2012 | [14C]ETHOFUMESATE - AEROBIC RATE OF DEGRADATION IN SOIL United Phosphorus Ltd., 13845.6130 Smithers Viscient, Massachusetts, USA GLP: yes Published: no | N | Y | New data requirement | UPL | Submitted for the purpose of renewal (2014) |
| KCA 7.1.1.1 /02 | Hein, W. | 2012 | 14C-ETHOFUMESATE: AEROBIC DEGRADATION IN NINE EUROPEAN SOILS AT 20 °C IN THE DARK United Phosphorus Ltd., AS231 RLP AgroScience GmbH GLP: yes Published: no | N | Y | New data requirement | UPL | Submitted for the purpose of renewal (2014) |
| KCA 7.1.1.2 /01 | Waring, A. R. | 1992 | ANAEROBIC SOIL METABOLISM (14C)-Ethofumesate Hazleton UK, Harrogate, North Yorkshire, United Kingdom Bayer CropScience, Report No.: A83390, Report includes Trial Nos.: 194/60 93B Edition Number: M-155658-01-1 Date: 1992-07-22 GLP/GEP: yes, unpublished ...also filed: KCA 7.1.2.1.3 /01 | N | N | - | Bayer CropScience | In DAR (1998) |
| KCA 7.1.1.3 /03 | Stupp, H. P.; Weuthen, M. | 2013 | [Phenyl-UL-14C]Ethofumesate: Phototransformation on soil Bayer CropScience, Report No.: EnSa-12-0221, Edition Number: M-455051-01-1 Date: 2013-05-23 GLP/GEP: yes, unpublished | N | Y | Required due to deficiencies of previous study and inconsistent results | Bayer CropScience | Submitted for the purpose of renewal (2014) |
| KCA 7.1.2.1.1 /06 | Waring, A. R. | 1992 | [14C]-ETHOFUMESATE: AEROBIC METABOLISM IN TWO SOILS AT TWO MOISTURE CONTENTS Hazleton UK; Bayer CropScience, Report No.: A83385, | N | N | - | Bayer CropScience | In DAR (1998) |

| Data Point | Author(s) | Year | Title Company Report No. Source (where different from company) GLP or GEP status Published or not | Vertebrate study Y/N | Data protection claimed Y/N | Justification if data protection is claimed | Owner | Previous evaluation |
|-------------------|---|------|--|-------------------------|--------------------------------|--|-------------------------|---|
| | | | Report includes Trial Nos.: 194/58 89B Edition Number: M-155653-01-1 Date: 1992-07-22 GLP/GEP: yes, unpublished ...also filed: KCA 7.1.1.1 /03 | | | | | |
| KCA 7.1.2.1.1 /07 | Waring, A. R. | 1993 | AEROBIC METABOLISM IN A STANDARD SOIL (SPEYER 2.2) (14C)-Ethofumesate Hazleton UK, Harrogate, North Yorkshire, United Kingdom Bayer CropScience, Report No.: A83398, Report includes Trial Nos.: 194/59 94B Edition Number: M-155666-01-1 Date: 1993-09-01 GLP/GEP: yes, unpublished ...also filed: KCA 7.1.1.1 /04 | N | N | - | Bayer CropScience | In DAR (1998) |
| KCA 7.1.2.1.1 /08 | Cameron, B. D.; Phillips, M.; Hall, B. E. | 1991 | DEGRADATION IN SOIL UNDER AEROBIC CONDITIONS 14C Ethofumesate Inveresk Research Int. Ltd., Tranent, Scotland Bayer CropScience, Report No.: A87600, Edition Number: M-161526-01-1 Date: 1991-08-08 GLP/GEP: yes, unpublished ...also filed: KCA 7.1.1.1 /02 | N | N | - | Bayer CropScience | In DAR (1998) |
| KCA 7.1.2.1.1 /13 | Menke, U.; Telscher, M. | 2008 | [Phenyl-UL-14C]ethofumesate (AE B049913): Time - dependent sorption in soils Bayer CropScience, Report No.: MEF-08/514, Edition Number: M-313317-01-1 Date: 2008-12-16 GLP/GEP: yes, unpublished ...also filed: KCA 7.1.1.1 /06 ...also filed: KCA 7.1.3.2 /01 | N | Y | New data requirement | Task Force Ethofumesate | Submitted for the purpose of renewal (2014) |
