Document Title

Summary of the fate and behaviour in the environment for Ethephon

Data Requirements

EU Regulation 1107/2009 & EU Regulation 283/2013
Document MCA
Section 7: Fate and behaviour in the environment

According to the guidance document SANCO 10181/2013 for preparing dossiers for the approval of a chemical active substance

Date

2017-07-24

Author(s)

[redacted]

Bayer AG
Crop Science Division

OWNERSHIP STATEMENT

This document, the data contained in it and copyright therein are owned by Bayer AG. No part of the document or any information contained therein may be disclosed to any third party without the prior written authorisation of Bayer AG.

The summaries and evaluations contained in this document are based on unpublished proprietary data submitted for the purpose of the assessment undertaken by the regulatory authority. Other registration authorities should not grant, amend, or renew a registration on the basis of the summaries and evaluation of unpublished proprietary data contained in this document unless they have received the data on which the summaries and evaluation are based, either:

- **From Bayer AG; or**
- **From other applicants once the period of data protection has expired.**

Version history

Date	Data points containing amendments or additions[1] and brief description	Document identifier and version number
2016-01-15	Initial document submitted for Annex I renewal Ethephon	M-544744-01-1
2017-06-XX	Amendment to report [redacted]; 2017; M-539124-02-1 (CA 7.1.3.1.1; p.36) and summary update included. Statements on RMS requests on pH dependency, adsorption/desorption and water/sediment are incorporated ([redacted]; 2017; M-587404-01-1; CA 7.1.3.1.1, CA 7.2.2.3) Change of legal entity fom Bayer CropScience AG to Bayer AG Crop Science Division	M-544744-02-1

[1] It is suggested that applicants adopt a similar approach to showing revisions and version history as outlined in SANCO/10180/2013 Chapter 4 How to revise an Assessment Report

Table of Contents

INTRODUCTION

Ethephon is a plant growth regulator and was included into Annex I of Directive 91/414 in 2006 (Directive 2006/85/EC, dated 23rd of October 2006, Entry into Force 1st of August 2007).

This dossier contains only summaries of studies, which were not available at the time of the first Annex I inclusion of ethephon and were, therefore, not evaluated during the first EU review of this compound. All other studies, which were already submitted by Bayer AG (formerly Bayer CropScience AG) for the first Annex I inclusion, are contained in the Monograph and in the Baseline Dossier (**P-012067-01**). These studies are summarised written in grey typeface in the dossier prepared for the renewal of approval.

The here presented and submitted studies used different synonyms and codes for the active substance ethephon, its metabolites and reference compounds. In order to present a common basis for the evaluation the following list summarises all names used.

Formula Report name used in summaries	**Codes used** *IUPAC index name* / Other names / codes
Ethephon	AE F016382 Ethephon technical concentrate Ethephon Base 250
Ethephon-2-hepa	HEPA, 2-HEPA (2-hydroxyethyl)phosphonic acid

In addition, a list of metabolites which contains the structures, the synonyms and code numbers attributed to the compound is presented in Document N3 of this dossier. The matrices in which the metabolites were identified are also included in this list.

CA 7 FATE AND BEHAVIOUR IN THE ENVIRONMENT

Information on the updated dossier for the current EU review of ethephon

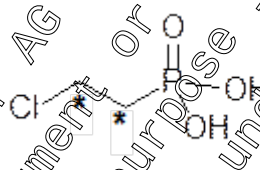
Data on the fate and behaviour of ethephon (AE F016382) in soil, water and air were evaluated during the previous EU review. For studies submitted during that review, please refer to the corresponding section in the Baseline Dossier provided by Bayer CropScience. This current MCA document summarizes the evaluations and decisions made during the previous EU review, and focuses on *additional* environmental fate studies which are now submitted for the current EU review.

The evaluations and decisions with regard to this section from the previous EU review can be found in the DAR of December 2004, its addendum of February 2006, and the EFSA Conclusion on ethephon dated September 2008.

An overview of the previously-evaluated data is provided in each chapter of this section. References for *previously-evaluated* studies are stated in grey text. Additional studies submitted for the current EU review are stated in black text. The latter have been submitted in order to fulfil current regulatory requirements. The numbering and the headings correspond to the new EU guidelines.

CA 7.1 Fate and behaviour in soil

The fate and behaviour of ethephon in soil has been investigated in a comprehensive series of laboratory studies and, when required, extended by data from field experiments. The laboratory studies on ethephon were all conducted with [^{14}C]-labelled active substance.



* Position of ^{14}C

Additionally, where required, a study has been conducted on a metabolite of ethephon.

CA 7.1.1 Route of degradation in soil

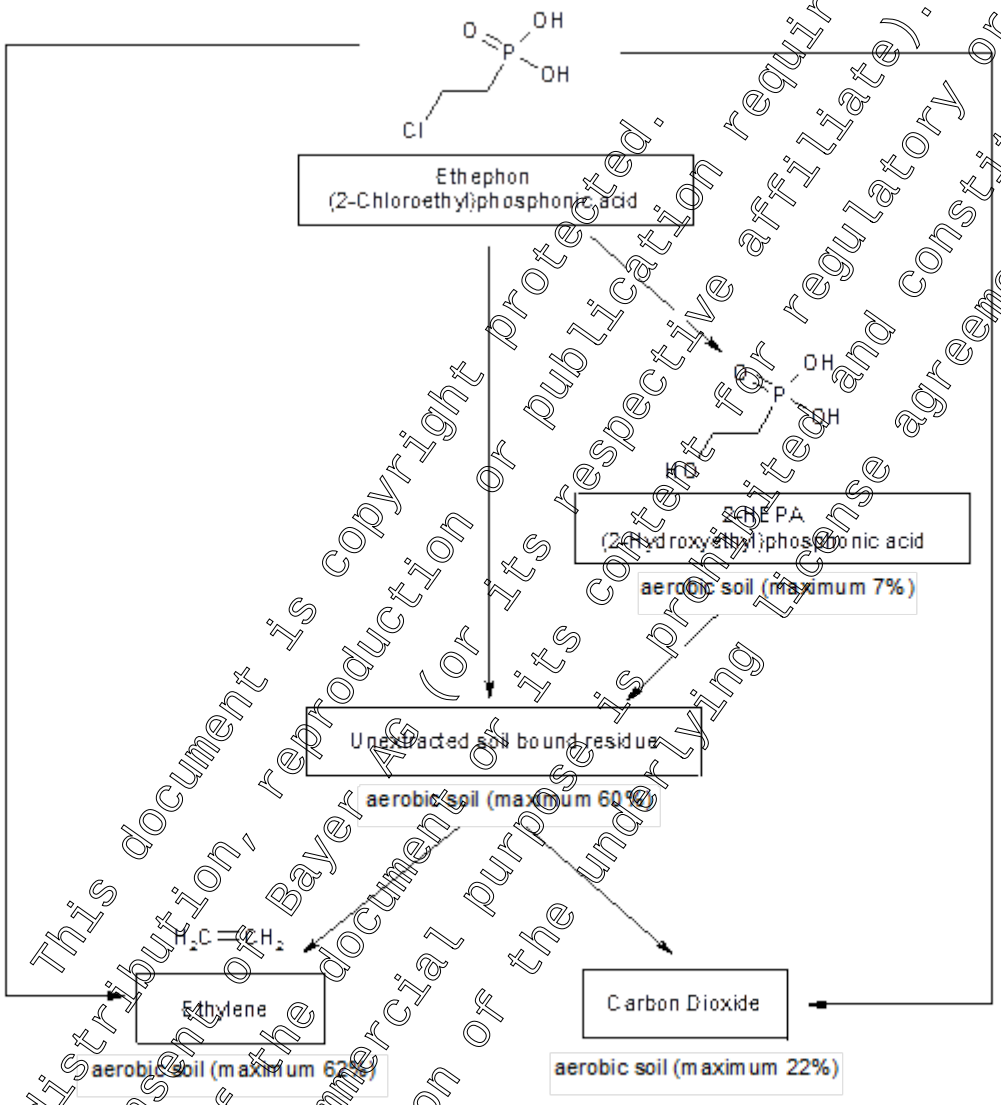
The main metabolic pathway of ethephon in soil was degradation to form ethylene (maximum 62%) and non-extractable soil residues (maximum 60%). Significant mineralisation to form carbon dioxide was observed in one soil (maximum 22%). A metabolite, 2-hydroxyethylphosphonic acid (HEPA), was detected in aerobic soil at a maximum of 7.4% at a single timepoint, but otherwise did not exceed 5%.

A similar pathway was observed under anaerobic conditions, where ethephon was rapidly degraded to form mainly ethylene (maximum 94%), with HEPA observed at a maximum of 4% AR.

In a soil photolysis study, ethephon was readily degraded with a similar decline seen under irradiated conditions and in dark controls indicating that photolytic degradation had only a minor effect on the degradation rate. HEPA was detected in irradiated samples (maximum 10.6% AR after 10 days) and > 5% at two consecutive timepoints in dark control samples (maximum 6% after 30 days). Ethylene and carbon dioxide were formed at maxima of 12% and 6%, respectively. No other metabolites exceeded 2%.

No other significant metabolites were detected in aerobic, anaerobic or soil photolysis laboratory studies.

Figure 7.1.1- 1: The proposed route of degradation for ethephon in soil



CA 7.1.1.1 Aerobic degradation

The route of degradation of ethephon in aerobic soil had been investigated in two studies under laboratory conditions in five soils at 20°C and 45% maximum water holding capacity (MWHC) and in one soil at 10°C and 45% MWHC (KCA 7.1.1.1 /01 and KCA 7.1.1.1 /02). These two studies were evaluated during the previous EU review and are listed below. No new information on the route of aerobic degradation in soil is submitted for the current EU review.

Report:	KCA 7.1.1.1/01; [redacted]; 2001; M-203033-01-1
Title:	Route and rate of degradation under aerobic conditions in one soil at 20 degrees C and 10 degrees C and in three contrasting soils at 20 degrees C (14C-Ethephon
Report No.:	C016772
Document No.:	M-203033-01-1
Guideline(s):	ED Council Directive 91/414/EEC as amended by Commission Directive 95/36/EEC of July 1995 US EPA OPPTS 835.4100
Guideline deviation(s):	not specified
GLP/GEP:	**yes**

Report:	KCA 7.1.1.1/02; [redacted]; 2003; M-232779-01-1
Title:	(14C)-Ethephon: Route and rate of degradation under aerobic conditions in one soil at 20 degrees C
Report No.:	C033199
Document No.:	M-232779-01-1
Guideline(s):	EU Council Directive 91/414/EEC as amended by Commission Directive 95/36/EC of July 1995, section 7, Sub-section 7.1.1.2. US EPA OPPTS 835.4100
Guideline deviation(s):	not specified
GLP/GEP:	**yes**

Two additional studies were considered unreliable by the RMS in the previous EU review ([redacted]; 1991, M-187639-01-1 and [redacted]; 2000, M-198831-01-1).

CA 7.1.1.2 Anaerobic degradation

The route of degradation of ethephon in anaerobic soil had been investigated in a study under flooded laboratory conditions in one soil at 20°C (KCA 7.1.1.2 /01). This study was evaluated during the previous EU review, and the reference is provided below.

Report:	KCA 7.1.1.2/01; [redacted] M.; 2001; M-204496-01-1
Title:	Route and rate of degradation in soil under anaerobic conditions at 20 degrees C (14C)-Ethephon
Report No.:	C013378
Document No.:	M-204496-01-1
Guideline(s):	EU (=EEC): 95/36/EEC, 7.1.1.1.2
Guideline deviation(s):	--
GLP/GEP:	**yes**

The data evaluation by the notifier considered the changes in data requirements since the time of the previous EU review. The current study guideline for anaerobic studies is OECD 307 with an aerobic phase for one half-life or 30 d (whichever is shorter) followed by anaerobic waterlogged phase of up to 120 d. The aerobic phase permits the behaviour of significant aerobic metabolites to be investigated under anaerobic conditions.

The existing anaerobic study for ethephon under flooded anaerobic conditions did not have an aerobic phase. In aerobic conditions no major metabolites other than ethylene and HEPA are detected within one half-life of parent in any aerobic soil. All other metabolites are < 1% within this time period. Under anaerobic conditions the same pathway was observed with ethylene (maximum 94.1%) and HEPA (maximum 3.7%) formed and no other metabolites exceeding 5%. Thus it is concluded the existing study is sufficient to fully understand the behaviour of ethephon in anaerobic soil. Hence, no new information on the route of anaerobic degradation in soil is submitted for the current EU review.

CA 7.1.1.3 Soil photolysis

The soil photolysis of ethephon had been investigated in a study under laboratory conditions in one soil at 20°C (KCA 7.1.1.2 /01). This study was evaluated during the previous EU review, and the reference is provided below.

Report:	KCA 7.1.1.3/01; [redacted]; [redacted] M.; 2001; M-199517-01-1
Title:	Photodegradation in soil (14C)-Ethephon
Report No.:	C010713
Document No.:	M-199517-01-1
Guideline(s):	EU (-TEC): 95/36/EC
Guideline deviation(s):	--
GLP/GEP:	yes

Under Regulation 283/2013 there are new values which trigger data requirements for metabolites. As a consequence, although no new information on soil photolysis is submitted, HEPA is now considered to be a major metabolite in soil, due to its occurrence at ≥10% (10.6%) of AR in irradiated samples and between 5 and 10% in two sequential measurements in dark control samples (KCA 7.1.1.3 /01).

CA 7.1.2 Rate of degradation in soil

CA 7.1.2.1 Laboratory studies

CA 7.1.2.1.1 Aerobic degradation of the active substance

The rate of degradation of ethephon in aerobic soil had been investigated in two studies under laboratory conditions in five soils (KCA 7.1.2.1.1 /01 and KCA 7.1.2.1.1 /02). These studies were evaluated during the previous EU review, and the references are provided below.

Report:	KCA 7.1.2.1.1/01; [redacted]; 2001; M-203033-01-1
Title:	Route and rate of degradation under aerobic conditions in one soil at 20 degrees C and 10 degrees C and in three contrasting soils at 20 degrees C (1a)-Ethephon
Report No.:	C016772
Document No.:	M-203033-01-1
Guideline(s):	ED Council Directive 91/414/EEC as amended by Commission Directive 95/36/EEC of July 1995 US EPA OPPTS 835.4100
Guideline deviation(s):	not specified
GLP/GEP:	**yes**

Report:	KCA 7.1.2.1.1/02; [redacted]; 2003; M-232779-01-1
Title:	(14C)-Ethephon: Route and rate of degradation under aerobic conditions in one soil at 20 degrees C
Report No.:	C033199
Document No.:	M-232779-01-1
Guideline(s):	EU Council Directive 91/414/EEC, as amended by Commission Directive 95/36/EC of July 1995 Section 7, Sub section 7.1.1.2. US EPA OPPTS 835.4100
Guideline deviation(s):	not specified
GLP/GEP:	**yes**

No new studies have been submitted for Annex I Renewal, however the experimental data generated in the aerobic soil degradation studies listed above have now been re-evaluated according to FOCUS kinetics guidance (KCA 7.1.2.1.1 /03). This re-evaluation is summarised below.

Report:	KCA 7.1.2.1.1/03; [redacted]; [redacted]; 2015; M-534660-01-1
Title:	Kinetic evaluation of aerobic metabolism of ethephon in soil according to FOCUS kinetics
Report No.:	EnSa-15-0138
Document No.:	M-534660-01-1
Guideline(s):	"Generic Guidance for Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration". Report of the FOCUS Work Group on Degradation Kinetics. EC Document Reference: None, version 1.1, 2014; "Guidance Document on Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration". Report of the FOCUS Work Group on Degradation Kinetics. EC Document Reference Sanco/10058/2005 version 2.0, 2006
Guideline deviation(s):	none
GLP/GEP:	**no**

Executive Summary

The aim of this study was to evaluate aerobic soil degradation data for ethephon to derive DT_{50} values according to FOCUS kinetics guidance.

The degradation behaviour of ethephon has been investigated in five soils under laboratory conditions [Burr, 2001 & Fitzmaurice, 2003].

Kinetic modelling evaluations (KinGUI v2.1) showed statistically valid results could be derived according to FOCUS Kinetics acceptance criteria. The DT_{50} values (20 °C and pF2) selected for use as modelling endpoints are summarised below.

Soil	pH ($CaCl_2$)	DT_{50} (days)
Sandy loam (00/14)	6.1	13.2
Loam (00/15)	5.0	47.9
Clay loam (00/16)	7.1	2.22
Loam (00/18)	6.7	32.8
Clay loam (03/01)	7.6	6.35
Geometric mean		12.4

I. MATERIALS AND METHODS

The experimental data generated in two aerobic soil laboratory studies [previously reviewed for the first approval of ethephon, Burr, 2001 & Fitzmaurice, 2003] were re-evaluated according to the FOCUS guidance document on degradation kinetics using the software KinGUI v2.1. The aim of this evaluation was to derive DT_{50} values for use as modelling and trigger endpoints.

The datasets evaluated for each of the soils are provided in Table 7.1.2- 1 to Table 7.1.2- 5. All soils were incubated at a temperature of 20 °C and a soil moisture content of 45% maximum water holding capacity. Optimisations were carried out for the initial residue (M_0) and the degradation rate constant (Kp) for ethephon in all datasets. Modelling endpoints were normalised to a soil moisture content of pF 2.

Table 7.1.2- 1: Summary of ethephon dataset from Soil 00/14 ([redacted], 2001)

Time (days)	Ethephon (% of applied radioactivity)
0	100.0 [A]
0.02 [B]	90.3
1	78.1
3	69.3
7	59.9
14	47.5
27	34.5
60	15.0
77	7.1
102	3.1
120	1.0
151	1.3
180	1.4

[A] Day 0 was set to 100 % applied radioactivity
[B] First sampling 30 minutes after application (in original studies named DAT 0)

Table 7.1.2- 2: Summary of ethephon dataset from Soil 00/15 ([redacted], 2001)

Time (days)	Ethephon (% of applied radioactivity)
0	100.0 [A]
0.02 [B]	73.1
1	65.8
3	63.2
7	54.9
14	50.5
27	44.2
60	41.3
77	38.2
102	33.1
120	20.7
151	17.2
180	12.4

[A] Day 0 was set to 100 % applied radioactivity
[B] First sampling 30 minutes after application (in original studies named DAT 0)

Table 7.1.2- 3: Summary of ethephon dataset from Soil 00/16 ([redacted], 2001)

Time (days)	Ethephon (% of applied radioactivity)
0	100.0 [A]
0.02 [B]	81.3
1	61.6
3	47.6
7	24.9
14	10.4
27	1.2
60	0.5
77	0.4

[A] Day 0 was set to 100 % applied radioactivity
[B] First sampling 30 minutes after application (in original studies named DAT 0)

Table 7.1.2- 4: Summary of ethephon dataset from Soil 00/18 ([redacted], 2001)

Time (days)	Ethephon (% of applied radioactivity)
0	100.0 [A]
0	100.0 [A]
0.02 [B]	76.9
0.02 [B]	84.7
1	67.6
1	65.3
3	65.7
3	64.6
7	46.6
7	47.6
14	49.1
14	45.2
28	41.6
28	41.7
56	31.2
56	30.5
80	28.8
80	30.9
100	17.1
100	29.6
123	23.2
123	19.8
152	14.9
152	14.4
180	7.0
180	1.7

[A] Day 0 was set to 100 % applied radioactivity
[B] First sampling 30 minutes after application (in original studies named DAT 0)

Table 7.1.2- 5: Summary of ethephon dataset from Soil 03/01 ([redacted], 2003)

Time (days)	Ethephon (% of applied radioactivity)
0	107.7 [A]
1	90.2
3	69.9
7	52.4
14	36.2
21	28.2
38	15.0
44	10.8

[A] Day 0 was set to material balance

II. RESULTS AND DISCUSSION

The modelling endpoints (DT_{50} values) for ethephon are summarised in Table 7.1.2- 6 and the trigger endpoints are summarised in Table 7.1.2- 7.

For Soils 00/14 and 00/16 the single first order model (SFO) showed a good visual fit, an acceptable Chi² error, significant parameter estimations and a random scatter of the data in the residual plot. It was therefore chosen as appropriate to derive modelling endpoints. For derivation of trigger endpoints the bi-phasic first order multi compartment model (FOMC) was tested and resulted in improved visual assessment and a lower Chi² error for both soils. The bi-phasic double first order in parallel model (DFOP) clearly improved the statistical relevance and visual assessment and was therefore chosen for derivation of trigger endpoints for soils 00/14 and 00/16.

For Soil 00/15 the visual assessment of the SFO model was reasonable, although the Chi² error was high and the residual data showed large scatter. However, as the fit was statistically significant the SFO model was accepted for derivation of modelling endpoints. The amount of applied radioactivity at the end of the study was > 10% and therefore the FOMC model was excluded. The bi-phasic DFOP model was tested and resulted in a clearly better visual assessment and lower Chi² error than the SFO fit. Consequently, the DFOP model was chosen as the best fit model for Soil 00/15.

For Soil 00/18 a reasonable visual fit with a high Chi² error and a large scatter of the residual data was obtained with the SFO model. However, the fit was statistically significant and therefore the SFO model was considered appropriate to derive modelling endpoints. For derivation of trigger endpoints the bi-phasic model FOMC was tested as a first step which resulted in a slightly improved visual fit and lower Chi² error. As a second step the DFOP model was tested which was statistically significant and provided an even lower Chi² error and a better visual assessment. The DFOP model was therefore chosen as the best fit model for soil 00/18.

For Soil 03/01 an acceptable visual fit, a good Chi² error, significant parameter estimation and a random scatter of the data in the residual plot were obtained from the SFO model. It was therefore considered appropriate to derive modelling endpoints. The bi-phasic model FOMC was tested as a first step for derivation of trigger endpoints and provided a much better visual assessment and Chi² error compared to the SFO model. The DFOP model was tested additionally and resulted in a very low Chi² error and excellent visual assessment with high statistical significance. It was therefore chosen as best fit model for the soil 03/01.

Table 7.1.2- 6: Ethephon modelling endpoint DT_{50} values

Soil	pH ($CaCl_2$)	Kinetic model	$DT_{50\ SFO}$ (days)	$DT_{50\ REF\ pF2\ \&\ 20°C}$ (days)	Minimum χ^2 error	Parameter Confidence / t-test	Visual
00/14	6.1	SFO	18.10	13.24	11.50	<0.001	Good
00/15	5.0	SFO	72.05	47.89	17.46	<0.001	Acceptable
00/16	7.1	SFO	3.53	2.22	13.27	<0.001	Good
00/18	6.7	SFO	49.36	32.81	20.47	<0.001	Acceptable
03/01	7.6	SFO	10.12	6.35	10.72	<0.001	Acceptable
Geometric mean			18.70	12.40			

Table 7.1.2- 7: Ethephon trigger endpoint DT_{50} values

Soil	pH ($CaCl_2$)	Kinetic model	Soil DT_{50} (days)	Soil DT_{90} (days)	Minimum χ^2 error	Parameter Confidence / t-test	Visual
00/14	6.1	DFOP	15.04	70.78	4.59	k_1 = 0.018 k_2 <0.001	Good
00/15	5.0	DFOP	42.04	257.10	11.29	k_1 = 0.155 k_2 <0.001	Good
00/16	7.1	DFOP	2.50	13.68	1.68	k_1 < 0.001 k_2 < 0.001	Good
00/18	6.7	DFOP	20.09	193.60	10.29	k_1 = 0.006 k_2 < 0.001	Good
03/01	7.6	DFOP	6.29	44.98	1.08	k_1 < 0.001 k_2 < 0.001	Good
Geometric mean			11.48	73.66			

No statistically significant correlation between the degradation half-life of ethephon and the pH value of the soils was detected using the German Input Decision tool (UBA, 2012). However, higher degradation rates were found for the soils with high pH and the lowest degradation rate was found for the soil with the lowest pH. As a precautionary approach, the worst case DT_{50} of 47.9 days for acidic soils (Soil 00/15) and a geometric mean DT_{50} of 3.8 days from the two alkaline soils (Soils 00/16 and 03/01) were used in separate modelling assessments for acidic and alkaline soils in line with FOCUS (2014) recommendations.

III. CONCLUSIONS

Kinetic modelling analysis of the data from five aerobic soils treated with ethephon provided acceptable model fits.

The modelling endpoints for PEC_{soil}, PEC_{gw} and PEC_{sw} derived from the aerobic soil data are summarised below.

PEC_{soil} endpoint:	Worst-case SFO DT_{50} value, un-normalised	72.1 days
FOCUS PEC_{gw} and PEC_{sw} endpoints:	Geometric mean DT_{50} value in all soils, normalised to pF 2 and 20 °C (n=5)	12.4 days
	Worst case DT_{50} value in loam soil (00/15, pH 5), normalised to pF 2 and 20 °C	47.9 days
	Geometric mean DT_{50} value in clay loam soil (00/16 & 03/01, pH > 7), normalised to pF 2 and 20 °C (n=2)	3.8 days

CA 7.1.2.1.2 Aerobic degradation of metabolites, breakdown and reaction products

For the metabolite HEPA, laboratory data on the rate of degradation in aerobic soil could not be derived from studies performed with the active substance. Hence, a new study with the metabolite separately-dosed to soil was performed for the current EU review (KCA 7.1.2.1.2/01). This study is summarised below.

Report:	KCA 7.1.2.1.2/01; [redacted]; [redacted]; 2015; M-533483-01-1
Title:	2-hydroxyethylphosphonic acid:: Aerobic degradation in four soils
Report No.:	EnSa-15-0130
Document No.:	M-533483-01-1
Guideline(s):	OECD Test Guideline No. 307 Commission Regulation (EU) No 283/2013 in accordance with Regulation (EC) No 1107/2009
Guideline deviation(s):	Due to the very fast degradation of the test item the duration of this study was limited to seven days after treatment with four sampling intervals only. This has no impact on the results of the study.
GLP/GEP:	**yes**

Executive Summary

The rate of degradation of 2-hydroxyethylphosphonic acid (HEPA) was determined in four soils under aerobic conditions under laboratory conditions. The soils were incubated in the dark at a temperature of 20.0 °C and a soil moisture content of 54.4% of maximum water holding capacity (MWHC) for 7 days.

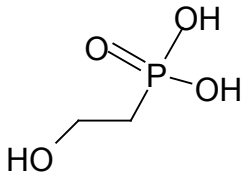
Soil	Soil pH ($CaCl_2$)	DT_{50} (days)	DT_{90} (days)
Laacher Hof AXXa (Sandy loam)	5.5	1.6	5.3
Höfchen am Hohensch (Silt loam)	6.0	1.9	6.2
Dollendorf II (Loam)	7.3	0.9	3.0
Laacher Hof Würmwiese (Sandy loam)	4.8	1.7	5.6

HEPA was very rapidly degraded in aerobic soil. ‘Best fit’ SFO degradation kinetics resulted in DT_{50} values ranging from 0.9 to 1.7 days and DT_{90} values from 3.0 to 6.2 days.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test material: 2-Hydroxyethylphosphonic acid



Chemical name (IUPAC) 2-Hydroxyethylphosphonic acid

Synonyms HEPA, 2-HEPA, AE F020271

Batch number: AE F020271 00 1B95 0001

Chemical purity: 95.3%

CA registry number: 22987-22-9

Application vehicle: Methanol:Water (1:1, v/v)

SMILES code: P(O)(O)(=O)CCO

2. Soils Four fresh agricultural soils collected from various sites in Germany were used for the study. The soils were selected to cover a range of pH, organic matter and clay content.

Parameter	Results/Units			
Soil Designation	Laacher Hof AXXa	Höfchen am Hohensch	Dollendorf II	Laacher Hof Wurmwiese
Soil Taxonomic Classification (USDA)	Sandy, mixed, mesic Typic Cambudoll	Loamy, mixed, mesic Typic Argudalf	Fine-loamy, mixed, active, frigid Typic Eutrudept	Loamy, mixed, mesic Typic Argudalf
Textural Class (USDA)	Sandy loam	Silt loam	Loam	Sandy loam
Sand [50 µm – 2 mm]	76%	32%	38%	52%
Silt [2 µm – 50 µm]	15%	55%	35%	31%
Clay [< 2 µm]	9%	13%	27%	17%
pH (soil/0.01 M $CaCl_2$)	5.5	6.0	7.3	4.8
pH (soil/water 1/1)	5.9	6.3	7.4	5.1
pH (saturated paste)	5.8	6.3	7.4	5.1
pH (soil/1 N KCl 1/1)	5.2	5.7	7.0	4.4
Organic Carbon (combustion)	1.5%	1.7%	5.1%	1.6%
Organic Matter [A]	2.6%	2.9%	8.8%	2.8%
Cation Exchange Capacity	7.9 meq/100 g	10.1 meq/100 g	19.5 meq/100 g	8.8 meq/100 g
Water Holding Capacity				
MWHC	49.0 g H_2O *ad* 100 g DW	59.6 g H_2O *ad* 100 g DW	83.0 g H_2O *ad* 100 g DW	57.1 g H_2O *ad* 100 g DW
1/10 bar (pF 2.0)	13.9%	31.8%	39.2%	20.3%
Bulk Density (disturbed)	1.16 g/cm^3	1.00 g/cm^3	0.90 g/cm^3	1.05 g/cm^3

Parameter	Results/Units			
Soil Designation	Laacher Hof AXXa	Höfchen am Hohenseh	Dollendorf II	Laacher Hof Wurmwiese
Biomass	424 mg microbial C/kg soil DW	4288 mg microbial C/kg soil DW	713 mg microbial C/kg soil DW	2214 mg microbial C/kg soil DW

[A] % organic matter = % organic carbon x 1.724 MWHC = Maximum water holding capacity

B. STUDY DESIGN AND METHODS

In-life dates

Study initiation date: 7 April 2015

Study completion date: 7 September 2015

Experimental start date: 13 April 2015

Experimental completion date: 28 August 2015

Experimental design

Parameter		Description
Duration of test		7 days. Study originally planned for 120 days. As degradation faster than originally assumed test stopped after 7 days.
Soil condition		Freshly sampled, soil sieved (≤ 2 mm), systems pre-incubated under test conditions for 10 days prior to treatment.
Soil sample weight		100 g dry weight equivalents per replicate
Test concentrations	kg test item/ha	1.2 kg test item/ha (based on maximum single field application rate of ethephon of 2.24 kg/ha, maximum occurrence of 10.6% of HEPA, and a 5 fold increase in rate for analytical reasons)
	µg test item/kg soil DW	Nominal: 2762 Actual: 2693
Control conditions (if used)		Samples for soil microbial biomass, untreated soil
Number of replications		Two per sampling interval
Test apparatus		300 mL Erlenmeyer flasks closed with polyurethane foam plugs
Traps for volatiles		None
Test material application	Identity of solvent	Methanol/water, 1/1 (v/v)
	Volume of application solution	400 µL per 100 g soil dry weight
	Application method	Dropwise application to the soil surface using an adjustable pipette
Traps for volatiles		None
Is there any indication of the test material absorbing to the walls of the test apparatus?		No
Experimental conditions	Temperature	20 °C
	Moisture content	54.4% MWHC
	Continuous darkness (Yes/No)	Dark

Sampling

Parameter		Description
Sampling intervals		Duplicate samples were processed and analyzed 0, 1, 3 and 7 days after treatment (DAT).
Soil sampling procedures		Complete treated samples were removed at each sampling time and extracted as detailed below.
Collection of volatiles		None
Sampling intervals / checks	Moisture content	Each sampling interval
	Sterile	Not applicable
	Other	Soil microbial biomass was determined for untreated soil at DAT-1
Sample storage before analysis		The soils were processed immediately after sampling. Soil extracts were analyzed by HPLC-MS/MS. Storage stability investigations were not necessary due to the use of an internal stable-labelled standard

Analytical procedures

Each sample was extracted as follows:

a) Soil was extracted three times at ambient temperature with 100 mL phosphate buffer (pH 7) using a mechanical shaker for 30 minutes. Soil and solvent were separated by centrifugation at 3480 g for 10 minutes after each extraction step.

b) The soil was then extracted twice with 100 mL phosphate buffer (pH 7) using a microwave at a temperature of 70 °C with a mechanical stirrer for 10 minutes. After each extraction step soil and solvent were separated by centrifugation as before.

c) All extracts were combined in a 500 mL volumetric cylinder, an internal reference standard added (2-hydroxyethyl-[1,1,2,2-d4]phosphonic acid) and the contents made up to volume.

An aliquot of the combined soil extract was transferred into a centrifugation tube and centrifuged at 25000 x g for 5 minutes. The clear supernatant was transferred into a HPLC vial and analyzed by HPLC-MS/MS.

At each sampling interval (except DAT-0) concurrent recovery samples were prepared at the LOQ and at the application rate. These samples were extracted and analysed alongside, and in the same manner, as the incubated samples.

The amount of HEPA in soil extracts was determined by HPLC-MS/MS in selected reaction monitoring (SRM) mode using an internal standard. The identity of HEPA was confirmed by HPLC-MS/MS including accurate mass determination.

The half-life (DT_{50}) of HEPA in each soil was determined using a simple first order (SFO), double first order in parallel (DFOP) and first order multi compartment (FOMC) models from the KinGUI kinetic modelling software.

II. RESULTS AND DISCUSSION

Analytical Methodology

The mean recoveries of HEPA at DAT-0 were between 82.9 and 105% of applied for all soils (see Table 7.1.2- 8). Extraction efficiency during the course of the study was demonstrated by concurrent recovery samples fortified with the test item at the LOQ (corresponding to 5% of the nominal application rate; 138 µg/kg) and at the application rate (100% of the nominal application rate; 2762 µg/kg). Overall recoveries ranged from 92.2 to 110% (mean 103% of applied).

The mass selective detector was operated in the negative electrospray ionization selected reaction monitoring mode (SRM), tuned for the mass transitions of HEPA and a significant product ion. The detector response of HEPA was linear over the concentration range determined (1 to 150% of the application rate) with a correlation coefficient of > 0.99. The accuracy and precision of the method was assessed on the basis of a set of recovery rates determined for all soils at the LOQ and nominal application rate. The mean recovery rates were in the range of 69.3 to 112% of applied for all soils and concentrations (overall mean 97.2% of applied, RSD 5.4%, n = 40). The relative standard deviations for each recovery set ranged from 3.5 to 6.4 for all soils, except for Dollendorf soil where it was 23.3%, showing a good overall repeatability of the method. Background levels of the test item in blank soil matrix was < 40% of the LOQ in all soils with no interference by other matrix components. The LOD in soil was set to 1/5 LOQ (corresponding to 1% of the nominal application rate; 27.62 µg/kg).

HEPA concentrations

The concentration of HEPA in soil extracts dissipated rapidly in all four soils. The amount in soil extracts decreased from 101% applied at DAT-0 to 8.4% at DAT-7 in soil Laacher Hof AXXa, from 99.0 to 9.0% applied in soil Höfchen am Hohenseh, from 82.9 to 6.2% applied in soil Dollendorf II and from 105 to 9.9% applied in soil Laacher Hof Wurmwiese. The quantities of HEPA extracted from each soil with time are shown in detail in Table 7.1.2- 8 as % of applied and in Table 7.1.2- 9 as µg/kg soil dw.

Table 7.1.2- 8: Degradation of HEPA in aerobic soil (as % of applied)

Soil (USDA soil texture)	Replicate	DAT			
		0	1	3	7
Laacher Hof AXXa (Sandy loam)	1	96.9	95.3	9.1	8.0
	2	105	96.4	10.5	8.8
	Mean	101	95.8	9.8	8.4
Höfchen am Hohenseh (Silt loam)	1	98.1	82.5	24.9	8.8
	2	100	80.5	27.8	9.3
	Mean	99.0	81.5	26.4	9.0
Dollendorf II (Loam)	1	82.4	38.2	5.3	5.4
	2	83.4	40.7	5.4	6.9
	Mean	82.9	39.4	5.3	6.2
Laacher Hof Wurmwiese (Sandy loam)	1	105	93.9	16.1	9.7
	2	105	94.2	18.4	10.0
	Mean	105	94.0	17.3	9.9

Table 7.1.2- 9: Degradation of HEPA in aerobic soil (as µg/kg soil dw)

Soil (USDA soil texture)	Replicate	DAT			
		0	1	3	7
Laacher Hof AXXa (Sandy loam)	1	2610	2564	246	216
	2	2819	2596	282	236
	Mean	2711	2580	263	226
Höfchen am Hohenseh (Silt loam)	1	2641	2223	671	236
	2	2692	2168	748	251
	Mean	2666	2194	710	244
Dollendorf II (Loam)	1	2220	1027	143	145
	2	2245	1095	144	187
	Mean	2232	1060	144	166
Laacher Hof Wurmwiese (Sandy loam)	1	2839	2527	435	261
	2	2828	2537	495	270
	Mean	2834	2532	465	265

Degradation kinetics

DT_{50} and DT_{90} values for the degradation of HEPA were determined following the recommendations of the FOCUS work group, with calculations performed according to the FOCUS guidance document on degradation kinetics using the software KinGUI version 2.1.

SFO kinetics showed 'best fit' to the data with no improvement for FOMC or double first order in parallel (DFOP) kinetics for all four soils.

Table 7.1.2- 10: 'Best-Fit' DT_{50} and DT_{90} values for HEPA in aerobic soil

Soil	Kinetic model	Soil pH ($CaCl_2$)	DT_{50} (days)	DT_{90} (days)	Min χ^2 error	Visual
Laacher Hof AXXa (Sandy loam)	SFO	5.5	1.6	5.3	25.2	Poor
Höfchen am Hohenseh (Silt loam)	SFO	6.0	1.9	6.2	10.2	Moderate
Dollendorf II (Loam)	SFO	7.3	0.9	3.0	8.0	Good
Laacher Hof Wurmwiese (Sandy loam)	SFO	4.8	1.7	5.6	18.9	Poor

III. CONCLUSIONS

HEPA was very rapidly degraded in aerobic soil. Best fit' SFO degradation kinetics resulted in DT_{50} values ranging from 0.9 to 1.7 days and DT_{90} values from 3.0 to 6.2 days.

A kinetic evaluation of the experimental data generated in the above aerobic soil study has been conducted according to FOCUS kinetics guidance with the aim of deriving DT_{50} values for use as modelling and trigger endpoints (KCA 7.1.2.1.2/02). This kinetic evaluation is summarised below.

Report:	KCA 7.1.2.1.2/02; [redacted]; [redacted]; 2015; M-534855-01-1
Title:	2-Hydroxyethylphosphonic acid - Kinetic evaluation of aerobic metabolism in soil according to FOCUS kinetics
Report No.:	EnSa-15-0788
Document No.:	M-534855-01-1
Guideline(s):	"Generic Guidance for Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration". Report of the FOCUS Work Group on Degradation Kinetics. EC Document Reference: None, version 1.1, 2014; "Guidance Document on Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration". Report of the FOCUS Work Group on Degradation Kinetics. EC Document Reference Sanco/10058/2005 version 2.0, 2006
Guideline deviation(s):	not applicable
GLP/GEP:	**no**

Executive Summary

The degradation behaviour of HEPA has been investigated in four soils under laboratory conditions [KCA 7.1.2.1.2/01, [redacted], 2015]. A kinetic evaluation of the study was conducted following FOCUS recommendations in order to derive kinetic parameters suitable for modelling and environmental risk assessments (modelling endpoints). The DT_{50} values (20 °C and pF2) selected for use as modelling endpoints are summarised below.

Soil	Soil pH ($CaCl_2$)	DT_{50} 20 °C and pF2 (days)
Laacher Hof AXXa (Sandy loam)	5.5	1.6
Höfchen am Hohenseh (Silt loam)	6.0	1.9
Dollendorf II (Loam)	7.3	0.9
Laacher Hof Wurmwiese (Sandy loam)	4.8	1.7
Geometric mean		1.5

I. MATERIALS AND METHODS

The experimental data generated in an aerobic soil laboratory study [KCA 7.1.2.1.2/01, [redacted], 2015] were evaluated according to the FOCUS guidance document on degradation kinetics using the software KinGUI v2.1. The aim of this evaluation was to derive DT_{50} values for use as modelling endpoints. Trigger endpoints were derived in the aerobic soil study and are also summarised here for completeness.

The datasets evaluated for each of the soils are provided in Table 7.1.2- 11 to Table 7.1.2- 14. All soils were incubated at a temperature of 20 °C and a soil moisture content of 54% maximum water holding capacity. Optimisations were carried out for the initial residue (M_0) and the degradation rate constant (k) for HEPA in all datasets. Normalisation of the modelling endpoints to 20°C and pF 2 was not required as the soils had been incubated at 20 °C and a soil moisture content above field capacity.