| KCA 7.1.2.1.2 /01 | Traub, M. | 2011 | AE C508493 (ethofumesate-2-hydroxy): Aerobic degradation in four European soils Eurofins Agroscience Services EcoChem GmbH, Niefern-Oeschelbronn, Germany Bayer CropScience, Report No.: S11-00957, Edition Number: M-431094-01-1 Date: 2011-11-30 GLP/GEP: yes, unpublished | N | Y | Required since a metabolite in new photolysis study. | Task Force Ethofumesate | Submitted for the purpose of renewal (2014) |
| KCA 7.1.2.1.2 /02 | Traub, M. | 2012 | AE C509607: Aerobic degradation in four European soils Eurofins-GAB GmbH, Niefern-Oeschelbronn, Germany Bayer CropScience, Report No.: S11-00958, Edition Number: M-431784-01-1 Date: 2012-04-17 GLP/GEP: yes, unpublished | N | Y | Metabolite not exceeding 5% AR in soil but potentially required to assess the behaviour in soil of succeeding metabolite NC20645 | Task Force Ethofumesate | Submitted for the purpose of renewal (2014) |
| KCA 7.1.2.1.2 /03 | Traub, M. | 2012 | Ethofumesate-carboxylic acid (as potassium salt: AE C639175): Aerobic degradation in four European soils Eurofins-GAB GmbH, Niefern- | N | Y | Required according to new metabolite | Task Force Ethofumesate | Submitted for the purpose of renewal |

| Data Point | Author(s) | Year | Title Company Report No. Source (where different from company) GLP or GEP status Published or not | Vertebrate study Y/N | Data protection claimed Y/N | Justification if data protection is claimed | Owner | Previous evaluation |
|------------------|----------------|------|---|-------------------------|-----------------------------------|--|-------------------|---|
| | | | Oeschelbronn, Germany Bayer CropScience, Report No.: S11-03264, Edition Number: M-432551-01-1 Date: 2012-05-22 GLP/GEP: yes, unpublished | | | identification triggers. | | (2014) |
| KCA 7.1.2.1.2/01 | Malekani, K. | 2013 | NC8493 (A METABOLITE OF ETHOFUMESATE) - AEROBIC RATE OF DEGRADATION IN THREE SOILS United Phosphorus Ltd., 13845.6134 Smithers Viscient, Massachusetts, USA GLP: yes Published: no | N | Y | Required since a metabolite in new photolysis study. | UPL | Submitted for the purpose of renewal (2014) |
| KCA 7.1.2.1.3/01 | Waring, A. R. | 1992 | ANAEROBIC SOIL METABOLISM (14C)-Ethofumesate Hazleton UK, Harrogate, North Yorkshire, United Kingdom Bayer CropScience, Report No.: A83390, Report includes Trial Nos.: 194/60 93B Edition Number: M-155658-01-1 Date: 1992-07-22 GLP/GEP: yes, unpublished ...also filed: KCA 7.1.1.2/01 | N | N | - | Bayer CropScience | In DAR (1998) |
| KCA 7.1.2.2.1/03 | Castro, L. E. | 1991 | DISSIPATION OF ETHOFUMESATE IN SOIL FOLLOWING USE OF NORTRON EC IN SUGAR BEET CULTIVATION USA 1989 Nor-Am Chemical Company, Pikeville, NC, USA Bayer CropScience, Report No.: A83366, Edition Number: M-155634-02-1 EPA MRID No.: 41997205 Date: 1991-03-05 ...Amended: 1991-08-23 GLP/GEP: yes, unpublished | N | N | - | Bayer CropScience | In DAR (1998) |
| KCA 7.1.2.2.1/05 | Snowdon, P. J. | 1991 | DECLINE OF ETHOFUMESATE RESIDUES IN SOIL FOLLOWING APPLICATION WITH A 50 SC FORMULATION IN THE UK 1990/91 Schering AG, Berlin, Germany Bayer CropScience, Report No.: A83357, Report includes Trial Nos.: 041/04/056 Edition Number: M-155626-01-1 Date: 1991-10-25 GLP/GEP: yes, unpublished | N | N | - | Bayer CropScience | In DAR (1998) |
| KCA 7.1.2.2.1/06 | Moede, J. | 1992 | DISSIPATION OF ETHOFUMESATE IN SOIL FOLLOWING TREATMENT OF AN EC CO-FORMULATION WITH PHENMEDIPHAM AND DESMEDIPHAM IN THE FEDERAL REPUBLIC OF GERMANY 1990 Schering AG, Berlin, Germany Bayer CropScience, Report No.: A83378, Report includes Trial Nos.: PF-R 91 076 Edition Number: M-155646-01-1 Date: 1992-01-13 GLP/GEP: yes, unpublished | N | N | - | Bayer CropScience | In DAR (1998) |
| KCA | Aldag, R. | 1992 | TESTS ON THE DEGRADATION OF | N | N | - | Bayer | In DAR |

| Data Point | Author(s) | Year | Title Company Report No. Source (where different from company) GLP or GEP status Published or not | Vertebrate study Y/N | Data protection claimed Y/N | Justification if data protection is claimed | Owner | Previous evaluation |
|------------------|--------------|-------|--|-------------------------|-----------------------------------|--|------------------------------------|---|
| 7.1.2.2.1/07 | | | ETHOFUMESATE IN THE TOPSOIL UNDER FIELD CONDITIONS AT FOUR DIFFERENT LOCATIONS. Kemira Agro Oy, Helsinki, FIN; Bayer CropScience, Report No.: A87554, Edition Number: M-161457-01-1 Date: 1992-11-10 GLP/GEP: no, unpublished | | | | CropScience | (1998) |
| KCA 7.1.2.2.1/15 | Schmitt, W. | 2008 | Kinetic evaluation of the soil dissipation of ethofumesate under field conditions Bayer CropScience, Report No.: MEF-08/334, Edition Number: M-305786-01-1 Date: 2008-08-13 GLP/GEP: no, unpublished | N | Y | Needed for risk assessment | Task Force Ethofumesate | Submitted for the purpose of renewal (2014) |
| KCA 7.1.2.2.1/16 | Schmitt, W. | 2013 | Kinetic evaluation of the soil dissipation of ethofumesate under field conditions (re-evaluation according to EFSA guidance 2010) Bayer CropScience, Report No.: EnSa-13-0274, Edition Number: M-455136-01-1 Date: 2013-05-29 GLP/GEP: no, unpublished | N | Y | Re-evaluation according to EFSA Guidance 2010 | Task Force Ethofumesate | Submitted for the purpose of renewal (2014) |
| KCA 7.1.2.2.1/01 | Andrews, G. | 2014 | ETHOFUMESATE: FIELD DISSIPATION STUDIES IN NORTHERN AND SOUTHERN EUROPE United Phosphorus Ltd., NZ/11/007 Battelle UK LTD. GLP: yes Published: no | N | Y | New data for active ingredient, not previously submitted nor evaluated | UPL | Submitted for the purpose of renewal (2014) |
| KCA 7.1.2.2.1/02 | Seibert, K. | 2012 | DETERMINATION OF SOIL CHARACTERISTICS United Phosphorus Ltd., BP 10/12 LUFA, Speyer, Germany GLP/GEP: no Published: no | N | Y | New data for active ingredient, not previously submitted nor evaluated | UPL | Submitted for the purpose of renewal (2014) |
| KCA 7.1.2.2.1/03 | Stangelj, A. | 2014a | KINETIC EVALUATION OF SOIL DISSIPATION STUDIES WITH ETHOFUMESATE ACCORDING TO RECOMMENDATIONS OF THE WORK GROUP ON DEGRADATION KINETICS OF FOCUS United Phosphorus Ltd., 210790-CA-0701020201-01 GAB Consulting GmbH, Lamstedt, Germany GLP/GEP: no Published: no | N | Y | New data for active ingredient, not previously submitted nor evaluated | UPL | Submitted for the purpose of renewal (2014) |
| KCA 7.1.3.1.1/01 | Muellert, J. | 1990 | Determination of adsorption/desorption for ethofumesate Fraunhofer Institut fuer Umweltchemie und Oekotoxikologie, Schmallingenberg, Germany Feinchemie Schebda, Report No.: OFC00004873, Edition Number: M-352102-01-1 Date: 1990-08-27 GLP/GEP: yes, unpublished | N | N | - | Adama (former Feinchemie Schwebda) | In DAR (1998) |
| KCA 7.1.3.1.1/02 | Bruhl, R. | 1984 | THE ADSORPTION AND DESORPTION OF ETHOFUMESATE IN SOIL. | N | N | - | Bayer CropScience | In DAR (1998) |

| Data Point | Author(s) | Year | Title Company Report No. Source (where different from company) GLP or GEP status Published or not | Vertebrate study Y/N | Data protection claimed Y/N | Justification if data protection is claimed | Owner | Previous evaluation |