Table 7.1.2- 11: Summary of HEPA dataset from Laacher Hof AXXa ([redacted], 2015)

Time (days)	HEPA (% of applied)
0	96.9
0	104.7
1	95.2
1	96.4
3	9.1
3	10.5
7	8.0
7	8.8

Table 7.1.2- 12: Summary of HEPA dataset from Höfchen am Hohenseh ([redacted], 2015)

Time (days)	HEPA (% of applied)
0	98.1
0	100.0
1	82.9
1	80.5
3	24.9
3	27.8
7	8.8
7	9.3

Table 7.1.2- 13: Summary of HEPA dataset from Dollendorf II ([redacted], 2015)

Time (days)	HEPA (% of applied)
0	82.4
0	83.4
1	38.2
1	40.7
3	5.3
3	5.4
7	5.4
7	6.9

Table 7.1.2- 14: Summary of HEPA dataset from Laacher Hof Wurmwiese ([redacted], 2015)

Time (days)	HEPA (% of applied)
0	105.4
0	105.0
1	93.9
1	94.2
3	16.1
3	18.4
7	9.7
7	10.0

II. RESULTS AND DISCUSSION

The modelling and trigger endpoints for HEPA are summarised in Table 7.1.2- 15. Model selection was conducted following the decision scheme defined in the FOCUS kinetics guidance document

The SFO model was used for all soils for the evaluation of modelling endpoints. Although the SFO fit was not optimal it was considered acceptable for all four soils as the residuals were randomly distributed around zero. Only four data points were available for each soil due to the very rapid degradation of HEPA which did not allow for further measurements. However, as acceptable fits were obtained with the data the endpoints are also considered acceptable.

The FOMC model did not show a better fit to the data compared to SFO in any of the soils. As measured residues were < 10 % at the end of the experiment no other biphasic models were tested.

Table 7.1.2- 15: HEPA trigger and modelling endpoint DT_{50} values

Soil	Kinetic model	$DT_{50\ SFO}$ (days)	$DT_{50\ REF\ pF2\ \&\ 20°C}$ (days)	Min χ^2 error	T-test	Visual
Laacher Hof AXXa (Sandy loam)	SFO	1.6	1.6	25.2	0.008	Poor
Höfchen am Hohenseh (Silt loam)	SFO	1.9	1.9	10.2	<0.001	Moderate
Dollendorf II (Loam)	SFO	0.9	0.9	8.0	<0.001	Good
Laacher Hof Wurmwiese (Sandy loam)	SFO	1.7	1.7	18.9	0.002	Poor
Geometric mean		1.5	1.5			

III. CONCLUSIONS

Kinetic modelling analysis of the data from four aerobic soils treated with HEPA provided acceptable model fits.

The modelling endpoints for PEC_{soil}, PEC_{gw} and PEC_{sw} derived from the aerobic soil data are summarised below.

PEC_{soil} endpoint:	Worst-case SFO DT_{50} value, un-normalised	1.9 days
FOCUS PEC_{gw} and PEC_{sw} endpoints:	Geometric mean DT_{50} value in all soils, normalised to pF 2 and 20 °C (n=4)	1.5 days

CA 7.1.2.1.3 Anaerobic degradation of the active substance

The rate of degradation of ethephon in anaerobic soil had been investigated in a study under flooded laboratory conditions in one soil at 20°C (KCA 7.1.2.1.3/01). The study was evaluated during the previous EU review, and the reference is provided below. The DT_{50} value for degradation of ethephon in flooded anaerobic soil was 2.2 days. No new information is submitted for the current EU review.

Report:	KCA 7.1.2.1.3/01; [redacted] M.; 2001; M-204496-01-1
Title:	Route and rate of degradation in soil under anaerobic conditions at 20 degrees (14C)-Ethephon
Report No.:	C013378
Document No.:	M-204496-01-1
Guideline(s):	EU (=EEC): 95/36/EEC, 7.1.1.1
Guideline deviation(s):	--
GLP/GEP:	**yes**

CA 7.1.2.1.4 Anaerobic degradation of metabolites, breakdown and reaction products

Under anaerobic conditions no metabolite exceeding 5% of applied was formed from the degradation of ethephon other than ethylene. Consequently no information has been submitted for Annex I Renewal.

CA 7.1.2.2 Field studies

CA 7.1.2.2.1 Soil dissipation studies

A US field dissipation study was evaluated during the previous EU review (KCA 7.1.2.2.1/01). The reference is provided below.

Report:	KCA 7.1.2.2.1/01; [redacted]; 1991; M-187653-01-1
Title:	A Terrestrial Field Soil Dissipation Study with Ethephon
Report No.:	R013288
Document No.:	M-187653-01-1
Guideline(s):	USEPA (=EPA); 164-1
Guideline deviation(s):	--
GLP/GEP:	**yes**

The data requirements for active substances stated in Regulation 283/2013 have changed since the previous EU review. Field dissipation studies are now required when laboratory degradation rates; $DegT_{50lab}$ or $DegT_{90lab}$ values in one or more soils (at 20 °C and pF 2) exceed 60 days and 200 days, respectively.

The degradation of ethephon under laboratory conditions is biphasic and in one of five soils the $DegT_{90lab}$ value exceeds 200 days. As a consequence a new European field dissipation study has been conducted for the current EU review (KCA 7.1.2.2.1/02). This study is summarised below.

Report:	KCA 7.1.2.2.1/02; [redacted]; [redacted]; 2015; M-514111-01-1
Title:	Terrestrial field dissipation study with Ethrel SL 480 (Active ingredient: Ethephon) on bare soil at 2 different sites in northern and 2 different sites in southern Europe
Report No.:	M-514111-01-1
Document No.:	M-514111-01-1
Guideline(s):	NAFTA Guidance Document for Conducting Terrestrial Field Dissipation Studies, Regulatory Directive DIR2006-01, March 2006 • EPA (Environmental Protection Agency) US: Fate, Transport and Transformation Test Guidelines, OPPTS 835.6100, Terrestrial Field Dissipation, October 2008 • SETAC – Procedures for Assessing the Environmental Fate and Ecotoxicity of Pesticides, March 1995 • EFSA Panel on Plant Protection Products; Guidance for evaluating laboratory and field dissipation studies to obtain DegT50 values of plant protection products in soil. EFSA Journal 2010;8(12):1936, 67 pp
Guideline deviation(s):	none
GLP/GEP:	**yes**

Executive Summary

The soil dissipation of ethephon under European field conditions was investigated after application of Ethrel SL 480 at four sites in Vélez-Málaga (Spain), Dugnolo di Mezzolara (Italy), Banbury (UK) and Bakum (Germany). A single application of Ethrel SL 480 was applied once to bare soil at each site in May 2013 at a nominal application rate of 1.0 L product/ha, equivalent to 480 g/ha ethephon. After application the plots received ≥ 10 mm water within 3 days either by irrigation or rainfall. Soil samples were collected to a depth of 30 cm for timepoints up to 4 months and analysed for ethephon. The limit of quantification (LOQ) and limit of determination (LOD) for ethephon were 5 and 1.5 µg/kg dry soil respectively.

Ethephon degraded rapidly in soil under field conditions at all sites. 'Best fit' simple first order degradation kinetics resulted in DT_{50} values ranging from 4.7 to 28.4 days and DT_{90} values from 15.7 to 94.5 days.

Trial	Location	Kinetic model	Soil pH ($CaCl_2$)	DT_{50} (days)	DT_{90} (days)	Min χ^2 error	Visual
13/02566990-01	Vélez-Málaga (Spain)	SFO	7.5	8.7	28.9	11.5	Good
13/02566990-02	Dugnolo di Mezzolara (Italy)	SFO	7.7	4.7	15.7	7.5	Good
13/02566990-03	Banbury (UK)	SFO	6.4	13.2	43.9	6.5	Good
13/02566990-04	Bakum (Germany)	SFO	5.6	28.4	94.5	3.1	Good

I. MATERIALS AND METHODS

A. MATERIALS

1.

Name (formulated product):	Ethrel SL 480
Active ingredient:	Ethephon
Nominal active ingredient content:	480.0 g a.s./L
Actual active ingredient content:	40.4 % wt/wt (487.7 g/L, density 1.208 kg/L at 20°C)
Expiry Date	2015-04-12
Specification ID	102000001940 - 02
Batch ID	NK49CX0211
Certificate of Analysis ID	13003918

B. STUDY DESIGN AND METHODS

In-life dates

Study initiation date: 19 April 2013

Study completion date: 27 January 2015

Experimental start date: 23 April 2013

Date of first application: 2 May 2013

Date of last analysis: 13 December 2014

Experimental design

A terrestrial field dissipation study with ethephon formulated as Ethrel SL 480, a soluble liquid concentrate containing 480 g a.s./L, was conducted under field conditions after application to bare soil at two Southern European sites, Vélez-Málaga in Spain (Trial 13/02566990-01) and Dugliolo di Mezzolara in Italy (Trial 13/02566990-02) and two Northern European sites, Banbury in the UK (Trial 13/02566990-03) and Bakum in Germany (Trial 13/02566990-04). At each site one treated plot and one control plot were maintained. Each treated plot was divided into 4 subplots.

Prior to application soil cores for soil characterisation (0-30 cm, 30-50 cm, 50-75 and 75 to *ca.* 100 cm) were taken. Details are provided below.

Soil Characterisation for Trial 13/02566990-01 in Vélez-Málaga (Spain)

Soil Property	Unit	Depth [cm]			
		0-30	30-50	50-75	75-95*
Soil type (USDA)		Sandy loam	Loam	Sandy loam	Sandy loam
Clay (<0.002 mm)	[%]	13.5	11.6	11.0	8.6
Silt (0.002-0.050 mm)	[%]	31.3	40.0	33.3	26.3
Sand (0.050-2.00 mm)	[%]	55.2	48.4	55.6	65.1
CEC	[mval BA/100 g]	14.2	12.2	10.0	10.4
Chalk	[% $CaCO_3$]	4.67	4.50	3.00	1.67
Organic carbon (TOC)	[% Carbon]	1.57	0.60	0.46	0.36
Inorganic carbon (TIC)	[% Carbon]	0.56	0.54	0.36	0.20
Total carbon (TC)	[% Carbon]	2.13	1.14	0.82	0.56
Organic matter (calc., TOC x 1.724)	[%]	2.71	1.03	0.79	0.62
pH ($CaCl_2$)		7.47	7.74	7.71	7.69
pH (H_2O)		8.22	8.76	8.77	8.70
WHC max (pF 0.05)	[Vol%]	41.8	48.2	45.7	38.6
WHC 0.1 bar (pF 2)	[Vol%]	26.9	26.3	24.1	23.8
WHC 0.33 bar (pF 2.5)	[Vol%]	24.0	21.7	20.4	17.2

Soil Characterisation for Trial 13/02566990-02 in Dugliolo di Mezzolara (Italy)

Soil Property	Unit	Depth [cm]			
		0-30	30-50	50-75	75-90*
Soil type (USDA)		Sandy loam	Sandy loam	Sand	Sand
Clay (<0.002 mm)	[%]	10.1	7.8	1.8	1.5
Silt (0.002-0.050 mm)	[%]	28.6	23.5	6.8	3.9
Sand (0.050-2.00 mm)	[%]	61.3	68.7	91.4	94.5
CEC	[mval BA/100 g]	7.3	5.9	3.4	2.2
Chalk	[% $CaCO_3$]	18.4	20.3	21.5	21.9
Organic carbon (TOC)	[% Carbon]	0.54	0.37	0.13	0.03
Inorganic carbon (TIC)	[% Carbon]	2.20	2.43	2.58	2.62
Total carbon (TC)	[% Carbon]	2.74	2.80	2.71	2.65
Organic matter (calc., TOC x 1.724)	[%]	0.93	0.64	0.22	0.05
pH ($CaCl_2$)		7.72	7.84	7.92	7.93
pH (H_2O)		8.43	8.76	8.91	8.94
WHC max (pF 0.05)	[Vol%]	40.1	40.9	35.4	32.5
WHC 0.1 bar (pF 2)	[Vol%]	28.6	28.1	18.1	12.7
WHC 0.33 bar (pF 2.5)	[Vol%]	15.0	13.4	6.2	4.9

Soil Characterisation for Trial 13/02566990-03 in Banbury (UK)

Soil Property	Unit	Depth [cm]			
		0-30	30-50	50-75	75-95*
Soil type (USDA)		Loam	Clay loam	Silt loam	Silt loam
Clay (<0.002 mm)	[%]	23.2	33.6	10.1	3.2
Silt (0.002-0.050 mm)	[%]	42.9	32.2	53.9	52.1
Sand (0.050-2.00 mm)	[%]	33.9	34.4	36.0	44.7
CEC	[mval BA/100 g]	23.3	20.1	22.1	21.2
Chalk	[% $CaCO_3$]	0.17	0.17	0.08	0.08
Organic carbon (TOC)	[% Carbon]	1.93	0.66	0.51	0.46
Inorganic carbon (TIC)	[% Carbon]	0.02	0.02	0.01	0.01
Total carbon (TC)	[% Carbon]	1.95	0.68	0.52	0.47
Organic matter (calc., TOC x 1.724)	[%]	3.33	1.14	0.88	0.79
pH ($CaCl_2$)		6.36	6.35	5.60	5.12
pH (H_2O)		7.09	7.09	6.17	5.70
WHC max (pF 0.05)	[Vol%]	57.3	58.5	55.3	60.0
WHC 0.1 bar (pF 2)	[Vol%]	39.6	42.2	49.1	43.6
WHC 0.33 bar (pF 2.5)	[Vol%]	32.7	36.5	41.1	33.0

Soil Characterisation for Trial 13/02566990-04 in Bakum (Germany)

Soil Property	Unit	Depth [cm]			
		0-30	30-50	50-75	75-100*
Soil type (USDA)		Sandy loam	Sandy loam	Loamy sand	Loamy sand
Clay (<0.002 mm)	[%]	5.4	2.4	3.9	6.3
Silt (0.002-0.050 mm)	[%]	35.9	30.9	14.4	11.4
Sand (0.050-2.00 mm)	[%]	58.7	66.7	81.6	82.2
CEC	[mval BA/100 g]	12.1	9.6	4.4	2.9
Chalk	[% $CaCO_3$]	0.17	0.08	<0.08	<0.08
Organic carbon (TOC)	[% Carbon]	1.88	0.98	0.20	0.12
Inorganic carbon (TIC)	[% Carbon]	0.02	0.01	<0.01	<0.01
Total carbon (TC)	[% Carbon]	1.90	0.99	0.20	0.12
Organic matter (calc., TOC x 1.724)	[%]	3.24	1.69	0.34	0.21
pH ($CaCl_2$)		5.57	5.60	5.46	4.75
pH (H_2O)		6.28	6.64	6.57	5.74
WHC max (pF 0.05)	[Vol%]	51.7	43.0	32.6	37.1
WHC 0.1 bar (pF 2)	[Vol%]	17.6	15.2	11.2	9.9
WHC 0.33 bar (pF 2.5)	[Vol%]	13.9	10.6	6.0	7.1

The formulation Ethrel SL 480 was applied once at a nominal rate equivalent to 480 g a.s/ha to bare soil plots. The treated plots size ranged from 360 m^2 to 480 m^2. After application the plots received ≥ 10 mm water within 3 days either by irrigation or rainfall.

Two baking trays (containing approximately 1 kg soil, 30 x 30 cm) were placed diagonally across each subplot immediately prior to treatment to provide soil samples for verification of the application rate. Aliquots (50 mL) of each spray tank mixture were taken before and after application.

Name	13/02566990-01	13/02566990-02	13/02566990-03	13/02566990-04
Trial location	Vélez-Málaga (Spain)	Dugliolo di Mezzolara (Italy)	Banbury (United Kingdom)	Bakum (Germany)
Coordinates	36° 44' 35.95" N 04° 06' 51.46" W	44° 37' 28.25'' N 11° 35' 16.48 E''	52° 05' 51" N 01° 26' 57'' W	52° 46' 17.8'' N 08° 14' 13.1'' E
Region	Southern Europe	Southern Europe	Northern Europe	Northern Europe
Treated plot size (m^2)	480	480	360	480
Number of subplots	4	4	4	4
Subplot size (m^2)	120	120	90	120
Application Date	6 May 2013	23 May 2013	17 May 2013	28 May 2013
Nominal application rate [L product/ha]	1.0	1.0	1.0	1.0
Water rate (L/ha)	450	450	400	300
Actual application rate [L product/ha]	1.027	0.966	1.025	1.033
Target (%)	+2.7	-0.6	+2.5	+3.3
Nominal application rate [g ethephon/ha]	480	480	480	480
Actual application rate [g ethephon/ha]	493	498	492	495.8
Equipment	Spraying boom AT0604	Spraying boom, ECHO SHR 170 SI, Code 414	Spraying boom UK S10	Spraying boom AT0606
Nozzle type / number	Air Mix 110-03, Flat Fan	AFC 02, Flat Fan	Flat Fan	Air Mix 110-02, Flat Fan

During the study the test areas were kept free from weeds by periodic application of the herbicide glyphosate, and on one occasion, dicamba to control weeds.

Climatic measurements were recorded by weather stations located at the test site (Italy) or within 2 to 350 m. When required the test sites were irrigated to reach 110% of the historical rainfall in each month. In the Southern European trials (Spain and Italy) additional irrigation of 10 mm per week was applied during July, August and September.

Sampling

Samples were taken at timepoints up to 4 months after application. At Day 0 soil cores of 110 mm diameter (32 replicate cores, 2 samples per subplot, 4 cores per sample) were taken immediately after application to a depth of 10 cm from the treated plots and eight from baking trays placed within the treated plots prior to application. At subsequent sampling dates soil cores were taken from 0-10 cm and 10-40 cm soil depth at sampling intervals up to 28 days, and from 0-10 cm and 10-60 cm soil depth at later sampling dates (60 to 120 days). At each timepoint soil cores of 110 mm diameter were taken from the 0-10 cm layer and 46 mm diameter from deeper soil depths. For each depth sixteen replicate soil cores (4 cores per subplot) were taken.

Samples from the treated plots were collected on the day of application and at further intervals of 3, 7, 14 (±1), 28 (±2), 60 (±3), 90 (±4) and 120 (±4) days after treatment (DAT). Soil cores from the control plots were taken 0 to 7 days before treatment. Soil cores were frozen within 24 hours of collection and shipped frozen to the analytical laboratory in Germany. The samples were then stored at < -18 ºC until required for analysis.

Soil cores from the treated plots were divided into 10 cm increments and horizons from each subplot combined and homogenized.

Analytical procedures

The analytical method BCS 00899 was used for the determination of ethephon in soil. Samples were extracted as follows:

(a) Aliquots (20 g) of soil sample were extracted with 40 mL water/phosphoric acid mixture (1000/7; v/v) in a microwave oven.
(b) An aliquot of extract (1.5 mL) was centrifuged at 15000 rpm for 5 minutes prior to analysis by HPLC-MS/MS

The analytical method was successfully validated according to Guidance Document SANCO/825/00 rev 8.1 for the determination of residues of ethephon in soil. The LOQ and LOD for ethephon were 5 and 1.5 µg/kg dry soil respectively.

Degradation kinetics

DT_{50} and DT_{90} values for the degradation of ethephon were determined following the recommendations of the FOCUS work group, with calculations performed according to the FOCUS guidance document on degradation kinetics using the software KinGUI version 2.1.

Measured values between the LOQ and the LOD were used directly. Residue levels below the LOD were set to ½ LOD, equivalent to 1.1 g/ha, as recommended by FOCUS.

SFO kinetics showed an excellent fit to the field data, with no improvement for FOMC or DFOP kinetics, so SFO kinetics were selected as 'best fit' for all four trials.

II. RESULTS AND DISCUSSION

The mean recovery found in the baking tray specimens used for verification of the application rate ranged from 82 ± 9.1 % of the nominal concentration in Banbury (UK) to 101 ± 10.8 % in Vélez-Málaga (Spain). Recovery rates of ethephon in the spray tank mixtures ranged from 87 % to 106 % of the nominal concentration in Vélez-Málaga (Spain), 77 % to 106 % in Dugliolo di Mezzolara (Italy), 97% to 102 % in Banbury (UK) and 98% to 106 % in Bakum (Germany).