|-----------------------------|---|----------|--|-------------------------|-----------------------------------|--|-----------------------------------|---|
| | | | Schering AG, Berlin, Germany Bayer CropScience, Report No.: A83285, Edition Number: M-155554-01-1 Date: 1984-10-23 GLP/GEP: no, unpublished | | | | | |
| KCA 7.1.3.1. 1 /03 | Allen, R. | 1988 | [14C]-ETHOFUMESATE: ADSORPTION/DESORPTION IN SOIL Hazleton UK; Bayer CropScience, Report No.: A83336, Report includes Trial Nos.: 194/18 64b Edition Number: M-155605-01-1 Date: 1988-01-14 GLP/GEP: yes, unpublished | N | N | - | Bayer CropSc ience | In DAR (1998) |
| KCA 7.1.3.1. 1 /04 | Cameron, B. D.; Mackie, J. A.; Hall, B. E. | 1991 | ADSORPTION/DESORPTION IN SOIL 14C-Ethofumesate Inveresk Research Int. Ltd., Tranent, Scotland Bayer CropScience, Report No.: A87601, Edition Number: M-161528-01-1 Date: 1991-10-10 GLP/GEP: yes, unpublished | N | N | - | Bayer CropSc ience | In DAR (1998) |
| KCA 7.1.3.1. 1 /05 | Hoven, A.; Vonk, J. W. | 1988 | ADSORPTION OF ETHOFUMESATE TO DITCH-BOTTOM SEDIMENT TNO, Delft, NLD; Bayer CropScience, Report No.: A87606, Edition Number: M-161536-01-1 Date: 1988-07-28 GLP/GEP: yes, unpublished | N | N | - | Bayer CropSc ience | In DAR (1998) |
| KCA 7.1.3.1. 1 /06 | Cameron, B. D.; Mackie, J. A.; Hall, B. E. | 1991 | Aged soil leaching 14C Ethofumesate Inveresk Research Int. Ltd., Tranent, Scotland Bayer CropScience, Report No.: A87602, Edition Number: M-161529-01-1 Date: 1991-06-12 GLP/GEP: yes, unpublished | N | N | - | Bayer CropSc ience | In DAR (1998) |
| KCA 7.1.3 .1.1/ 01 | Hellstern, J. | 20 07 | ADSORPTION/DESORPTION OF 14C-ETHOFUMESATE ON SOIL - ADVANCED TEST AgriChem B.V., B01912 RCC Ltd. GLP: yes Published: no | N | Y | New data for active ingredient, not previously submitted nor evaluated | ACM * | Submitted for the purpose of renewal (2014) |
| KCA 7.1.3.1. 2 /01 | Hein, W.; Moendel, M.; D'Ambrosio, A. | 2011 | [phenyl-UL-14C] AE C508493: Adsorption/desorption in five different soils RLP AgroScience GmbH, Neustadt a. d. Weinstraße, Germany Bayer CropScience, Report No.: AS201, Edition Number: M-431772-01-1 Date: 2011-12-22 GLP/GEP: yes, unpublished | N | Y | Required according to new metabolite identification triggers. | Bayer CropSc ience | Submitted for the purpose of renewal (2014) |
| KCA 7.1.3.1. 2 /02 | Moendel, M.; D'Ambrosio, A. | 2012 | [phenyl-UL-14C] AE C509607: Adsorption/desorption in five different soils RLP AgroScience GmbH, Neustadt a. d. Weinstraße, Germany BCS, Report No.: AS202, | N | Y | Metabolite not exceeding 5% AR in soil but required to assess the behaviour in soil of | Task Force Ethofu mesate | Submitted for the purpose of renewal (2014) |

| Data Point | Author(s) | Year | Title Company Report No. Source (where different from company) GLP or GEP status Published or not | Vertebrate study Y/N | Data protection claimed Y/N | Justification if data protection is claimed | Owner | Previous evaluation |
|--------------------------|--|------|--|-------------------------|-----------------------------------|---|-----------------------------------|---|
| | | | Edition Number: M-446351-01-1 Date: 2012-07-19 GLP/GEP: yes, unpublished | | | succeeding metabolite ETO- carboxylic acid | | |
| KCA 7.1.3.1. 2 /03 | Moendel, M.; D'Ambrosio, A. | 2012 | [phenyl-UL-14C] AE C639175: Adsorption/desorption in five different soils RLP AgroScience GmbH, Neustadt a. d. Weinstraße, Germany Bayer CropScience, Report No.: AS204, Edition Number: M-446350-01-1 Date: 2012-06-25 GLP/GEP: yes, unpublished | N | Y | Required according to new metabolite identification triggers. | Task Force Ethofu mesate | Submitted for the purpose of renewal (2014) |
| KCA 7.1.3.2 /01 | Menke, U.; Telscher, M. | 2008 | [Phenyl-UL-14C]ethofumesate (AE B049913): Time - dependent sorption in soils Bayer CropScience, Report No.: MEF-08/514, Edition Number: M-313317-01-1 Date: 2008-12-16 GLP/GEP: yes, unpublished ...also filed: KCA 7.1.1.1 /06 ...also filed: KCA 7.1.2.1.1 /13 | N | Y | Investigation of increase of sorption behavior (aged sorption) in soil, metabolism and degradation rate, study considered as necessary to re-evaluate leaching and metabolism using fresh soils. | Task Force Ethofu mesate | Submitted for the purpose of renewal (2014) |
| KCA 7.1.4.1. 2 /01 | Mackie, J. A.; Hall, B. E. | 1992 | AGED SOIL LEACHING OF [14C]- ETHOFUMESATE Inveresk Research Int. Ltd., Tranent, Scotland Bayer CropScience, Report No.: A83391, Report includes Trial Nos.: 95B Edition Number: M-155659-01-1 Date: 1992-08-04 GLP/GEP: yes, unpublished | N | N | - | Bayer CropSc ience | In DAR (1998) |
| KCA 7.1.4.2 /01 | Allen, R.; MacKenzie, E.; Hibbert, L.; Lander, G. | 1995 | ETHOFUMESATE SC 50% W/V CR 19035/1 and CR 18654/1 LEACHING IN SOIL LYSIMETERS MAINTAINED UNDER OUTDOOR CONDITIONS Hoechst Schering AgrEvo GmbH, Frankfurt am Main, Germany Bayer CropScience, Report No.: A89221, Report includes Trial Nos.: ENVIR/97B Edition Number: M-164392-01-1 Date: 1995-03-31 GLP/GEP: yes, unpublished | N | N | - | Bayer CropSc ience | In DAR (1998) |
| KCA 7.1.4.2 /02 | Burgener, A. | 1994 | MOBILITY AND DEGRADATION IN SOIL IN OUTDOOR LYSIMETER 14C- Ethofumesate RCC Umweltchemie AG, Itingen, Switzerland Bayer CropScience, Report No.: A87603, Edition Number: M-161530-01-1 Date: 1994-11-01 GLP/GEP: no, unpublished | N | N | - | Bayer CropSc ience | In DAR (1998) |
| KCA | Burgener, A. | 1997 | Report amendment to 14C-ethofumesate: | N | N | - | Bayer | In DAR |

| Data Point | Author(s) | Year | Title Company Report No. Source (where different from company) GLP or GEP status Published or not | Vertebrate study Y/N | Data protection claimed Y/N | Justification if data protection is claimed | Owner | Previous evaluation |
|-----------------|----------------------------|-------|--|-------------------------|--------------------------------|---|-------------------------|---|
| 7.1.4.2 /03 | | | Mobility and Degradation in soil in outdoor lysimeters RCC Umweltchemie AG, Itingen, Switzerland Bayer CropScience, Report No.: A91247, Report includes Trial Nos.: ENVIR/113B Edition Number: M-167946-02-1 Date: 1997-07-25 GLP/GEP: yes, unpublished | | | | CropScience | (1998) |
| KCA 7.1.4.2 /04 | Stupp, H. P.; Junge, T. | 2013 | [Phenyl-UL-14C]ethofumesate: Investigation of metabolites previously detected in lysimeter leachates by an outdoor experiment with three EU soils Bayer CropScience, Report No.: EnSa-13-0234, Edition Number: M-461417-01-1 Date: 2013-08-01 GLP/GEP: yes, unpublished | N | Y | Required to assess the unidentified Peak A detected in previous lysimeter studies | Task Force Ethofumesate | Submitted for the purpose of renewal (2014) |
| KCA 7.1.4 .2/01 | Parsons, R. | 2003a | 14C-ETHOFUMESATE AND 2-OXO-ETHOFUMESATE: MOBILITY AND DEGRADATION IN SOIL IN FIELD LYSIMETERS United Phosphorus Ltd., ACE01-012 Agrochemical Experimentation Ltd. Essex, UK GLP: yes Published: no | N | Y | New data for active ingredient, not previously submitted nor evaluated | UPL | Submitted for the purpose of renewal (2014) |