Levels of residues in the four replicate treated subplots were generally in good agreement throughout the trials. Measured concentrations of ethephon (µg/kg) were converted to ethephon (g/ha) based on measured soil density. The results are presented in Table 7.1.2- 16 to Table 7.1.2- 19.

Measured ethephon concentrations in soil at Day 0 represented between 53-54% of the nominal application rate at Banbury (UK) to 85-87% at Bakum (Germany). Ethephon residues declined from between 300.1 and 352.8 g/ha at 0 DAT to below the LOQ after 92 days in Vélez-Málaga (Spain), between 316.4 and 324.0 g/ha to below the LOQ after 27 days in Dugliolo di Mezzolara (Italy), from between 252.9 and 261.5 g/ha to below the LOQ after 95 days in trial Banbury (UK) and from between 409.8 and 415.6 g/ha to below 10 % of the DAT 0 concentrations after 90 days in Bakum (Germany).

No ethephon residues were detected below 20 cm soil depth in any sample.

Table 7.1.2- 16: Ethephon residues in soil samples from Trial 13/02566990-01 (Vélez-Málaga, Spain)

DAT	Sample Date	Replicate	Ethephon [g/ha]				
			0-10 cm	10-20 cm	20-30 cm	Total	Total Mean
0	6 May 13	A	385.3	-	-	385.3	352.8
		B	304.0	-	-	304.0	
		C	365.8	-	-	365.8	
		D	356.3	-	-	356.3	
0R	6 May 13	A	305.6	-	-	305.6	300.1
		B	279.5	-	-	279.5	
		C	327.5	-	-	327.5	
		D	287.8	-	-	287.8	
3	9 May 13	A	248.9	284.0	< LOD (1.1)	534.0	291.4
		B	182.4	27.2	< LOD (1.1)	210.7	
		C	200.7	(4.6)	< LOD (1.1)	206.4	
		D	210.2	(3.2)	< LOD (1.1)	214.5	
7	13 May 13	A	167.8	18.6	< LOD (1.1)	187.5	174.3
		B	98.5	56.0	< LOD (1.1)	155.6	
		C	136.3	< LOD (1.1)	< LOD (1.1)	138.5	
		D	141.1	< LOD (1.1)	< LOD (1.1)	143.3	
15	21 May 13	A	91.2	18.4	< LOD (1.1)	110.7	106.0
		B	102.9	14.0	< LOD (1.1)	118.0	
		C	95.4	5.2	< LOD (1.1)	101.7	
		D	90.2	(2.4)	< LOD (1.1)	93.7	
29	4 June 13	A	35.1	11.9	< LOD (1.1)	48.1	42.5
		B	33.4	10.0	< LOD (1.1)	44.5	
		C	27.4	15.4	< LOD (1.1)	43.9	
		D	24.9	8.6	< LOD (1.1)	33.6	
64	9 July 13	A	10.4	< LOD (1.1)	< LOD	11.5	9.5
		B	10.1	< LOD (1.1)	< LOD	11.2	
		C	7.0	< LOD (1.1)	< LOD	8.1	
		D	6.3	< LOD (1.1)	< LOD	7.4	
92	6 Aug 13	A	5.4	< LOD (1.1)	< LOD	6.5	(5.2)
		B	(4.3)	< LOD (1.1)	< LOD	(5.4)	
		C	(3.7)	< LOD (1.1)	< LOD	(4.8)	
		D	(3.0)	< LOD (1.1)	< LOD	(4.1)	
120	3 Sept 13	A	(3.9)	< LOD (1.1)	< LOD	(5.0)	(3.9)
		B	(3.6)	< LOD (1.1)	< LOD	(4.7)	
		C	(2.0)	< LOD (1.1)	< LOD	(3.1)	
		D	(1.7)	< LOD (1.1)	< LOD	(2.8)	

- = not sampled NA = not analysed
Values in brackets calculated from concentrations < LOQ
Values < LOD, concentrations equivalent to ½ LOD added (1.1 g/ha) according to FOCUS kinetics criteria

Table 7.1.2- 17: Ethephon residues in soil samples from Trial 13/02566990-02 (Dugliolo di Mezzolara, Italy)

DAT	Sample Date	Replicate	Ethephon [g/ha]				
			0-10 cm	10-20 cm	20-30 cm	Total	Total Mean
0	23 May 13	A	332.2	-	-	332.2	324.0
		B	311.6	-	-	311.6	
		C	327.2	-	-	327.2	
		D	324.9	-	-	324.9	
0R	23 May 13	A	280.9	-	-	280.9	316.4
		B	293.0	-	-	293.0	
		C	376.6	-	-	376.6	
		D	315.1	-	-	315.1	
3	26 May 13	A	236.2	< LOD (1.1)	< LOD	237.3	230.8
		B	229.2	< LOD (1.1)	< LOD	230.3	
		C	209.5	< LOD (1.1)	< LOD	210.6	
		D	243.8	< LOD (1.1)	< LOD	244.9	
7	30 May 13	A	100.7	< LOD (1.1)	< LOD	101.8	100.9
		B	106.4	< LOD (1.1)	< LOD	107.5	
		C	92.4	< LOD (1.1)	< LOD	93.5	
		D	99.9	< LOD (1.1)	< LOD	101.0	
14	6 June 13	A	40.4	< LOD (1.1)	< LOD	41.5	39.5
		B	36.6	< LOD (1.1)	< LOD	37.7	
		C	37.3	< LOD (1.1)	< LOD	38.4	
		D	39.2	< LOD (1.1)	< LOD	40.3	
27	19 June 13	A	(5.5)	< LOD (1.1)	< LOD	(6.6)	(6.8)
		B	(5.8)	< LOD (1.1)	< LOD	(6.9)	
		C	(5.9)	< LOD (1.1)	< LOD	(7.0)	
		D	(5.7)	< LOD (1.1)	< LOD	(6.8)	
60	22 July 13	A	< LOD (1.1)	< LOD	< LOD	(1.1)	(1.1)
		B	< LOD (1.1)	< LOD	< LOD	(1.1)	
		C	< LOD (1.1)	< LOD	< LOD	(1.1)	
		D	< LOD (1.1)	< LOD	< LOD	(1.1)	

- = not sampled NA = not analysed
Values in brackets calculated from concentrations < LOQ
Values < LOD, concentrations equivalent to ½ LOD added (1.1 g/ha) according to FOCUS kinetics criteria

Table 7.1.2- 18: Ethephon residues in soil samples from Trial 13/02566990-03 (Banbury, UK)

DAT	Sample Date	Replicate	Ethephon [g/ha]				
			0-10 cm	10-20 cm	20-30 cm	Total	Total Mean
0	17 May 13	A	271.3	-	-	271.3	261.5
		B	257.4	-	-	257.4	
		C	244.0	-	-	244.0	
		D	273.3	-	-	273.3	
0R	17 May 13	A	236.8	-	-	236.8	252.9
		B	258.2	-	-	258.2	
		C	276.7	-	-	276.7	
		D	239.8	-	-	239.8	
3	20 May 13	A	196.3	< LOD (1.1)	< LOD	197.4	195.0
		B	211.3	< LOD (1.1)	< LOD	212.4	
		C	179.5	< LOD (1.1)	< LOD	180.6	
		D	188.7	< LOD (1.1)	< LOD	189.8	
7	24 May 13	A	172.0	< LOD (1.1)	< LOD	173.1	171.5
		B	179.6	< LOD (1.1)	< LOD	180.7	
		C	168.3	< LOD (1.1)	< LOD	169.4	
		D	161.8	< LOD (1.1)	< LOD	162.9	
13	30 May 13	A	121.0	< LOD (1.1)	< LOD	122.1	138.4
		B	159.0	< LOD (1.1)	< LOD	160.1	
		C	129.4	(2.2)	< LOD (1.1)	132.7	
		D	131.0	< LOD (1.1)	< LOD	132.1	
28	14 June 13	A	52.8	< LOD (1.1)	< LOD	53.9	53.4
		B	47.8	< LOD (1.1)	< LOD	48.9	
		C	58.3	< LOD (1.1)	< LOD	59.4	
		D	54.7	< LOD (1.1)	< LOD	55.8	
63	19 July 13	A	13.5	< LOD (1.1)	< LOD	14.6	12.2
		B	14.8	< LOD (1.1)	< LOD	15.9	
		C	12.5	< LOD (1.1)	< LOD	13.6	
		D	8.1	< LOD (1.1)	< LOD	9.2	
94	19 Aug 13	A	5.8	< LOD (1.1)	< LOD	6.9	(4.4)
		B	5.0	< LOD (1.1)	< LOD	6.1	
		C	3.8	< LOD (1.1)	< LOD	4.9	
		D	2.8	< LOD (1.1)	< LOD	3.9	
124	18 Sept 13	A	5.3	< LOD (1.1)	< LOD	6.4	(4.1)
		B	4.7	< LOD (1.1)	< LOD	5.8	
		C	3.8	< LOD (1.1)	< LOD	4.9	
		D	2.7	< LOD (1.1)	< LOD	3.8	

- = not sampled NA = not analysed
Values in brackets calculated from concentrations < LOQ
Values < LOD, concentrations equivalent to ½ LOD added (1.1 g/ha) according to FOCUS kinetics criteria

Table 7.1.2- 19: Ethephon residues in soil samples from Trial 13/02566990-04 (Bakum, Germany)

DAT	Sample Date	Replicate	Ethephon [g/ha]				
			0-10 cm	10-20 cm	20-30 cm	Total	Total Mean
0	28 May 13	A	410.1	-	-	410.1	415.6
		B	404.5	-	-	404.5	
		C	414.3	-	-	414.3	
		D	433.5	-	-	433.5	
0R	28 May 13	A	437.0	-	-	437.0	409.8
		B	387.0	-	-	387.0	
		C	409.7	-	-	409.7	
		D	405.6	-	-	405.6	
3	31 May 13	A	378.6	< LOD (1.1)	< LOD	379.7	391.6
		B	392.5	< LOD (1.1)	< LOD	393.6	
		C	409.6	< LOD (1.1)	< LOD	410.7	
		D	381.4	< LOD (1.1)	< LOD	382.5	
7	4 June 13	A	322.3	< LOD (1.1)	< LOD	323.4	327.4
		B	319.9	< LOD (1.1)	< LOD	321.0	
		C	333.8	< LOD (1.1)	< LOD	334.9	
		D	329.0	< LOD (1.1)	< LOD	330.1	
14	11 June 13	A	263.5	< LOD (1.1)	< LOD	264.6	284.6
		B	282.1	< LOD (1.1)	< LOD	283.2	
		C	309.8	< LOD (1.1)	< LOD	310.9	
		D	278.5	< LOD (1.1)	< LOD	279.6	
27	24 June 13	A	234.5	< LOD (1.1)	< LOD	235.6	220.8
		B	207.8	< LOD (1.1)	< LOD	208.9	
		C	245.0	< LOD (1.1)	< LOD	246.1	
		D	191.5	< LOD (1.1)	< LOD	192.6	
59	26 July 13	A	81.0	< LOD (1.1)	< LOD	82.1	99.2
		B	73.9	< LOD (1.1)	< LOD	75.0	
		C	106.5	< LOD (1.1)	< LOD	107.6	
		D	131.0	< LOD (1.1)	< LOD	132.1	
90	26 Aug 13	A	28.7	< LOD (1.1)	< LOD	29.8	42.0
		B	26.9	< LOD (1.1)	< LOD	28.0	
		C	43.5	< LOD (1.1)	< LOD	44.6	
		D	64.3	< LOD (1.1)	< LOD	65.4	
121	26 Sept 13	A	21.6	< LOD (1.1)	< LOD	22.7	27.7
		B	19.9	< LOD (1.1)	< LOD	21.0	
		C	31.3	< LOD (1.1)	< LOD	32.4	
		D	33.4	< LOD (1.1)	< LOD	34.5	

- = not sampled NA = not analysed
Values in brackets calculated from concentrations < LOQ
Values < LOD, concentrations equivalent to ½ LOD added (1.1 g/ha) according to FOCUS kinetics criteria

DT_{50} and DT_{90} values for ethephon in soil were estimated according to the FOCUS guidance document on degradation kinetics using the KinGUI version 2.1 software. Based on chi^2 confidence criterion and visual inspection the SFO model was selected as being the best-fit for all four trials. DT_{50} values ranged from 4.7 to 28.4 days. The kinetics results are presented in the following table:

Table 7.1.2- 20: 'Best-Fit' DT_{50} and DT_{90} values for ethephon in European Field Dissipation Trials

Trial	Location	Kinetic model	Soil pH ($CaCl_2$)	DT_{50} (days)	DT_{90} (days)	Min χ^2 error	Visual
13/02566990-01	Vélez-Málaga (Spain)	SFO	7.5	8.7	28.9	11.5	Good
13/02566990-02	Dugliolo di Mezzolara (Italy)	SFO	7.7	4.7	15.7	7.5	Good
13/02566990-03	Banbury (UK)	SFO	6.4	13.2	43.9	6.5	Good
13/02566990-04	Bakum (Germany)	SFO	5.6	28.4	94.5	3.1	Good

III. CONCLUSIONS

Ethephon degraded rapidly in soil under field conditions at all sites. A single application of Ethrel SL 480, equivalent to 480 g/ha of ethephon, was made at each site in May 2013. 'Best fit' SFO degradation kinetics resulted in DT_{50} values ranging from 4.7 to 28.4 days and DT_{90} values from 15.7 to 94.5 days.

CA 7.1.2.2.2 Soil accumulation studies

Soil accumulation studies are required where it is established from soil dissipation studies that the $DisT_{90field}$ in one or more soils is greater than one year. Dissipation studies conducted in Europe and the US show the $DisT_{90field}$ for ethephon will not exceed this trigger and therefore soil accumulation studies are not required.

CA 7.1.3 Adsorption and desorption in soil

CA 7.1.3.1 Adsorption and desorption

CA 7.1.3.1.1 Adsorption and desorption of the active substance

A new study investigating the adsorption and desorption of ethephon in soil had been conducted since the previous EU review (KCA 7.1.3.1.1/01).

In the previous adsorption desorption study with ethephon all the soils used were acidic, with the pH of some soils artificially adjusted by the addition of hydrochloric acid prior to sieving. A portion of the silt and clay fractions in one soil was removed by sieving to 0.053 mm to artificially create a loamy sand soil. The silt and clay fractions removed were then sieved to 2 mm to artificially create a clay soil. Additionally the relationship assumed between organic carbon and organic matter in the study was not standard; % Organic Carbon = (% Organic Matter / 1.8) - 0.1944 rather than % Organic Carbon = (% Organic Matter / 1.724). For these reasons the previous study is ~~considered to be~~ supported ~~superseded~~ by Document KCA 7.1.3.1.1/02. This new study is summarised below.

Report:	KCA 7.1.3.1.1/02; [redacted]; 2017; M-539124-02-1
Title:	Final report amendment 1 - [UL-14C]ethephon: Adsorption/desorption on four soils
Report No.:	S15-04002
Document No.:	M-539124-02-1
Guideline(s):	OECD Test Guideline No. 106; Commission Regulation (EU) No 283/2013 in accordance with Regulation (EC) No 1107/2009; US EPA OCSPP Test Guideline No. 835.1230
Guideline deviation(s):	none
GLP/GEP:	**yes**

Executive Summary

The adsorption/desorption characteristics of [UL-^{14}C]-ethephon was studied in four different German soils: Laacher Hof AXXa (sandy loam), Dollendorf II (loam), Hoefchen am Hohenseh 4a (silt loam) and Laacher Hof Wurmwiese (loam) in the dark at 23 ± 2 °C using the batch equilibrium method.

Soil	Soil ID	Source	Texture (USDA)	pH *	OC [%]
Laacher Hof AXXa	AX	Monheim, Germany	sandy loam	6.3	2.0
Dollendorf II	DD	Blankenheim, Germany	loam	7.3	5.1
Hoefchen am Hohenseh 4a	HH	Burscheid, Germany	silt loam	6.1	2.1
Laacher Hof Wurmwiese	WW	Monheim, Germany	loam	5.1	2.0

* pH values were derived from aqueous 0.01 M $CaCl_2$ suspensions

The adsorption phase of the study was carried out using air-dried, sterilized soils, equilibrated in aqueous 0.01 M $CaCl_2$ solution at a soil-to-solution ratio of 1:10. [UL-^{14}C]-ethephon was applied in aqueous 0.01 M $CaCl_2$ solution at nominal test concentrations of 1.0, 0.3, 0.1, 0.03 and 0.01 mg/L. The adsorption phase was equilibrated for 2 hours (soil WW) or 5 hours (soils AX, HH, DD). A desorption step was only conducted for soil AX for 5 hours, due to the limited stability of the test item observed for the other soils.

Material balances were quantitative ranging from 92.1% to 100.2% AR. Ethephon was sufficiently stable throughout the study for all soils with parental mass balances ranging from 87.3 ~~89.5~~ to 91.8% AR. No adsorption to the surface of the test vessels was observed.

The Freundlich adsorption and desorption constants for ethephon in soil are summarised below.

Soil	Adsorption				Desorption			
	K_f [mL/g]	K_{foc} [mL/g]	1/n	R^2	K_{fdes} [mL/g]	K_{focdes} [mL/g]	1/n	R^2
Laacher Hof AXXa	6.1	306.5	1.0007	0.9953	15.3	766.2	1.0647	0.9947
Dollendorf II	5.2	101.9	1.045	0.9953	n.p.	n.p.	n.p.	n.p.
Hoefchen am Hohenseh 4a	13.0	621.1	0.9718	0.9992	n.p.	n.p.	n.p.	n.p.
Laacher Hof Wurmwiese	6.8	342.3	0.9896	0.9983	n.p.	n.p.	n.p.	n.p.
Mean	**7.8**	**342.9**	**1.0018**	**0.9970**	**15.3**	**766.2**	**1.0647**	**0.9947**

n.p. not performed

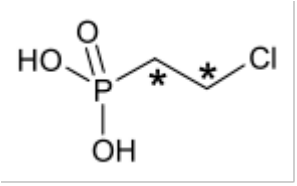
In general the organic matter in soil, determined as organic carbon content, is the most important component responsible for binding organic chemicals. However, ethephon is a diprotic acid (pK_{a1} = 2.8, pK_{a2} = 7.2) and the predominant species under environmental conditions are the negatively charged mono-anion (below pH 7.2) and di-anion (above pH 7.2). Based on its Log P_{ow} the molecule has a very low lipophilicity. The adsorption of ethephon is predominantly based on non-specific interactions with the soil but the binding to the soil organic matter may be a significant process as well. Therefore, the adsorption coefficients K_F were correlated with the organic carbon content of the soil. The K_{Foc} values ranged from 101.9 to 621.1 mL/g (arithmetic mean 342.9 mL/g). ~~and binding to the soil organic matter is a subordinated process only. This is confirmed by the narrow range of K_f values (9.3 to 11.0 mL/g) measured across four soils, without correlation to organic carbon content. Thus adsorption coefficients K_f for ethephon were not normalised to the organic carbon content of the soil.~~

There was no significant correlation between pH and adsorption for the investigated soils.

~~Ethephon was strongly adsorbed to soil with a mean K_F value of 10 mL/g~~. Ethephon can be classified as being of low mobility in soil using the Briggs classification scale to assess potential mobility in soil.

I. MATERIALS AND METHODS

1. Test Material: [UL-^{14}C]ethephon



* indicates position of ^{14}C radiolabel

Chemical name (IUPAC): (2-chloroethyl)phosphonic acid
Synonyms AE F016382
Batch number: KML 9960
Specific activity: 4.28 MBq/mg
Radiochemical Purity: 98%
CA registry number: 16672-87-0
Stability of test compound: Stable, determined within study
Application vehicle: Methanol with 1% formic acid

2. Soils Four agricultural soils collected from various sites in Germany were used for the study. The soils were selected to cover a range of pH, organic matter and clay content. All soils were sterilized by gamma-irradiation prior to use.

Parameter	Results/Units			
Soil Designation	Laacher Hof AXXa	Dollendorf II	Höfchen am Hohenseh	Laacher Hof Wurmwiese
Soil ID	AX	DI	HH	WW
Batch ID	20130830	20140321	20140321	20140321
Geographic Location (City / State / Country)	Monheim am Rhein / North Rhine Westphalia / Germany	Blankenheim / North Rhine Westphalia / Germany	Burscheid / North Rhine Westphalia / Germany	Monheim am Rhein / North Rhine Westphalia / Germany
GPS Coordinates	N 051° 04.645' E 006° 53.530'	N 050° 22.785' E 006° 42.790'	N 051° 04.013' E 007° 06.305'	N 051° 04.857' E 006° 55.251'
Textural Class (USDA)	Sandy loam	Loam	Silt loam	Loam
Sand [50 µm – 2 mm]	72%	29%	19%	50%
Silt [2 µm – 50 µm]	19%	44%	66%	32%
Clay [< 2 µm]	9%	27%	15%	18%
pH (Soil/0.01 M $CaCl_2$ 1/2)	6.3	7.3	6.1	5.1
pH (Soil/Water 1/1)	6.5	7.4	6.4	5.4
pH (Saturated Paste)	6.5	7.4	6.3	5.5
pH (Soil/1 N KCl 1/1)	6.1	7.0	5.7	4.8
Organic Carbon (combustion)	2.0%	5.1%	2.1%	2.0%
Organic Matter [A]	3.4%	8.8%	4.8%	3.4%
Cation Exchange Capacity	9.0 meq/100 g	21.5 meq/100 g	11.3 meq/100 g	10.4 meq/100 g

Parameter	Results/Units			
Water Holding Capacity				
MWHC	47.7 g H_2O *ad* 100 g DW	85.0 g H_2O *ad* 100 g DW	57.7 g H_2O *ad* 100 g DW	59.2 g H_2O *ad* 100 g DW
1/3 bar	10.7%	32.8%	22.7%	17.2%
1/10 bar (pF 2.0)	15.9%	39.2%	36.6%	24.4%
Bulk Density (disturbed)	1.21 g/cm^3	0.98 g/cm^3	1.12 g/cm^3	1.12 g/cm^3

[A] % organic matter = % organic carbon x 1.724 MWHC = Maximum water holding capacity

B. STUDY DESIGN AND METHODS

In-life dates

Study initiation date:	19 June 2015
Study completion date:	3 December 2015
Experimental start date:	29 June 2015
Experimental completion date:	25 August 2015
Final Report Amendment 1:	14 June 2017

Experimental design

The stability in aqueous solution, adsorption to glassware, soil to solution ratio, equilibration time, parental mass balance and overall material balance were determined in preliminary testing. The stability of ethephon was confirmed in 0.01M calcium chloride solution over 48 hours. No significant adsorption of ethephon to glassware occurred in soil-free control samples.

The test to establish a suitable equilibration time was conducted at a soil solution ratio of 1:10 in all four soils. Adsorption equilibrium plateau concentrations were not reached within 48 hours with the amount of radioactivity in soil was steadily increasing due to the formation of non-extractable residues. In order to achieve an acceptable parental mass balance the adsorption equilibrium time was limited to 5 hours for soil AX, DD and HH and 2 hours for soil WW. Due to the limited stability of ethephon a desorption step was only conducted for soil AX. Five hours were considered appropriate as desorption equilibration time, equal to the adsorption equilibration time.

Mean parental mass balances at these times were 91.8, 90.3, 87.3 and 89.5% AR for soil AX, DD, HH and WW, respectively. It was concluded that no significant degradation of ethephon occurred over the duration of the study. Material balances were 98.0% AR for soil AX, 92.1% AR for soil DD, 100.2% AR for soil HH and 99.1% AR for soil WW.

A soil solution ratio of 1:10 was selected for all soils in the definitive test. With an equilibration time of 2 (Soil WW) to 5 hours (Soils AX, HH and DD) the amount of test substance adsorbed ranged between 26 and 60%. The aqueous supernatant after adsorption and desorption was separated by centrifugation and the amount of test item in the supernatants was analysed by liquid scintillation counting (LSC). The sorption parameters were calculated using Freundlich isotherms.

Adsorption phase

Parameter	Description
Soil condition	Soils were air-dried, sieved to ≤ 2 mm, sterilized by gamma-irradiation and pre-equilibrated for 20 hours with aqueous 0.01 M $CaCl_2$ solution.
Soil sample weight	2 g (dry weight) per replicate

Parameter		Description
Equilibration solution		0.01M $CaCl_2$ (20 mL per replicate)
Control		No soil (test item in 0.01M $CaCl_2$ only)
Test item concentration	Nominal application rates	Nominal concentrations in test solution: 0.01 mg/L, 0.03 mg/L, 0.1 mg/L, 0.3 mg/L, and 1.0 mg/L
	Analytically measured concentrations	Concentrations in test solution: 0.009 mg/L, 0.03 mg/L, 0.10 mg/L, 0.32 mg/L, and 1.07 mg/L
Identity and concentration of co-solvent		Methanol with 1% formic acid, solvent concentration in test solution between 0.0008 and 0.00002% (v:v).
Soil: Solution ratio		1:10 i.e. 2 g soil dry weight equivalent to 20 mL solution (corrected for soil moisture)
pH of the equilibration solution	Initial	pH of aqueous 0.01 M CaCl2 solution without soil: 7.0
	Final	pH with soil and test item after adsorption equilibrium: Range 4.87 – 6.78
Number of replicates	Control	N/A
	Treatments	Duplicate
Equilibration conditions	Time	5 hours (soils AX, DD and HH), 2 hours (soil WW)
	Temperature	23.6 °C
	Dark	Yes
	Shaking method	Mechanical flatbed shaker, 130 rpm
Method of separation of supernatant		Centrifugation
Centrifugation	Speed (g)	1295 x g
	Duration	4 minutes
	Method of separating supernatant	Supernatant was carefully decanted.

Desorption phase

Parameter		Description
Soil samples from adsorption phase used		Yes
Amount of test item present in the adsorbed state/adsorbed amount (mg a.i./kg soil)		The amounts of test item adsorbed to soil after adsorption ranged from 34.2 to 41.9% AR
Number of desorption cycles		1 (Soil AX only)
Equilibrium solution and quantity used per treatment for desorption		The decanted solution was replaced by fresh aqueous 0.01 M $CaCl_2$ solution. A total volume of 20 mL was used as equilibration solution.
Soil: Solution ratio		1:10 i.e. 2 g soil dry weight equivalent to 20 mL solution (corrected for soil moisture)
Number of replicates	Control	N/A
	Treatments	Duplicate
Desorption Equilibration conditions	Time	5 hours
	Temperature	23.6 °C
	Dark	Yes
	Shaking method	Mechanical flatbed shaker, 130 rpm
Method of separation of supernatant		Centrifugation
Centrifugation	Speed (g)	1295 x g
	Duration	4 minutes
	Method of separating supernatant	Supernatant was carefully decanted.

Analytical procedures

The amount of radioactivity in supernatants and soil extracts was quantified by LSC. Before chromatographic analysis aqueous samples were stabilized with formic acid (0.1% of nominal total volume) and analysed immediately.

Radioactivity in the soil pellet was extracted in selected soil samples to establish the parental mass balance in soil samples from the equilibrium time preliminary test over 48 hours. Samples were extracted as follows:

a) Soil from 1, 2 and 5 hour timepoints was extracted three times at ambient temperature using a mechanical shaker for 30 minutes with 20 mL aqueous formic acid (1% v/v) followed by a final extraction with 15 mL of acetone.

b) Soil from 24 and 48 hour timepoints was extracted twice at ambient temperature using a mechanical shaker for 30 minutes with 20 mL aqueous formic acid (1% v/v), twice with 20 mL acetonitrile/water 1:1 acidified with formic acid (final acid concentration 1%), followed by a final extraction with 15 mL of acetone.

c) Radioactivity remaining unextracted in the soil pellet was determined by combustion and LSC to establish the material balance.

As ethephon was found to bind irreversibly to the solid phase scintillator of the radioactivity detector it was not possible to use HPLC with radiodetection to measure the stability directly. The adsorption of the test item to the scintillator increased the base line from run to run and could not be reduced by the washing the system with water or organic solvents. A very intensive washing procedure was required to reduce the background down to a minimum. The washing could not be included in routine washing methods and thus, measuring all samples on a routine basis was not possible but was done for selected

samples. The absence of a transformation product in those HPLC runs confirmed the stability of the test item. Furthermore, the amount of ethephon in supernatants and soil extracts determined by HPLC-MS/MS were compared with those derived by LSC measurement, assuming the test item was stable. All HPLC-MS/MS results were in full agreement with the LSC measurement, confirming test item stability. ~~Furthermore, test item stability was proven by HPLC analysis with radiodetection of selected samples.~~

II. RESULTS AND DISCUSSION

The recovery of radioactivity was quantitative, with mean values of ~~ranging from~~ 98.0% AR for soil AX, 92.1% AR for soil DD, 100.2% AR for soil HH and 99.1% AR for soil WW. It was concluded that no significant degradation of ethephon occurred over the duration of the study. Mean parental mass balances were 91.8, 90.3, 87.3 and 89.5% AR for soil AX, DD, HH and WW, respectively. A summary of the recoveries and parental mass balance data is presented in the table below:

Table 7.1.3- 1: Preliminary Test: Summary of Results from Adsorption Kinetics, Parental Mass Balance and Material Balance for all Soils

Parameters Mean values [% AR]	Adsorption time (hours) 1	2	5	24	48
Soil I (AX)					
Amount adsorbed to soil [1]	18.6	20.2	*25.6*	30.8	46.1
Non-extractable residues [2]	3.9	5.4	*6.2*	7.5	8.6
Parental Mass Balance [2]	94.0	92.7	*91.8*	89.6	83.2
Overall Material Balance [2]	98.0	98.7	*98.0*	97.0	91.8
Soil DD					
Amount adsorbed to soil [1]	16.3	18.4	*23.7*	36.7	50.2
Non-extractable residues [2]	1.4	1.6	*1.8*	4.2	5.7
Parental Mass Balance [2]	94.2	93.6	*90.2*	76.6	51.2
Overall Material Balance [2]	95.5	95.5	*92.1*	80.8	56.9
Soil HH					
Amount adsorbed to soil [1]	39.3	45.0	*50.7*	59.2	66.6
Non-extractable residues [2]	10.6	12.3	*12.8*	27.9	30.3
Parental Mass Balance [2]	90.4	87.2	*87.3*	75.2	72.9
Overall Material Balance [2]	101.0	99.5	*100.2*	103.1	103.2
Soil WW					
Amount adsorbed to soil [1]	27.2	*31.0*	37.8	46.7	57.0
Non-extractable residues [2]	7.2	*9.6*	12.0	23.6	23.2
Parental Mass Balance [2]	92.4	*89.4*	88.3	80.7	77.9
Overall Material Balance [2]	99.5	*99.1*	100.3	104.3	101.0

[1] Values taken from preliminary adsorption equilibrium test
[2] Values taken from preliminary parental mass balance test
[3] values in italic indicate the equilibrium time of the definitive test

In the definitive adsorption test 34.2 – 41.9% AR, 26.0 – 33.7% AR, 55.7 – 60.2% AR and 38.6 – 42.9% AR were adsorbed in soil AX, DD, HH and WW, respectively.

The Freundlich adsorption and desorption constants for ethephon in soil are summarised below.

Table 7.1.3- 2: Adsorption and desorption constants for ethephon in soil

Soil Texture (USDA)	pH	OC [%]	Adsorption				Desorption			
			K_f [mL/g]	K_{foc} [mL/g]	1/n	R^2	K_{fdes} [mL/g]	K_{focdes} [mL/g]	1/n	R^2
Laacher Hof AXXa (sandy loam)	6.3	2.0	6.1	306.5	1.0007	0.9953	15.3	766.2	1.0647	0.9947
Dollendorf II (loam)	7.3	5.1	5.2	101.9	1.045	0.9953	n.p.	n.p.	n.p.	n.p.
Hoefchen am Hohenseh 4a (silt loam)	6.1	2.1	13.0	621.1	0.9718	0.9992	n.p.	n.p.	n.p.	n.p.
Laacher Hof Wurmwiese (loam)	5.1	2.0	6.8	342.3	0.9896	0.9983	n.p.	n.p.	n.p.	n.p.
Mean			7.8	342.9	1.0018	0.9970	15.3	766.2	1.0647	0.9947

n.p. not performed

In general the organic matter in soil, determined as organic carbon content, is the most important component responsible for binding organic chemicals. However, ethephon is a diprotic acid (pK_{a1} = 2.8, pK_{a2} = 7.2) and the predominant species under environmental conditions are the negatively charged mono-anion (below pH 7.2) and di-anion (above pH 7.2). The log P_{OW} values of ethephon are ≤ - 0.63 demonstrating the molecule has a very low lipophilicity. Thus, the adsorption of ethephon is believed to be predominantly based on non-specific interactions with soil but the binding to the soil organic matter may be a significant process as well. Therefore, the adsorption coefficients K_F were correlated with the organic carbon content of the soil. The K_{foc} values ranged from 101.9 to 621.1 mL/g (arithmetic mean 342.9 mL/g), ~~and binding to the soil organic matter is a subordinated process only. This is confirmed by the narrow range of K_F values (9.3 to 11.0 mL/g) measured across four soils, without correlation to organic carbon content. Thus adsorption coefficients K_F for ethephon were not normalised to the organic carbon content of the soil.~~

There was no significant correlation between pH and adsorption for the investigated soils.

III. CONCLUSIONS

~~Ethephon was strongly adsorbed to soil with a mean KF value of 10 mL/g and mean slope (1/n) of 0.8619. Using the Briggs classification scale to assess a chemical's potential mobility in soil (based on its KF), ethephon can be classified as being of low mobility in the soils examined.~~

The adsorption constants $K_{F\,(ads)}$ of ethephon for the tested soils calculated based on the Freundlich isotherms ranged from 5.2 to 13.0 mL/g (arithmetic mean 7.8 mL/g). The desorption constant $K_{F(des)}$ of ethephon could only be determined for soil AX and was in the same order of magnitude than the respective adsorption constant.

There was no significant correlation between pH and adsorption for the investigated soils. Ethephon was stable during the definitive test. The parental mass balance was ≥87% AR. No major degradation product was observed.

Using the Briggs classifications for the estimation of the mobility of chemicals in soil based on K_F values, ethephon can be classified as low mobile for adsorption in all tested soils and low mobile for desorption in soil AX.

Report:	KCA 7.1.3.1.1/03; [redacted]; 2017; M-587404-01-1
Title:	Discussion of comments provided by RMS (the Netherlands) in the draft RAR - Volume 3 - Annex B (AS / PPP) - Ethephon - B.8 Environmental fate and behaviour
Report No.:	M-587404-01-1
Document No.:	M-587404-01-1
Guideline(s):	none
Guideline deviation(s):	--
GLP/GEP:	**no**

1. Discussion of the validity of the adsorption/ desorption study performed by [redacted] (2015), listed in Annex Point KCA 7.1.4.1 /02 and considered as not acceptable by RMS

a) The Freundlich exponent and adsorption value were transposed in error in the original report. The corrected values can be found in the Final report Amendment 1. New K_{foc} values have been calculated from the corrected K_F values. Please find the corrected values in the table below:

Table 7.1.3- 3: Corrected Adsorption Parameters for Ethephon

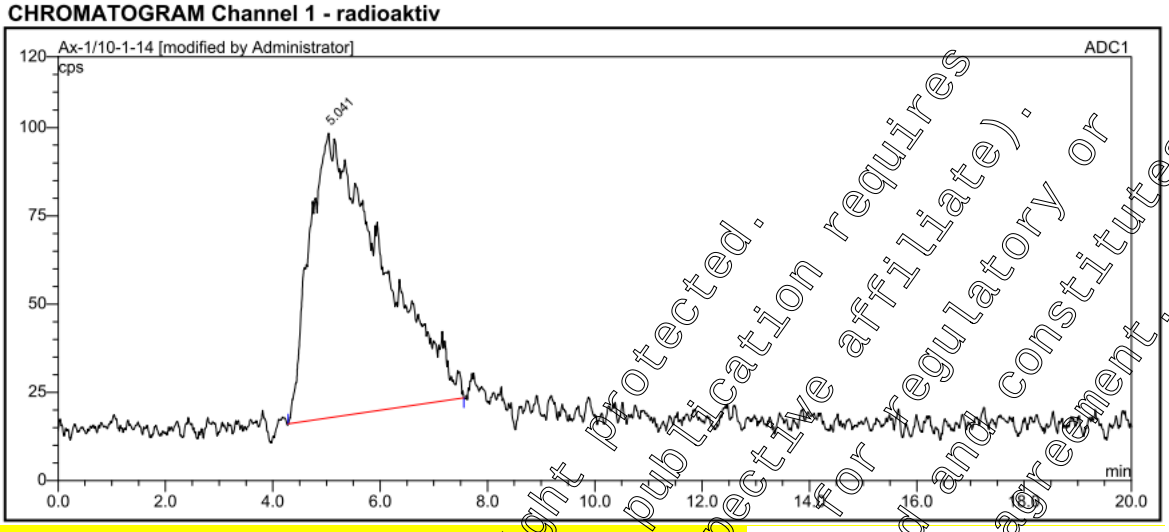
Soil	pH ($CaCl_2$)	OC	log K_f	K_f	K_{foc}	1/n
AX	6.3	2.0	0.79	6.2	**306.5**	**1.0007**
DD	7.3	5.1	0.72	5.2	**101.9**	**1.045**
HH	6.1	2.1	1.12	13.0	**621.1**	**0.9718**
WW	5.1	2.0	0.84	6.8	**342.3**	**0.9896**

b) The applicant does not agree to the statement made by the RMS that the substance is unstable during the equilibration times chosen for the main study. The reasons are discussed below:

Degradation of test item in supernatants and soil extracts

Sufficient stability of the test item in the sterilised systems was shown during the performance of the parental mass balance test. As it was not possible to demonstrate stability of the test item using HPLC/radiodetection due to adsorption effects of the test item to the solid phase scintillator of the radioactivity detector, the stability of the test item was confirmed by LC-MS/MS detection. Further details on this procedure will be included in an amendment to the study report. Available results from HPLC/radiodetection show no peak besides the peak of ethephon (Figure 7.1.3- 1).

Figure 7.1.3- 1: Representative HPLC/radiodetection Chromatogram of Test Item in Supernatant of Soil AX



Supernatant (not diluted) of soil AX after 5 hours of incubation,
Sample ID: AX-1/10-1-14 CaCl2; File ID: 20150828-S15-04002-S01

Tables 8 to Table 11 in the study report reveal that in all cases the amounts of the test item (test item in solution [% AA]) determined by LC-MS/MS are higher or similar to the radioactivity determined in solution (radioactivity in solution [% AR]). This confirms that the test item represents the major part of the radioactivity in the supernatant solution and soil extracts and that no further components are present. A summary of the parental mass balance test is shown in Table 12 in the study report and in Table 7.1.3- 4 below.

Table 7.1.3- 4: Preliminary Test; Summary of Results from Adsorption Kinetics, Parental Mass Balance and Material Balance for all Soils (Table 12 in study report)

Parameters	Adsorption time (hours)				
Mean values [% AR]	**1**	**2**	**5**	**24**	**48**
Soil (AX)					
Amount adsorbed to soil	18.6	20.2	25.3	30.8	46.1
Non-extractable residues	3.9	5.4	6.2	7.5	8.6
Parental Mass Balance	94.0	92.7	**91.8**	89.6	83.2
Overall Material Balance	98.0	98.7	98.0	97.0	91.8
Soil DD					
Amount adsorbed to soil	16.3	18.4	23.7	36.7	50.2
Non-extractable residues	1.4	1.6	1.8	4.2	5.7
Parental Mass Balance	94.2	93.6	**90.2**	76.6	51.2
Overall Material Balance	95.5	95.5	92.1	80.8	56.9
Soil HH					
Amount adsorbed to soil	39.3	45.0	50.7	59.2	66.6
Non-extractable residues	10.6	12.3	12.8	27.9	30.3
Parental Mass Balance	90.4	87.2	**87.3**	75.2	72.9

Parameters	Adsorption time (hours)				
Mean values [% AR]	**1**	**2**	**5**	**24**	**48**
Overall Material Balance	101.0	99.5	100.2	103.1	103.2
Soil WW					
Amount adsorbed to soil	27.2	31.0	37.8	46.7	57.0
Non-extractable residues	7.2	9.6	12.0	23.6	23.2
Parental Mass Balance	92.4	**89.4**	88.3	80.7	77.9
Overall Material Balance	99.5	99.1	100.3	104.8	101.0

Parental mass balances, i.e. the amount of test item in the extracts (highlighted in bold), were shown to be >90% for soils AX (91.8% after 5 h) and DD (90.2% after 5 h) and thus the requirements of the OECD 106 guidance regarding stability are considered to be fully met. NER were present in these soils with 6.2 and 1.8% AR, respectively which is not considered to be unacceptable high. Please note that the effect of temperature is discussed below.