| KCA 7.1.4 .2/02 | Parsons, R. | 2003b | 14C-ETHOFUMESATE AND 2-OXO-ETHOFUMESATE: MOBILITY AND DEGRADATION IN SOIL IN FIELD LYSIMETERS. FINAL ANALYTICAL REPORT United Phosphorus Ltd., ACE-01-012 Agrochemical Experimentation Ltd. Essex, UK GLP: yes Published: no | N | Y | New data for active ingredient, not previously submitted nor evaluated | UPL | Submitted for the purpose of renewal (2014) |
| KCA 7.1.4 .2/03 | Diehl, M. | 2005 | ETHOFUMESATE: MOBILITY AND DEGRADATION IN SOIL IN OUTDOOR LYSIMETERS AgriChem B.V., 836695 RCC Ltd. GLP: yes Published: no | N | Y | New data for active ingredient, not previously submitted nor evaluated | ACM* | Submitted for the purpose of renewal (2014) |
| KCA 7.1.4 .2/04 | Diehl, M. | 2006 | ETHOFUMESATE: MOBILITY AND DEGRADATION IN SOIL IN OUTDOOR LYSIMETERS (SECOND AMENDMENT) AgriChem B.V., October 2006, 836695 RCC Ltd. GLP/GEP: no Published: no | N | Y | New data for active ingredient, not previously submitted nor evaluated | ACM* | Submitted for the purpose of renewal (2014) |
| KCA 7.2.1 .1/01 | Macdonald, E., Craig, W.B. | 2002 | ETHOFUMESATE DETERMINATION OF THE PHYSICO-CHEMICAL PROPERTIES OF ETHOFUMESATE AgriChem B.V., 21131 Inveresk Research International, Tranent, Scotland GLP: yes Published: no | no | yes | New data for active ingredient, not previously submitted nor evaluated | ACM* | Submitted for the purpose of renewal (2014) |
| KCA 7.2.1.2 | Howarth, R.; Tremain, S. | 1991 | TECHNICAL ETHOFUMESATE: DETERMINATION OF PHYSICO- | N | N | - | Bayer CropScience | In DAR (1998) |

| Data Point | Author(s) | Year | Title Company Report No. Source (where different from company) GLP or GEP status Published or not | Vertebrate study Y/N | Data protection claimed Y/N | Justification if data protection is claimed | Owner | Previous evaluation |
|-----------------|---------------------------|------|---|-------------------------|-----------------------------------|---|-------------------------|---|
| /03 | P.; Bartlett, A. J. | | CHEMICAL PROPERTIES Safepharm Lab. Ltd., Derby, United Kingdom Bayer CropScience, Report No.: A87526, Report includes Trial Nos.: 245/25 Edition Number: M-161417-01-1 Date: 1991-01-07 GLP/GEP: yes, unpublished ...also filed: KCA 2.1 /02 ...also filed: KCA 2.2 /02 ...also filed: KCA 2.5 /03 ...also filed: KCA 2.7 /02 ...also filed: KCA 2.8 /03 | | | | ience | |
| KCA 7.2.1.2 /04 | Keirs, D. C. | 2000 | Aqueous photolysis (14C)-ethofumesate Inveresk Research Int. Ltd., Tranent, Scotland Bayer CropScience, Report No.: C009667, Edition Number: M-199018-01-1 EPA MRID No.: 46157901 Date: 2000-09-13 GLP/GEP: yes, unpublished ...also filed: KCA 2.8 /01 | N | N | - | Bayer CropScience | In DAR (1998) |
| KCA 7.2.1.2 /06 | Weuthen, M.; Stupp, H. P. | 2013 | [Phenyl-UL-14C]Ethofumesate: Phototransformation in water Bayer CropScience, Report No.: EnSa-12-0228, Edition Number: M-453458-01-1 Date: 2013-04-19 GLP/GEP: yes, unpublished | N | Y | Required due to not identified transformation products in Previous study (up to 50% AR) | Task Force Ethofumesate | Submitted for the purpose of renewal (2014) |