For soils HH and WW, the parental mass balances were with 87.3 and 89.3% AR very close to the 90% requested by the test guidelines and are thus considered to be also valid. The slightly lower parental mass balances mainly result from the formation of NER which accounted for 12.8 and 9.6% AR, respectively.

Mean material balances were 98.0% AR for soil AX after 5 h, 92.1% AR for soil DD after 5 h, 100.2% AR for soil HH after 5 h and 99.1% AR for soil WW after 2 h. The complete material balances found for all soils demonstrated that there was no significant loss of radioactivity from the test systems or during sample processing which would have been expected in case of a significant formation of the major transformation product ethylene.

After the periods chosen as equilibration time in the definitive test (5 hours for soils AX, DD and HH, 2 hours for soil WW), the parental mass balances decrease <90% in all soils. This indicates that degradation started after completion of the definitive test. Overall the equilibration times chosen for the definitive test can be seen as a compromise between fulfilling the requirements for stability and reaching the adsorption equilibrium (see below).

Adsorption kinetics

The results of the adsorption kinetics test revealed that the adsorption equilibrium of ethephon (plateau concentrations) was not reached within the 48 hours of the test. The table below shows that after 5 and 2 hours the adsorbed amounts still increase. This demonstrates that the adsorption measured at the equilibrium times of the definitive test generally underestimates the sorption of ethephon.

Thus the applicant does not agree to the statement made by the RMS that the study generally overestimates adsorption due to the mentioned stability issues.

Table 7.1.3- 5: Results of Preliminary Adsorption Equilibrium (Table 7 in study report)

Soil ID/ Time [h]	Amount of Test Item Adsorbed [% AR]				
	1	2	5	24	48
AX	18.6	20.3	25.3	30.8	46.1
DD	16.3	18.5	23.2	36.7	50.2
HH	39.3	45.0	50.7	59.2	66.6
WW	27.2	31.2	37.8	46.7	57.0

Influence of temperature:

The RMS addressed the fact that the preliminary tests and the definitive test were performed at slightly different temperatures. Due to the following reasons, the temperature change is not considered relevant:

- All preliminary tests and the main test were performed at temperatures between 20 and 25°C as required by the test guidelines. It is a common procedure to directly compare K_{foc} values determined in this temperature range. A temperature correction is not necessary.
- The radioactivities in the supernatants obtained in the parental mass balance test (temperature: 19.7 to 20.4°C) were compared with the results of Tier 3 (temperature: 22.9 to 24.0°C) and presented in the table below:

Table 7.1.3- 6: Comparison of radioactivity in supernatants: parental mass balance test and definitive test

Soil	AX	DD	HH	WW
Equilibration time	5 h	5 h	5 h	2 h
RA in solution in parental mass balance test (% AR) presented in Table 8 to Table 11 in the study report	59.7	67.4	47.7	53.6
RA in solution in Tier 3, highest test item concentration (% AR) presented in Table 13 (100 - % adsorbed)	64.1	68.7	44.3	61.4
Difference (% AR)	4.4	-1.3	3.4	-7.8

The comparison shows that for the soils AX, DD and HH the radioactivity in the supernatants is similar (difference <5% AR; for soil WW the difference is somewhat larger. However, there is no trend visible which could be assigned to temperature.

Also in an comparison of KOC values determined within the preliminary adsorption equilibrium test with the K_{foc} values determined in the definitive test (justifiable as adsorption is almost linear) no trend which might have been caused by temperature is visible (see table below).

Table 7.1.3- 7: Comparison of K_{oc} values determined in preliminary Adsorption Equilibrium Test with K_{Foc} values from definitive test

Soil	pH ($CaCl_2$)	OC	K_{OC} [mL/g] (equilibrium test)	K_{Foc} [mL/g] (definitive test)
AX	6.3	2.0	274 (5 h)	306.5
DD	7.3	5.1	145 (5 h)	101.9
HH	6.1	2.1	433 (5 h)	621.1
WW	5.1	2.0	339 (2 h)	342.3

Conclusion: The difference in temperature is not expected to have influenced the test item behavior significantly.

Results from hydrolysis study:

The hydrolysis data provided by Das, Y.T. (1990) in Annex Point KCA 7.2.1.1/01 show that after 6 hours, the test item still accounts for > 90% at pH 7 and 25°C (see table below). This supports the findings of the adsorption/desorption study in which was shown that the test item is stable for about 2-5 hours under sterilised conditions and that the main degradation started after completion of the definitive test.

Table 7.1.3- 8: Quantification of [ethyl(U)-^{14}C]Ethephon, measured in the test solutions at three pH values at each sampling time (at 25°C)

pH = 5		pH = 7		pH = 9	
Sampling hour	**Average of two replicates**	**Sampling hour**	**Average of two replicates**	**Sampling hour**	**Average of two replicates**
0	99.9±1.3	0	98.4±0.8	0	101.2±0.9
12	96.0±0.2	6	90.1±0.0	1.5	96.2±1.9
36	94.6±1.2	12	79.5±1.4	3	90.4±2.7
84	91.3±0.4	24	66.1±0.0	6	82.6±2.6
168	85.7±0.1	48	38.2±2.1	12	73.8±6.2
252	84.8±0.9	72	32.8±1.1	24	42.6±0.9
360	81.7±0.1	168	13.4±0.1	48	24.6±0.1
504	78.4±0.4				
720	73.6±0.1				

2. pH dependency

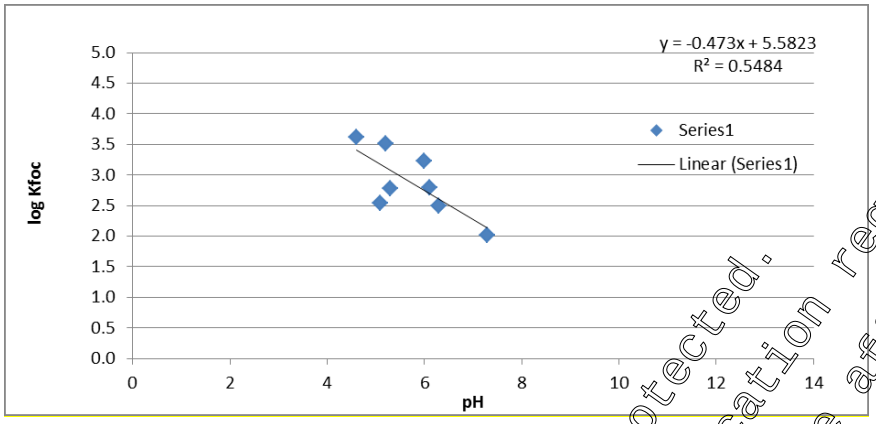
Under the assumption that the results of the new adsorption/desorption study can be considered valid, all adsorption data available for ethephon were checked for their pH dependency using the Table and Figures below:

Table 7.1.3- 9: Dependence on pH value

Study	Soil	pH	K_{foc} [ml/g]	log K_{foc}	1/n
Das Y.T. (1991)	Clay	5.2 a)	3220	3.51	0.987
	Silt loam	5.3 a)	608	2.78	1.017
	Sandy loam	4.6 a)	4078	3.61	0.977
	Sandy loam (sediment)	6 a)	1676	3.22	0.987
[redacted] (2015)	AX (sandy loam)	6.3 ($CaCl_2$)	306.5 b)	2.49	1.0007
	DB (loam) c)	7.3 ($CaCl_2$)	101.9 b)	2.01	1.0450
	HH (silt loam)	6.1 ($CaCl_2$)	621.1 b)	2.79	0.9718
	WW (loam)	5.1 ($CaCl_2$)	342.3 b)	2.53	0.9896
		Geometric mean	**980.6**	**Average:**	**0.9900**

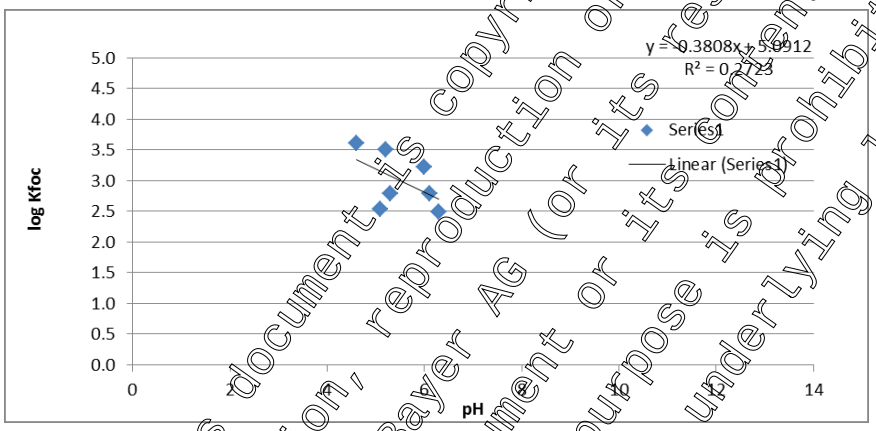
a) medium not known
b) re-calculated based on values in Figure 17-20 in the report
c) excluded from calculation of geometric mean and average

Figure 7.1.3- 2: Dependence on pH value including all soils



As the correlation is generally weak and seems to be mainly caused by the data point with the highest pH (soil Dollendorf) the data were also plotted without this soil:

Figure 7.1.3- 3: Dependence on pH value without soil Dollendorf (pH 7.3)



In Figure 3 there is no pH-dependency visible for the soils with pH < 6 or around 6.
Thus the applicant proposes the following procedure for modelling to address the pH dependency:

Divide the soils in pH < 7 and soils with pH > 7:
K_{foc} for soils with pH < 7: 980.6 mL/g (geomean, n < 7), 1/n: 0.99 (arithmetic mean, n= 7)
K_{foc} for soils with pH > 7: 102 mL/g (value for one soil > pH 7), 1/n = 1.045
(soil Dollendorf investigated in the new study, parental mass balance sufficient and NER only 1.8% after 5 h)

Conclusion: Based on the results of the two available adsorption studies, it can be concluded that soils with pH < 7 do not show a pH dependency and can be grouped for the PEC calculations.
As ethephon has a pka_2 value of 7.2, a lower adsorption can generally be expected at higher pH values. This assumption was confirmed with the lower K_{foc} value observed for soil DD having a pH value of 7.3 (in 0.01 M CaCl2). For the risk assessment the applicant thus proposes to use the value of 102 mL/g for soils with a pH > 7. This is the worst case of all available results. The parental mass balance and the low amounts of NER formed in this soil confirm the stability of ethephon under study conditions.

The section of the statement referring to water/sediment studies is presented in Annex Point KCA 7.2.2.3/03.

CA 7.1.3.1.2 Adsorption and desorption of metabolites, breakdown and reaction products

The adsorption and desorption of HEPA had been investigated in four soils and an aquatic sediment at 25 °C (KCA 7.1.3.1.2 /01). This study was evaluated during the previous EU review, and the reference is provided below. No new information on the adsorption and desorption in soil is submitted for the current EU review.

Report:	KCA 7.1.3.1.2/01; [redacted]; [redacted]; 1996; M-166197-01-1
Title:	2-Hydroxyethylphosphonic acid (ethephon metabolite) - Adsorption / desorption study.
Report No.:	R004445
Document No.:	M-166197-01-1
Guideline(s):	USEPA (=EPA): FIFRA, N, 163-1
Guideline deviation(s):	--
GLP/GEP:	**yes**

CA 7.1.3.2 Aged sorption

An assessment of aged sorption is an optional higher tier study which is not required for ethephon.

CA 7.1.4 Mobility in soil

CA 7.1.4.1 Column leaching studies

CA 7.1.4.1.1 Column leaching of the active substance

Soil adsorption coefficient values established for ethephon are provided in CA 7.1.3.1.1. Therefore, column leaching studies are not required.

CA 7.1.4.1.2 Column leaching of metabolites, breakdown and reaction products

Soil adsorption coefficient values established for HEPA are provided in CA 7.1.3.1.2. Therefore, column leaching studies are not required.

CA 7.1.4.2 Lysimeter studies

The potential mobility of ethephon and its metabolites has been assessed by modelling which confirmed that the compound does not constitute a risk to groundwater. Therefore a lysimeter study is not required.

CA 7.1.4.3 Field leaching studies

The potential mobility of ethephon and its metabolites has been assessed by modelling which confirmed that the compound does not constitute a risk to groundwater. Therefore a field leaching study is not required.

CA 7.2 Fate and behaviour in water and sediment

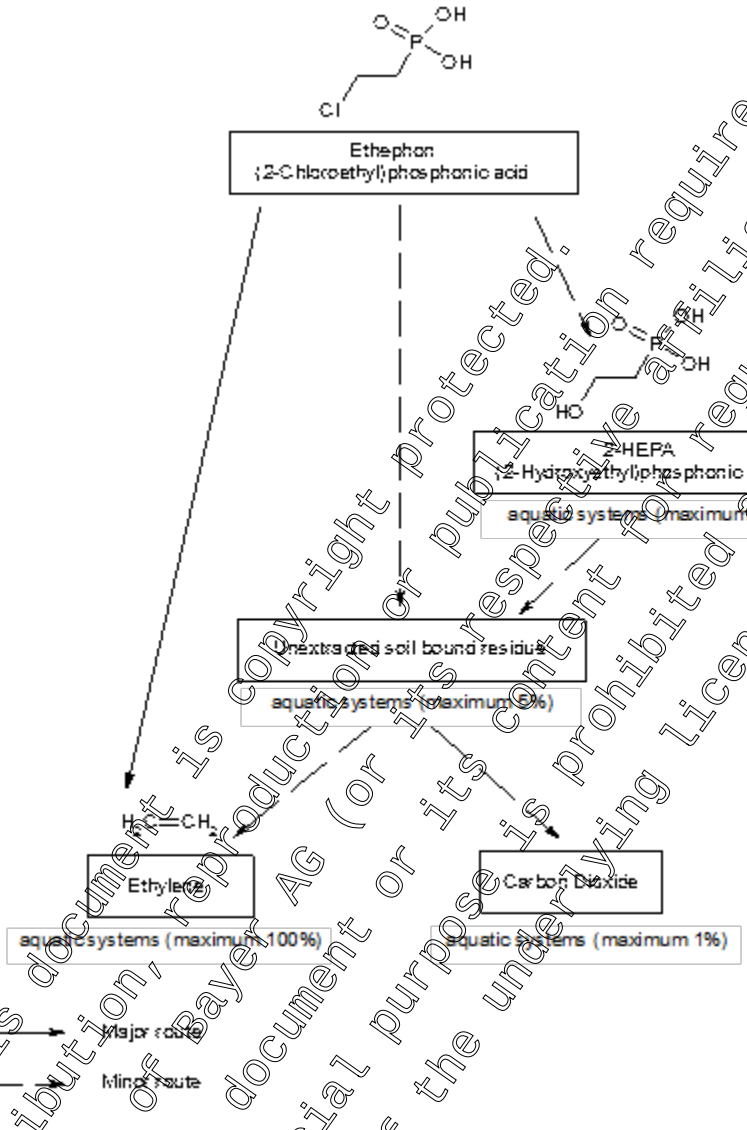
The fate and behaviour of ethephon in aquatic systems has been investigated under abiotic and biotic conditions. Studies were evaluated during the previous EU review. Two additional laboratory studies are provided for the current EU review (an aqueous photolysis study in natural water, and a study on aerobic mineralisation in surface water).

In sterile aqueous buffer solution at 25°C, ethephon was found to be stable to hydrolysis under acidic conditions but to hydrolyse rapidly to ethylene in neutral and alkali conditions, with DT_{50} values of 73.5 days at pH 5, 2.4 days at pH 7 and 1.0 day at pH 9. The photolytic degradation of ethephon in water has been investigated under sterile conditions in acetate buffer solution at pH 5 and in natural water at pH 7.5 at 25 ºC. The rate of degradation of ethephon was largely dependent on the pH of the test systems with similar half-lives observed in non-irradiated and irradiated experiments and it can be concluded that photolysis does not play a significant role in the breakdown of ethephon in aquatic systems. Ethylene was the only major degradation product. In a natural water study not previously evaluated, the metabolite HEPA was detected in both irradiated samples and dark controls, at a maximum of 7.4% AR. In irradiated samples it exceeded 5% at the two final timepoints.

Ethephon was found to be not readily biodegradable according to OECD Test Guideline 301D. In a new aerobic mineralisation study (OECD 309) the fate of ethephon was investigated in natural water at pH 7.8. The degradation rate was independent of concentration and very similar in the biotic and sterile systems. Ethephon was very rapidly degraded to ethylene with no other significant metabolites formed. Mineralisation was a minor route of degradation.

In two water / sediment systems (pH of water phase 8.9 and 6.8) ethephon was rapidly degraded to ethylene which accounted for over 95% of the applied material at the end of the study with no other significant products formed in water sediment systems. Very little ethephon transferred from the water to the underlying sediment, with a maximum of 6% of applied ethephon detected in sediment. HEPA was detected in the water phase of one of the systems at a maximum of 1.4% AR.

Figure 7.2- 1: The proposed route of degradation for ethephon in aquatic systems



CA 7.2.1 Route and rate of degradation in aquatic systems (chemical and photochemical degradation)

CA 7.2.1.1 Hydrolytic degradation

The hydrolysis of ethephon had been investigated in sterile aqueous buffer at pH 5, 7 and 9 at a temperature of 25 °C (KCA 7.2.1.1/01). The study was evaluated during the previous EU review, and the reference is provided below. No new information is submitted for the current EU review.

Report:	KCA 7.2.1.1/01; [redacted]; 1990; M-187629-01-1
Title:	Hydrolysis of [Ethyl(U)-14C]Ethephon in Aqueous Solutions buffered at pH 5, 7 and 9
Report No.:	R013276
Document No.:	M-187629-01-1
Guideline(s):	USEPA (=EPA): 161-1
Guideline deviation(s):	--
GLP/GEP:	**yes**

CA 7.2.1.2 Direct photochemical degradation

The aqueous photolysis of ethephon had been studied in sterile aqueous buffer at pH 5 at a temperature of 25 °C (KCA 7.2.1.2/01). The study was evaluated during the previous EU review and the reference is provided below. No new information is submitted for the current EU review.

Report:	KCA 7.2.1.2/01; [redacted]; 1990; M-187632-01-1
Title:	Photodegradation of [Ethyl(U)-14C]Ethephon in Aqueous Solution Buffered at pH 5 under artificial Sunlight
Report No.:	R013277
Document No.:	M-187632-01-1
Guideline(s):	USEPA (=EPA): 161-2
Guideline deviation(s):	--
GLP/GEP:	**yes**

CA 7.2.1.3 Indirect photochemical degradation

An aqueous photolysis study in natural water was conducted with ethephon as required under Japanese regulations. The study was conducted after the previous EU review and so it is now submitted for this current EU review. The study is summarised below.

Report:	KCA 7.2.1.3/01; [redacted]; [redacted]; 2005; M-249376-01-1
Title:	(14C)-ethephon: Aqueous photolysis in natural water
Report No.:	C047940
Document No.:	M-249376-01-1
Guideline(s):	JMAF: 13 Seisan No. 3986, (2001), 2-6-2, (2001)
Guideline deviation(s):	--
GLP/GEP:	**yes**

Executive Summary

The photolysis of [^{14}C]-ethephon was investigated in sterile natural water. The compound was applied to water at a nominal rate of 1 mg/L. Test samples were continuously irradiated with light from a xenon arc lamp, which emitted light that was filtered to give a spectral distribution close to that of natural sunlight. The pH of the water was 7.5. Samples were maintained at 25 °C and the illumination was continued for up to 6.5 days, equivalent to 30.8 days natural sunlight (Japan).

Duplicate samples were taken at time 0 and 157 hours. Single samples were taken at 4, 6, 24, 28, 48 and 61 hours. A set of control samples were incubated under the same conditions but kept in the dark. Single samples were taken at 24, 48 and 168 hours for non-irradiated samples.

Overall mean recoveries throughout the experiment were 97% and 96% for the irradiated and non-irradiated samples, respectively.