| KCA 7.2.1.2 /07 | Hellpointner, E. | 2013 | Ethofumesate: Assessment of the environmental half-life of the direct photodegradation in water Bayer CropScience, Report No.: EnSa-13-0355, Edition Number: M-461408-01-1 Date: 2013-08-06 GLP/GEP: yes, unpublished ...also filed: KCA 2.4 /11 | N | Y | Theoretical estimation of half-life in aqueous photolysis | Task Force Ethofumesate | Submitted for the purpose of renewal (2014) |
| KCA 7.2.1.2 /01 | Peizhi, L. | 2013 | PHOTODEGRADATION OF [14C]ETHOFUMESATE IN WATER, BASED ON THE OECD 316 DIRECT PHOTOLYSIS GUIDELINE TIER II - GENERATION AND CHARACTERIZATION OF PHOTOPRODUCTS United Phosphorus Ltd., 13845.6132 Smithers Viscient, Massachusetts, USA GLP: yes Published: no | N | Y | New data for active ingredient, not previously submitted nor evaluated | UPL | Submitted for the purpose of renewal (2014) |
| KCA 7.2.2.1 /01 | Bogers, M. | 1993 | READY BIODEGRADABILITY: 28 DAYS CLOSED BOTTLE TEST WITH ETHOFUMESATE RCC Notox B.V., s'Hertogenbosch, Netherlands Bayer CropScience, Report No.: A87607, Edition Number: M-161538-01-1 Date: 1993-03-31 GLP/GEP: yes, unpublished | N | N | - | Bayer CropScience | In DAR (1998) |
| KCA 7.2.2.1 /02 | Wuethrich, V. | 1993 | DETERMINATION OF BIOCHEMICAL AND CHEMICAL OXYGEN DEMAND OF ETHOFUMESATE DISPERSED IN WATER | N | N | - | Bayer CropScience | In DAR (1998) |

| Data Point | Author(s) | Year | Title Company Report No. Source (where different from company) GLP or GEP status Published or not | Vertebrate study Y/N | Data protection claimed Y/N | Justification if data protection is claimed | Owner | Previous evaluation |
|-----------------------|-------------------------------------|----------|---|-------------------------|-----------------------------------|---|---|---|
| | | | RCC Umweltchemie AG, Itingen, Switzerland Bayer CropScience, Report No.: A87608, Edition Number: M-161539-01-1 Date: 1993-04-28 GLP/GEP: yes, unpublished | | | | | |
| KCA 7.2.2.1 /03 | Douglas, M. T.; Sewell, I. G. | 1989 | ASSESSMENT OF READY BIODEGRADABILITY OF ETHOFUMESATE Huntingdon Research Centre Ltd., Huntingdon, United Kingdom Bayer CropScience, Report No.: A83351, Report includes Trial Nos.: 80B Edition Number: M-155620-01-1 Date: 1989-10-17 GLP/GEP: yes, unpublished | N | N | - | Bayer CropSc ience | In DAR (1998) |
| KCA 7.2.2.2 /01 | Fahrbach, M. | 2012 | [14C]Ethofumesate: Aerobic mineralization in surface water Harlan Laboratories Ltd., Itingen, Switzerland Bayer CropScience, Report No.: D25330, Edition Number: M-439697-01-1 Date: 2012-07-31 GLP/GEP: yes, unpublished | N | Y | New regulatory requirement | Task Force Ethofu mesate | Submitted for the purpose of renewal (2014) |
| KCA 7.2.2 .2/01 | Caviezel, A. | 20 13 | [14C]ETHOFUMESATE - AEROBIC MINERALISATION IN SURFACE WATER United Phosphorus Ltd., 20130080 Innovative Environmental Services (IES) Ltd. GLP: yes Published: no | N | Y | New data for active ingredient, not previously submitted nor evaluated | UPL | Submitted for the purpose of renewal (2014) |
| KCA 7.2.2.3 /02 | Kellner, G. | 1995 | DEGRADATION AND METABOLISM OF 14C ETHOFUMESATE IN AQUATIC SYSTEMS RCC Umweltchemie GmbH & Co. KG, Rossdorf, Germany Bayer CropScience, Report No.: A87625, Edition Number: M-161568-01-1 Date: 1995-05-18 GLP/GEP: yes, unpublished | N | N | - | Bayer CropSc ience | In DAR (1998) |
| KCA 7.2.2.3 /05 | Blech, S. | 1996 | Ethofumesate - Fate and behaviour in water/sediment A&M, Labor fuer Analytik und Metabolismusforschung Service GmbH, Bergheim, Germany Feinchemie Schebda , Report No.: OFC00004877, Edition Number: M-352106-01-1 Date: 1996-07-31 GLP/GEP: yes, unpublished | N | N | - | Adama (former Feinche mie Schwe bda) | In DAR (1998) |
| KCA 7.2.2.3 /06 | Stupp, H. P. Weuthen, M. | 2012 | [Phenyl-UL-14C]Ethofumesate:Aerobic aquatic metabolism Bayer CropScience, Report No.: EnSa-12-0334, Edition Number: M-443554-01-1 Date: 2012-11-29 GLP/GEP: yes, unpublished | N | Y | Required due to deficiencies in previous studies (metabolites not identified) | Task Force Ethofu mesate | Submitted for the purpose of renewal (2014) |
| KCA 7.2.2.3 /07 | Chapple, A.C. | 2013 | Kinetic evaluation of the degradation of ethofumesate in an aerobic water-sediment system Bayer CropScience, | N | Y | Required for new water/sedime nt studies | Task Force Ethofu mesate | Submitted for the purpose of renewal |

| Data Point | Author(s) | Year | Title Company Report No. Source (where different from company) GLP or GEP status Published or not | Vertebrate study Y/N | Data protection claimed Y/N | Justification if data protection is claimed | Owner | Previous evaluation |
|-----------------|--|------|--|-------------------------|-----------------------------------|--|-------------------------|---|
| | | | Report No.: EnSa-13-0250, Edition Number: M-459125-01-1 Date: 2013-07-01 GLP/GEP: no, unpublished | | | | | (2014) |
| KCA 7.2.2.3 /08 | Schmitt, W. | 2008 | Kinetic evaluation of the degradation of ethofumesate in an aerobic water/sediment system Bayer CropScience, Report No.: MEF-08/247, Edition Number: M-301623-01-1 Date: 2008-05-13 GLP/GEP: no, unpublished | N | Y | Required for new water/sediment studies | Task Force Ethofumesate | Submitted for the purpose of renewal (2014) |
| KCA 7.2.2.3 /01 | Heintze, A. | 2003 | DEGRADATION AND METABOLISM OF ETHOFUMESATE IN TWO WATER/SEDIMENT SYSTEMS UNDER AEROBIC CONDITIONS - LABORATORY TEST United Phosphorus Ltd., 20011407/01-CUWS GAB Biotechn. GmbH & IFU Umweltanalytik GmbH, Germany GLP: yes Published: no | N | Y | New data for active ingredient, not previously submitted nor evaluated | UPL | Submitted for the purpose of renewal (2014) |
| KCA 7.2.2.3 /02 | Stangelj, A. | 2014 | CALCULATIONS OF ENVIRONMENTAL FATE ENDPOINTS IN WATER/SEDIMENT SYSTEMS FOR ETHOFUMESATE ACCORDING TO RECOMMENDATIONS OF THE FOCUS WORKING GROUP ON DEGRADATION KINETICS United Phosphorus Ltd., 118608-CA-07020203-01 GAB Consulting GmbH, Lamstedt, Germany GLP/GEP: no Published: no | N | Y | New data for active ingredient, not previously submitted nor evaluated | UPL | Submitted for the purpose of renewal (2014) |
| KCA 7.3.1 /01 | Brehm, M. | 1992 | ESTIMATION OF THE PHOTOCHEMICAL- OXIDATIVE DEGRADATION OF ETHOFUMESATE (SCHERING CODE NO ZK 49 913) IN THE ATMOSPHERE Schering AG, Berlin, Germany Bayer CropScience, Report No.: A83382, Report includes Trial Nos.: 92/076 Edition Number: M-155650-01-1 Date: 1992-06-04 GLP/GEP: no, unpublished ...also filed: KCA 2.14 /02 ...also filed: KCA Section 2 /01 | N | N | - | Bayer CropScience | In DAR (1998) |
| KCA 7.5 /09 | Schafer, R.; Von Der Ohe, P.; Kuhne, R.; Schuurmann, G.; Liess, M. | 2011 | Occurrence and Toxicity of 331 Organic Pollutants in Large Rivers of North Germany over a Decade (1994 to 2004). Journal: Environ. Sci. Technol., Volume:45, Issue:14, Pages:6167-6174, Year:2011, Report No.: M-458649-01-1, Edition Number: M-458649-01-1 Date: 2011-12-31 GLP/GEP: no, published | N | N | - | LIT | Submitted for the purpose of renewal (2014) |

*... AgriChem B.V. has become part of UPL in 2012

LIT...Literature