[^{14}C]-Ethephon was rapidly degraded to [^{14}C]-ethylene which formed 88 and 92% AR after *ca.* 7 days incubation in irradiated and dark controls groups, respectively. Mineralization was a minor route of degradation, with [^{14}C]-carbon dioxide accounting for < 1% AR. HEPA was detected in both irradiated samples and dark controls, at a maximum of 7.4% AR. In irradiated samples it exceeded 5% at the two final timepoints. A second degradate, characterized as dissolved ethylene based on its retention time, reached a maximum of 5.4% but did not exceed 5% at any other timepoint.

The degradation rate of ethephon observed in the non-irradiated system was very similar to that seen in the irradiated experiment.

Test System	SFO		
	DT_{50} (days)	**DT_{90} (days)**	**r^2**
Irradiated	0.74	2.47	0.999
Dark control	0.73	2.43	0.998

It can be concluded that ethephon is very rapidly hydrolysed in natural water to ethylene at pH 7.5 and that photolysis would not play a significant role in the breakdown of ethephon in natural systems.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test material: [UL-^{14}C] Ethephon

Chemical name 2-Chloroethylphosphosphonic acid

Specific activity: 4.28 MBq/mg

Lot or batch number: BECH 1605

Radiochemical purity: 98%

CA registry number: 16672-87-0

Application vehicle: Acetonitrile

2. Water Natural water from Reservoir Pond at Boarded Barns Farm, Fyfield Road, Ongar, Essex was used. Water was sieved through a 0.22 µm Millipore filter to sterilize prior to use.

Characteristics of the test water

Name		Reservoir Pond
Origin		Boarded Barns Farm, Ongar, Essex.
Ordnance Survey reference		TL 562047
Date of collection		3rd November 2004
Dissolved Organic Carbon		24.7 mg/L
Dissolved Organic Matter c		42.58 mg/L
Total Phosphorus		< 0.05 mg/L
Total Nitrogen		32.2 mg/L
Nitrate		< 1.0 mg/L
Total Hardness		232.0 mg/L $CaCO_3$
Electrical Conductivity		484 µS cm^{-1}
pH		7.5
Residue on Evaporation		0.028 % w/w
Suspended Solids		0.0001 % w/w
Dissolved Oxygen	At collection	94% Saturated
	After sterilisation and re-aeration	97% Saturated

B. STUDY DESIGN AND METHODS

In-life dates

Study initiation date: 9 November 2004

Study completion date: 29 March 2005

Experimental start date: 10 November 2004

Experimental completion date: 20 March 2005

Experimental design

Parameter		Description
Nature of light source		Xenon lamp
Emission wavelength spectrum		290-800 nm
Measured light intensity (300 - 800 nm)		327 W/m^2
Light intensity t (300 - 400 nm)		11.25% x 327 W/m^2 =36.8 W/m^2
Filters used		UV filter
Relationship to natural sunlight		Similar spectral distribution
Duration of the test		157 hours (30 days sunlight equivalent)
Test system		Sterile natural water (sterilized by filtration), pH 7.5
Test concentration (mg/L)		0.87 mg/L in dark controls 1.0 mg/L in irradiated samples
Control conditions		Darkness
Number of replicates	Irradiated	Duplicate at 0 and 157 h, single at other timepoints
	Darkness	Duplicate at 0, single at other timepoints
Test apparatus	Irradiated	Glass photolysis vessels of capacity 60mL, quartz lids for irradiated vessels.
	Darkness	Glass calibrated tubes

Parameter		Description
Traps for CO_2 & organic volatiles		Four pyridinium hydrogen bromide perbromide traps (PHBPB, for ethylene) and a 2M sodium hydroxide trap (2M KOH, for carbon dioxide)
Preparation of test medium	Volume per vessel	50 mL
	Method of sterilisation	Filtration
Test material application	Identity of solvent	Acetonitrile co-solvent (0.2% v/v)
	Volume of application solution	100 µL
	Application method	Positive displacement Gilson pipette
Indication of test material adsorbing to walls of test apparatus		No
Experimental conditions	Temperature (°C)	25 ± 2
	Continuous irradiation	Yes

Sampling

Parameter		Description
Sampling intervals	Irradiated	0, 4, 6, 24, 28, 48, 61 and 157 hours
	Darkness	0, 24, 48 and 168 hours
Sampling procedures		Complete samples removed at each timepoint
Collection of CO_2 and volatile organics		Complete trap system removed at each timepoint. Additional trap changes carried out at 24, 48, 72 and 96 hours after treatment.
Sample storage before analysis		HPLC profiles were obtained immediately.
Verification of sterility		Sterility was confirmed at each timepoint.

Description of analytical procedures

At each sampling time, the amount of radioactivity in water and volatile traps was quantified by LSC. The metabolic profile was determined by HPLC with radiodetector. The identity of ethephon and HEPA was confirmed in selected samples by LC-MS.

The half-lives (DT_{50}) of [^{14}C]-ethephon in irradiated samples and dark controls were determined using a single first order (SFO) kinetic model.

II. RESULTS AND DISCUSSION

The total recoveries and distribution of radioactivity are shown in detail in Table 7.2.1- 1 to Table 7.2.1- 2.

Mass Balance

Total radioactivity	Sum of activity in the water phase, and that trapped in volatile traps as ^{14}C-ethylene in the PHBPB traps and as $^{14}CO_2$ in the 2M KOH traps.
Recovery at 0 DAT	Range 98.6 to 102.3% AR - Average 100.4% AR
Overall recovery (all samples)	Irradiated: Range 90.0 to 102.4% AR - Average 96.9% AR Dark control: Range 90.1 to 102.3% AR - Average 96.0% AR

Volatilisation

Ethephon rapidly degraded to form [^{14}C]-ethylene in both irradiated samples and dark controls (87.6 and 92.2% AR). Only small amounts of $^{14}CO_2$ were formed.		
$^{14}CO_2$ evolved at end of test	Irradiated Water	0.28% AR
	Dark Control	Not stated, negligible
^{14}C-Ethylene evolved at end of test	Irradiated Water	87.6% AR
	Dark Control	92.2% AR

Transformation of Parent Material

[^{14}C]-Ethephon was rapidly degraded to [^{14}C]-ethylene which formed 88 and 92% AR after *ca.* 7 days incubation in irradiated and dark controls groups, respectively. Mineralisation was a minor route of degradation, with [^{14}C]-carbon dioxide accounting for < 1% AR.

Minor amounts of HEPA were detected in both irradiated samples and dark controls (maximum 5.2% and 7.4%, respectively). In irradiated water samples HEPA exceeded 5% at the final two timepoints and thus has been included in aquatic risk assessments. The maximum level of HEPA was observed in the dark control samples (7.4% after 24 hours) but the metabolite did not exceed 5% at two consecutive timepoints. A second degradate, characterized as dissolved ethylene based on its retention time, reached a maximum of 5.4% after 4 hours but did not exceed 5% at any other timepoint.

The results are presented in Table 7.2.1- 3 to Table 7.2.1- 4.

DT_{50} of ethephon in natural water

The degradation of ethephon observed in the dark control experiment was very similar to that seen in the irradiated experiment. SFO DT_{50} values for ethephon in sterile natural water at pH 7.5 were 0.74 days under irradiated conditions and 0.73 days in dark controls. The results are presented in Table 7.2.1- 5. The decline of ethephon observed in the study was due to hydrolysis with the degradation rate independent of the light conditions.

Table 7.2.1- 1: Distribution and recovery of [^{14}C]-ethephon in irradiated natural water

Incubation time (hours)	Replicate	Days Sunlight *	% of applied radioactivity		
			Water phase	Ethylene	Total Recovery
0	A	0	98.62	-	98.62
	B		102.25	-	102.25
	Mean		100.44	-	100.44
4	A	0.79	89.13	7.04	96.17
6	A	1.18	79.34	10.67	90.01
24	A	4.74	45.55	50.83	96.38
28	A	5.53	39.87	62.53	102.40
48	A	9.45	20.59	74.74	95.33
61	A	12.04	12.26	87.45	99.71
157	A	31.0	6.72	91.30	98.02
	B		6.76	83.87	90.63
	Mean		6.74	87.59	94.32

* 1 day in the suntest = 4.74 sunlight equivalent days, Japan

Table 7.2.1- 2: Distribution and recovery of [^{14}C]-ethephon in dark controls

Incubation time (hours)	Replicate	Days	% of applied radioactivity		
			Water phase	Ethylene	Total Recovery
0	A	0	98.62	-	98.62
	B		102.25	-	102.25
	Mean		100.44		100.44
24	A	1	44.38	45.70	90.07
48	A	2	21.42	74.01	95.43
168	A	7	5.89	92.16	98.05

Table 7.2.1- 3: Composition of radioactivity in irradiated natural water

Incubation time (hours)	Replicate	% of applied radioactivity			
		Water phase	Ethephon	HEPA RRT 0.35	Unknown RRT 0.23
0	A	98.62	96.78	-	1.84
	B	102.25	101.48	-	0.77
	Mean	100.44	99.13	-	1.31
4	A	89.13	83.37	0.38	5.38
6	A	79.34	75.04	0.32	3.98
24	A	45.55	40.03	2.08	3.43
28	A	39.87	33.26	2.12	4.49
48	A	20.59	16.25	2.85	1.49
61	A	12.26	6.63	5.03	0.60
157	A	6.72	3.07	3.65	-
	B	6.76	-	6.76	-
	Mean	6.74	1.53	5.20	-

Table 7.2.1- 4: Composition of radioactivity in dark controls

Incubation time (hours)	Replicate	% of applied radioactivity			
		Water phase	Ethephon	HEPA RRT 0.35	Unknown RRT 0.23
0	A	98.62	96.78	-	1.84
	B	102.25	101.48	-	0.77
	Mean	100.44	99.13	-	1.31
24	A	44.38	35.10	7.44	1.84
48	A	21.42	18.89	1.02	1.51
168	A	5.89	-	5.89	-

Table 7.2.1- 5: Summary of DT_{50} values for [^{14}C]-ethephon in natural water systems

Test System	SFO		
	DT_{50} (days)	DT_{90} (days)	r^2
Irradiated	0.74	2.47	0.999
Dark control	0.73	2.43	0.998

Conclusions

The rate of photodegradation of [^{14}C]-ethephon was investigated in sterile natural water at pH 7.5. The compound was applied to water at nominal rate of 1 mg/L. Test samples were continuously irradiated at 25 °C for up to 6.5 days. Control samples were incubated under similar conditions in the dark.

[^{14}C]-Ethephon was rapidly degraded to ethylene which formed 88 and 92% AR after *ca.* 7 days incubation in irradiated and dark controls groups, respectively. HEPA was detected in both irradiated samples and dark controls, at a maximum of 7.4% AR. In irradiated samples it exceeded 5% at the two final timepoints.

The degradation of ethephon observed in the non-irradiated system was identical to that seen in the irradiated experiment, with DT_{50} values of 0.73 and 0.74 days. It can be concluded that ethephon is very rapidly hydrolysed in natural water systems to ethylene at pH 7.5 and that photolysis would not play a significant role in the breakdown of ethephon in natural systems.

CA 7.2.2 Route and rate of biological degradation in aquatic systems

CA 7.2.2.1 "Ready biodegradability"

The ready biodegradability of ethephon had been studied in a closed bottle test according to OECD 301 D (KCA 7.2.2.1/01). This study was evaluated during the previous EU review, and the reference is provided below. No new information is submitted for the current EU review.

Report:	KCA 7.2.2.1/01; [redacted]; 2002; M-212566-01-1
Title:	Study on the "ready biodegradability" of Ethephon
Report No.:	C022156
Document No.:	M-212566-01-1
Guideline(s):	OECD 301D
Guideline deviation(s):	--
GLP/GEP:	**yes**

CA 7.2.2.2 Aerobic mineralisation in surface water

An assessment of aerobic mineralisation in surface water is new study requirement under Regulation 1107/2009. An aerobic mineralization study (OECD 309) was performed for the current EU review (KCA 7.2.2.2/01). This new study is summarised below.

Report:	KCA 7.2.2.2/01; [redacted]; 2015; M-532463-01-1
Title:	[UL-^{14}C]ethephon - Aerobic mineralisation and metabolism in surface water - Final report
Report No.:	AS420
Document No.:	M-532463-01-1
Guideline(s):	OECD Guideline for Testing of Chemicals, No 309 Aerobic Mineralisation in Surface Water, Apr. 13, 2004
Guideline deviation(s):	not specified
GLP/GEP:	**yes**

Executive Summary

The extent of mineralisation and the rate and route of degradation of [^{14}C]-ethephon was investigated in Kellmetschweiher natural water at pH 7.8. The compound was applied to the water at nominal rates of 10 and 100 µg/L (low and high concentrations respectively). The higher application rate was also applied to a sterilised test system. The systems were incubated under aerobic conditions and maintained at 20 °C for 5 days. For each system, duplicate samples were taken at 1, 3, 6, 12, 24, 72 and 120 hours for analysis.

Separate test systems were treated with [^{14}C]-sodium benzoate at 100 µg/L. The compound was completely degraded within 120 hours, indicating a viable microbial population was present in the water.

The mean overall mass balance values for the low and high test concentrations were 96.7% AR (low concentration) and 93.4% AR (high concentration) with ranges of 93.6 to 99.8 8 % AR and 87.4 to 98.3 % AR respectively. The mass balance value for the sterilised incubation group was 96.0% AR.

[^{14}C]-Ethephon was very rapidly degraded to [^{14}C]-ethylene, which reached 75 to 86% AR after 5 days. No other metabolite exceeded 3% AR. Mineralisation was a minor route of degradation, with [^{14}C]-carbon dioxide accounting for < 2% AR.

The degradation rates ($DegT_{50}$) of ethephon were estimated using CAKE (version 2.0) software by fitting SFO kinetics to the data. The degradation rate was independent of concentration and very similar in the biotic and sterile systems. The results are summarised below:

System	Test concentration (µg/L)	SFO		
		$DegT_{50}$ (hours)	$DegT_{90}$ (hours)	Chi^2
Kellmetschweiher natural water	10	21.1	70.1	4.82
	100	19.0	63.0	3.59
	Sterile	23.5	78.1	2.11

I. MATERIALS AND METHODS

A. MATERIALS

1. **Test material:** [UL-^{14}C] Ethephon
   Chemical name 2-Chloroethylphosphosphonic acid
   Specific activity: 4.28 MBq/mg
   Lot or batch number: KML 9785 / CFQ 13687
   Radiochemical purity: 98% HPLC
   CA registry number: 16672-87-0
   Application vehicle: Acetonitrile
2. **Water** Natural water from the "Kellmetschweiher" pond located near the town of Schifferstadt was used. Water was sieved through a 0.1 mm mesh prior to use.

Characteristics of the test water

Name	Pond Kellmetschweiher
Origin	Near the town of Schifferstadt Rhineland-Palatinate Germany
Geographical coordinates:	49°21'52.78"N 8°19'58.94"E
Date of collection	Apr. 09, 2015
Weather conditions	Sunny
Water temperature	16.2°C
pH at sampling site	7.77
RedOx-potential [mV]	204 mV
Oxygen content and saturation [mg/L] [%]	10.21 mg/L, 106%
Hardness °dH	9.3°dH [1.66 mmol/L]
Total Nitrogen (TNb)	< 1.0*
Total Phosphorus [mg/L]	< 0.05*
Total Ammonium [mg/L]	0.12
Total Nitrate [mg/L]	< 0.5*
Dissolved Orthophosphate [mg/L]	≤ 0.03*
Total Organic Carbon (TOC) [mg/L]	10.5
Dissolved Organic Carbon (DOC) [mg/L]	10.5
Biochemical Oxygen Demand after 5 days (BOD5) [mg/L]	< 3*
Chemical Oxygen Demand (COD) [mg/L]	33.9
Total Nitrite [mg/L]	≤ 0.01*

* Limit of quantification

B. STUDY DESIGN AND METHODS

In-life dates

Study initiation date: 9 April 2015

Study completion date: 21 July 2015

Experimental start date: 13 April 2015

Experimental completion date: 23 June 2015

Experimental design

Parameter		Description
Duration of test		5 days
Concentration in test system	100 µg/L dose level	121.4 - 123.1 µg/L
	10 µg/L dose level	7.20 - 7.30 µg/L
	Sterile controls	131.03 - 131.65 µg/L
	[^{14}C]-Sodium benzoate	101.47 µg/L
Number of replications		Duplicate test system for each dose level
Test apparatus		1 L glass flasks (internal diameter 10 cm), surface area 78.5 cm^2
Volume of natural water per vessel		400 ml
Test material application	Identity of solvent	Acetonitrile
	Volume of application solution	108 µL for 100 µg/L dose level 72 µL for 10 µg/L dose level 111 µL for sterile controls
	Application method	Pipette
Traps for CO_2 and organic volatiles		[^{14}C]-Ethephon: Flow through trapping system with series of volatile traps: 1 x 2N NaOH, 5 x pyridinium hydrobromide perbromide in glacial acetic acid (PHBPB),1 x 3% sodium thiosulfate solution ($Na_2S_2O_3$) [^{14}C]-Sodium benzoate: Static system with soda lime trap
Is there any indication of the test material absorbing to the walls of the test apparatus?		No
Experimental conditions	Temperature	20 °C, Range 21.3 - 25.2 °C
	Lighting	[^{14}C]-Ethephon: Diffuse light conditions as test conducted in fume hood (due to safety reasons) [^{14}C]-Sodium benzoate: Dark

Sampling

Parameter		Description
Sampling intervals by treatment	[^{14}C]-Ethephon: Low and high concentrations	Duplicate aliquots collected at 1, 3, 6, 12, 24 and 72 hours. At 120 hours the remaining water samples collected. All PHBPB traps sampled when aliquots removed for analysis. At 120 hours PHBPB, NaOH and $Na_2S_2O_3$ traps taken.
	[^{14}C]-Ethephon: Sterilised	Duplicate aliquots collected at 1, 3, 6, 24 and 72 hours. At 120 hours the remaining water samples collected. All PHBPB traps sampled when aliquots removed for analysis. At 120 hours PHBPB, NaOH and $Na_2S_2O_3$ traps taken.
	[^{14}C]-Sodium benzoate	Duplicate samples collected at 1, 3, 6, 24, 72 and 120 hours
	Blank controls	Water quality measurements at 0 and 120 hours.
Sampling procedures		Aliquots were removed at each sampling time. The amount of radioactivity was quantified by LSC. A sub-aliquot was analysed by HPLC or HPLC-MS/MS. Sub-aliquots were acidified with 25 µL acid (pH 1).
Quantification of radioactivity in trapping solutions		LSC

Description of analytical procedures

At each sampling time, the amount of radioactivity in water and volatile traps was quantified by LSC. The metabolic profile in the high dose and sterile control groups was determined by HPLC with radiodetector. In the low dose group levels of ethephon were determined by HPLC-MS/MS.

The amount of sodium benzoate remaining at each timepoint was measured by HPLC. At the final timepoint [^{14}C]-carbon dioxide bound to soda lime traps was liberated by addition of 6M HCl and then trapped in scintillation cocktail prior to quantification by LSC.

A mass balance for each test system was calculated by the summation of radioactivity remaining in the water, in aliquots of water previously removed for sampling and in volatiles traps.

The half-lives (DegT_{50}) of [^{14}C]-ethephon (from the HPLC or HPLC-MS/MS analysis) were determined using a SFO kinetic model using the software CAKE version 2.0.

II. RESULTS AND DISCUSSION

The total recoveries and distribution of radioactivity from each water system are shown in detail in Table 7.2.2- 1 to Table 7.2.2- 3.

Mass Balance

Total radioactivity	Sum of activity in the water phase, in aliquots of water removed for sampling and that trapped in volatile traps as ^{14}C-ethylene in the PHBPB traps, as $^{14}CO_2$ in the 2N NaOH traps and trace amounts of radioactivity in the $Na_2S_2O_8$ traps.	
Mean Recovery at 0 DAT	Natural Water (100 µg/L)	98.0% AR
	Natural Water (10 µg/L)	98.1% AR
	Sterile Natural Water (100 µg/L)	98.9% AR
Overall recovery (all samples)	Natural Water (100 µg/L)	Mean 93.4% AR, Range 87.4 to 98.3 % AR
	Natural Water (10 µg/L)	Mean 96.8% AR, Range 93.6 to 99.8 % AR
	Sterile Natural Water (100 µg/L)	Mean 96.0% AR, Range 91.7 to 99.3 % AR

Radioactive Residues

Volatile Degradation Products

Ethephon rapidly degraded to form [^{14}C]-ethylene (~ 74% AR) in all test systems. Only small amounts of $^{14}CO_2$ were formed.		
$^{14}CO_2$ evolved at end of test	Natural Water (100 µg/L)	1.3% AR
	Natural Water (10 µg/L)	1.2% AR
	Sterilised Natural Water (100 µg/L)	0.9% AR
^{14}C-Ethylene evolved at end of test	Natural Water (100 µg/L)	74.5% AR
	Natural Water (10 µg/L)	85.5% AR
	Sterilised Natural Water (100 µg/L)	80.0% AR

Transformation of Parent Material in Water Phase

In all groups [^{14}C]-ethephon was rapidly degraded to [^{14}C]-ethylene which formed 74, 86 and 80% AR after 5 days incubation in the low, high and sterile dose groups, respectively. An unidentified degradation product was observed once at a maximum of 2.2% AR after 24 hours in the high dose group and at 3.0% AR after 72 hours in the sterile group. Mineralisation was a minor route of degradation, with [^{14}C]-carbon dioxide accounting for < 2% AR.

The results are presented in Table 7.2.2- 4 to Table 7.2.2- 6.

Degradation of [^{14}C]-Sodium benzoate

[^{14}C]-Sodium benzoate was completely degraded within 120 hours indicating a viable microbial population was established.

DegT$_{50}$ of ethephon in natural water systems

The single first-order DegT$_{50}$ values ranged from 19 to 23.5 hours. The results are presented in Table 7.2.2- 7. The degradation rate was independent of concentration and very similar in the biotic and sterile groups.

Table 7.2.2- 1: Distribution and recovery of [^{14}C]-ethephon in natural water (High dose 100 µg/L)

Incubation time (hours)	Replicate	% of applied radioactivity					
		Water phase	Water aliquots removed [A]	PHBPB traps [A]	2N NaOH traps	$Na_2S_2O_3$ traps	Total
1	A	95.88	2.05	0.36	-	-	98.28
	B	95.97	1.51	0.19	-	-	97.66
	Mean	95.92	1.78	0.27	-	-	97.97
3	A	88.60	3.62	2.06	-	-	94.28
	B	89.38	3.05	4.14	-	-	96.58
	Mean	88.99	3.33	3.10	-	-	95.43
6	A	77.71	5.06	11.85	-	-	94.62
	B	78.20	4.51	11.91	-	-	94.62
	Mean	77.95	4.79	11.88	-	-	94.62
12	A	62.87	6.35	23.65	-	-	92.87
	B	63.28	5.79	25.58	-	-	94.65
	Mean	63.07	6.07	24.62	-	-	93.76
24	A	41.16	7.09	44.72	-	-	92.97
	B	40.90	7.10	45.44	-	-	93.44
	Mean	41.03	7.10	45.08	-	-	93.21
72	A	10.84	7.80	70.53	-	0.32	89.50
	B	10.84	7.81	67.77	-	1.02	87.43
	Mean	10.84	7.81	69.15	-	0.67	88.47
120	A	5.80	8.00	75.91	1.28	0.32	91.32
	B	5.77	7.99	73.03	1.36	1.02	89.17
	Mean	5.79	8.00	74.47	1.32	0.67	90.25

[A] Cumulative total - = not sampled

Table 7.2.2- 2: Distribution and recovery of [^{14}C]-ethephon in natural water (Low dose 10 µg/L)

Incubation time (hours)	Replicate	% of applied radioactivity					
		Water phase	Water aliquots removed [A]	PHBPB traps [A]	2N NaOH traps	$Na_2S_2O_3$ traps	Total
1	A	95.48	1.47	0.65	-	-	97.61
	B	96.40	1.48	0.65	-	-	98.52
	Mean	95.94	1.48	0.65	-	-	98.07
3	A	88.60	2.86	4.86	-	-	96.31
	B	88.65	2.92	5.19	-	-	96.75
	Mean	88.62	2.89	5.02	-	-	96.53
6	A	78.54	4.22	12.60	-	-	95.35
	B	77.47	4.28	11.80	-	-	93.55
	Mean	78.01	4.25	12.20	-	-	94.45
12	A	62.43	5.46	25.66	-	-	93.55
	B	61.90	5.51	29.69	-	-	97.10
	Mean	62.16	5.48	27.68	-	-	95.33
24	A	41.62	6.45	47.26	-	-	95.33
	B	41.01	6.50	49.89	-	-	97.39
	Mean	41.31	6.48	48.57	-	-	96.36
72	A	19.27	7.12	73.27	-	-	99.66
	B	13.17	7.16	78.88	-	-	99.21
	Mean	16.22	7.14	76.08	-	-	99.44
120	A	3.33	7.44	83.85	0.94	0.00	95.56
	B	3.67	7.37	87.16	1.36	0.19	99.75
	Mean	3.50	7.40	85.50	1.15	0.10	97.66

[A] Cumulative total - = not sampled

Table 7.2.2- 3: Distribution and recovery of [^{14}C]-ethephon in natural water (High dose 100 µg/L sterile)

Incubation time (hours)	Replicate	% of applied radioactivity					
		Water phase	Water aliquots removed [A]	PHBPB traps [A]	2N NaOH traps	$Na_2S_2O_3$ traps	Total
1	A	96.55	1.56	0.45	-	-	98.57
	B	97.03	1.54	0.74	-	-	99.31
	Mean	96.79	1.55	0.59	-	-	98.94
3	A	89.79	3.12	3.95	-	-	96.86
	B	90.68	3.13	4.41	-	-	98.23
	Mean	90.24	3.12	4.18	-	-	97.54
6	A	79.81	4.56	12.03	-	-	96.40
	B	80.35	4.63	12.16	-	-	97.14
	Mean	80.08	4.59	12.09	-	-	96.77
24	A	46.37	5.34	40.67	-	-	92.37
	B	48.48	6.31	41.99	-	-	96.70
	Mean	47.42	5.83	41.29	-	-	94.54
72	A	15.13	6.12	70.49	-	-	91.74
	B	17.01	8.00	70.80	-	-	95.81
	Mean	16.07	7.06	70.65	-	-	93.78
120	A	3.25	6.37	81.53	1.09	0.00	92.25
	B	9.31	8.29	78.40	0.65	0.01	96.66
	Mean	6.28	7.33	79.96	0.87	0.00	94.46

[A] Cumulative total - not sampled

Table 7.2.2- 4: Characterisation of radioactive residues in natural water (High dose 100 µg/L)

Incubation time (hours)	Replicate	% of applied radioactivity			
		Water phase	Ethephon	Unknown RT 6.8-7.5	Total
1	A	95.88	95.88	-	95.88
	B	95.97	95.97	-	95.97
	Mean	95.92	95.92		95.92
3	A	88.6	88.60	-	88.60
	B	89.38	89.38	-	89.38
	Mean	88.99	88.99	-	88.99
6	A	77.71	77.71	-	77.71
	B	78.20	78.20	-	78.20
	Mean	77.95	77.95	-	77.95
12	A	62.87	62.87	-	62.87
	B	63.28	63.28	-	63.28
	Mean	63.07	63.07	-	63.07
24	A	41.16	39.62	1.54	41.16
	B	40.90	38.09	2.81	40.90
	Mean	41.03	38.86	2.18	41.04
72	A	10.84	10.84	-	10.84
	B	10.84	10.84	-	10.84
	Mean	10.84	10.84	-	10.84
120	A	5.80	5.80	-	5.80
	B	5.77	5.77	-	5.77
	Mean	5.79	5.79	-	5.79

- = not detected

Table 7.2.2- 5: Characterisation of radioactive residues in natural water (High dose 100 µg/L sterile)

Incubation time (hours)	Replicate	% of applied radioactivity			
		Water phase	Ethephon	Unknown RT 6.8-7.5	Total
1	A	96.55	96.55	-	96.55
	B	97.03	97.03	-	97.03
	Mean	96.79	96.79	-	96.79
3	A	89.79	89.79	-	89.79
	B	90.68	90.68	-	90.68
	Mean	90.24	90.24	-	90.24
6	A	79.81	79.81	-	79.81
	B	80.35	80.35	-	80.35
	Mean	80.08	80.08	-	80.08
12	A	46.37	46.37	-	46.37
	B	48.48	48.48	-	48.48
	Mean	47.42	47.42	-	47.42
72	A	15.13	11.67	3.46	15.13
	B	17.01	14.53	2.48	17.01
	Mean	16.07	13.10	2.97	16.07
120	A	3.25	3.25	-	3.25
	B	9.31	9.31	-	9.31
	Mean	6.28	6.28	-	6.28

- = not detected

Table 7.2.2- 6: Determination of ethephon in natural water (Low dose 10 µg/L)

Incubation time (hours)	Replicate	Water phase
		Ethephon (µg/L)
1	A	5.14
	B	5.12
	Mean	5.13
3	A	4.93
	B	4.87
	Mean	4.90
6	A	3.80
	B	4.11
	Mean	3.95
12	A	3.40
	B	3.65
	Mean	3.52
24	A	2.65
	B	2.95
	Mean	2.80
72	A	1.87
	B	1.95
	Mean	1.91
120	A	0.26
	B	0.26
	Mean	0.26

Table 7.2.2- 7: Summary of $DegT_{50}$ values for [^{14}C]-ethephon in natural water systems

System	Test concentration (µg/L)	SFO		
		$DegT_{50}$ (hours)	$DegT_{90}$ (hours)	Chi^2
Kellmetschweiher natural water	10	21.1	70.1	4.82
	100	19.0	63.0	3.59
	Sterile	23.5	78.1	2.11

III. CONCLUSIONS

The extent of mineralisation and the rate and route of degradation of [^{14}C]-ethephon was investigated in Kellmetschweiher natural water at pH 7.8. The compound was applied to the water at nominal rates of 10 and 100 µg/L (low and high, respectively). The 100 µg/L rate was also applied to sterilised natural water. The systems were incubated under aerobic conditions and maintained at 20 °C for 5 days.

Mean mass balance from each incubation group were quantitative, ranging from 93 to 97%.

[^{14}C]-ethephon was very rapidly degraded to [^{14}C]-ethylene, which reached 75 to 86% AR after 5 days. No other metabolite exceeded 3% AR. Mineralisation was a minor route of degradation, with [^{14}C]-carbon dioxide accounting for < 2% AR.

$DegT_{50}$ values for ethephon in natural water ranged from 19 to 23.5 hours. The degradation rate was independent of concentration and very similar in the biotic and sterile systems.

CA 7.2.2.3 Water/sediment study

The degradation and fate of ethephon had been investigated in two aerobic water sediment systems under laboratory conditions (KCA 7.2.2.3/01). This study was evaluated during the previous EU review, and the reference is provided below. No new studies are submitted for the current EU review. The need to investigate acidic water/sediment systems is discussed (KCA 7.2.2.3/03).

Report:	KCA 7.2.2.3/01; [redacted]; [redacted]; [redacted], 2000; M-199017-01-1
Title:	Degradation and retention in two water/sediment systems (14C)-Ethephon
Report No.:	C010433
Document No.:	M-199017-01-1
Guideline(s):	Dutch Guidelines for the Submission of Applications for Registration of Pesticides, Part G Section 2.1.(1). March 1995 and EU Council Directive 91/414/ECC, as amended by Commission Directive 95/36/ECC of July 1995, Section 7.2.1.3.2. US EPA OPPTS 835.4300
Guideline deviation(s):	not specified
GLP/GEP:	**yes**

The experimental data generated in the above water sediment study have now been re-evaluated according to FOCUS kinetics guidance (KCA 7.2.2.3/02) for the current EU review. This re-evaluation is summarised below.

Report:	KCA 7.2.2.3/02, [redacted]; [redacted]; 2015; M-534853-01-1
Title:	Ethephon (ETP) - Kinetic evaluation of degradation and dissipation behaviour in water / sediment systems according to FOCUS kinetics
Report No.:	EnSa-15-0164
Document No.:	M-534853-01-1
Guideline(s):	"Generic Guidance for Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration". Report of the FOCUS Work Group on Degradation Kinetics. EC Document Reference: None, version 1.1, 2014; "Guidance Document on Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration". Report of the FOCUS Work Group on Degradation Kinetics. EC Document Reference Sanco/10058/2005 version 2.0, 2006
Guideline deviation(s):	not applicable
GLP/GEP:	**no**

Executive Summary

The aim of this study was to evaluate water sediment degradation data for ethephon to derive DT_{50} values according to FOCUS kinetics guidance. The degradation and dissipation behaviour of ethephon in the aquatic environment had been investigated in two aerobic water sediment systems, Manningtree and Ongar, which were incubated under laboratory conditions at 20 °C in the dark [KCA 7.2.2.3/01, [redacted] *et al.*, 2000]. Other than ethylene, no major metabolites were detected in either system. The metabolite HEPA was detected at a maximum of 1.4% in the water phase of the Ongar system.

Following FOCUS recommendations, level P-I degradation half-lives for the total system and level P-I dissipation half-lives for the water and sediment phases were determined. SFO fits were statistically significant and provided good visual fits to the data.

Additionally a level P-II two-compartmental approach to estimate degradation in the water column and sediment compartments was undertaken. The evaluations resulted in very good fits for the water phase and moderate fits in the sediment phase. However in the Ongar sediment compartment the degradation and transfer rates were not significantly different from zero and thus were not considered further.

Modelling and trigger endpoints are summarised below:

Water sediment system	Whole system (days)		χ^2	Water (days)		χ^2	Sediment (days)		χ^2	Model
	DT_{50}	DT_{90}		DT_{50}	DT_{90}		DT_{50}	DT_{90}		
Manningtree (P-I)	2.98	9.89	2.48	2.56	8.50	1.43	8.75	29.1	5.55	SFO
Manningtree (P-II)	-	-		3.12 [B]	10.4	1.53	2.16	7.16	18.05	SFO
Ongar (P-I)	2.61	8.67	5.88	2.19	7.27	5.19	7.65	25.4	5.28	SFO
Mean (P-I)	2.79 [A,C]	9.26		2.37	7.86		8.18	27.2		

A) Suitable for use in FOCUS Steps 1-2 of the modelling assessment and as trigger endpoints
B) Suitable for use in FOCUS Step 3 of the modelling assessment for degradation in the water phase
C) Suitable for use in FOCUS Step 3 of the modelling assessment for degradation in the sediment phase

I. MATERIALS AND METHODS

The experimental data generated in an aerobic water sediment study [previously reviewed for the first approval of ethephon, [redacted] *et al*., 2000] were re-evaluated according to the FOCUS guidance document on degradation kinetics using the software KinGUI v2.1. The aim of this evaluation was to derive DT_{50} values for use as modelling and trigger endpoints.

The datasets evaluated for each water sediment system are provided in Table 7.2.2- 8 to Table 7.2.2- 9. Transfer of ethephon from the water phase to sediment was low. The maximum occurrence in sediment was 5.91 % in Manningtree at day 2 and 6.02 % in Ongar at day 4.

Table 7.2.2- 8: Summary of ethephon dataset from Manningtree water sediment system ([redacted] *et al*., 2000)

Time (days)	Total system [A] (% of applied radioactivity)	Water phase (% of applied radioactivity)	Time from Peak (days)	Sediment phase (% of applied radioactivity)
0	98.53 [B]	98.53 [B]	-	-
0.25	97.95	94.88	-	-
1	81.80	76.67	-	-
2	63.28	57.37	0 [C]	5.91
4	39.73	34.23	2	5.50
8	14.49	11.01	6	3.48
14	5.02	2.43	12	2.59
30	1.09	0.62	28	0.47

A Values of total system are the sum of concentrations in water and sediment phase.
B Values at day 0 were set to material balance.
C For sediment the initial value (listed as Time from Peak 0 days) was the time at which maximum concentration was reached after application.

Table 7.2.2- 9: Summary of ethephon dataset from Ongar water sediment system (Lowden *et al.*, 2000)

Time (days)	Total system [A] (% of applied radioactivity)	Water phase (% of applied radioactivity)	Time from Peak (days)	Sediment phase (% of applied radioactivity)
0	98.72 [B]	98.72 [B]	-	-
0.25	100.47	96.96	-	-
1	78.54	73.12	-	-
2	61.39	55.57	-	-
4	31.45	25.43	0 [C]	6.02
8	12.96	8.72	4	4.24
14	9.60	7.43	10	2.17
30	1.77	0.86	26	0.91

[A] Values of total system are the sum of concentrations in water and sediment phase.
[B] Values at day 0 were set to material balance.
[C] Day 0 was set to corresponding time at which maximum concentration was reached after application.

II. RESULTS AND DISCUSSION

Degradation/Dissipation Kinetics One-Compartmental Approach (Level P-I)

For degradation rates in the total system and dissipation rates in the water and sediment phases, SFO fits were statistically significant and provided good visual fits to the data. The bi-phasic FOMC model was tested but in all cases resulted in no improvement of fit or statistics.

DT_{50} values for ethephon are summarised in Table 7.2.2- 10 for degradation in the total system; in Table 7.2.2- 11 for dissipation in water phase and in Table 7.2.2- 12 for dissipation in the sediment phase.

Table 7.2.2- 10: Degradation Kinetics Total System (level P-I)

Water Sediment System	Kinetic model	DT_{50} (days)	DT_{90} (days)	Min χ^2 error	Parameter Confidence / t-test	Visual
Manningtree	SFO	2.98	9.89	2.5	<0.001	Good
Ongar	SFO	2.61	8.67	5.9	<0.001	Good
Geometric mean		2.79	9.26			

Table 7.2.2- 11: Dissipation Kinetics Water Phase (level P-I)

Water Sediment System	Kinetic model	DT_{50} (days)	DT_{90} (days)	Min χ^2 error	Parameter Confidence / t-test	Visual
Manningtree	SFO	2.56	8.50	1.4	<0.001	Good
Ongar	SFO	2.19	7.27	5.2	<0.001	Good
Geometric mean		2.37	7.86			

Table 7.2.2- 12: Dissipation Kinetics Sediment Phase (level P-I)

Water Sediment System	Kinetic model	DT_{50} (days)	DT_{90} (days)	Min χ^2 error	Parameter Confidence / t-test	Visual
Manningtree	SFO	8.75	29.05	5.5	0.002	Good
Ongar	SFO	7.65	25.42	5.3	0.007	Good
Geometric mean		8.18	27.17			

Degradation Kinetics Two-Compartmental Approach (Level P-II)

A two-compartmental approach was used to estimate the degradation of ethephon in water and sediment compartment in parallel, including partitioning processes via reaction rates. SFO kinetics was used to describe degradation separately in the water and sediment phase, as well as reversible transfer or partitioning between these compartments.

The evaluation resulted in a very good fit to the measured data of ethephon in the water phase, visually as well as statistically (χ^2 error and t-test). The fit to the measured data of ethephon in the sediment phase, however, was moderate for both aquatic systems and resulted in relatively high, but acceptable, χ^2 errors of 18% and 15%. Correlations could be observed between transfer and degradation rates. In the Manningtree system, significant degradation in the sediment and no back-transfer to the water phase were predicted by the model. However in the Ongar system the degradation rate from sediment to sink and the transfer rate from sediment to water were not significantly different from zero and thus were not recommended for use in exposure assessments.

Table 7.2.2- 13: Degradation Kinetics Water and Sediment Phase (level P-II)

Water Sediment System	Compartment	Kinetic model	DT_{50} (days)	DT_{90} (days)	Min χ^2 error	Parameter Confidence / t-test	Visual
Manningtree	Water	SFO	3.12	10.35	1.5	<0.001	Good
	Sediment	SFO	2.16 [a]	7.16	18.0	0.024	Acceptable
Ongar	Water	SFO	2.32 [b]	7.69 [b]	5.3	<0.001	Good
	Sediment	SFO	>1000 [c]	>1000 [c]	14.6	0.5	Acceptable

[a] No trigger endpoints estimated from level P-II – use level P-I DegT50 in sediment instead
[b] Not considered for endpoint estimation as not all rate constants of this system were reliable
[c] Not reliable / not considered for endpoint estimation

The geometric mean total system $DegT_{50}$ values of 2.79 days was deemed appropriate for water, sediment, and total system for FOCUS surface water Step 1 and 2 calculations. For FOCUS Step 3 modelling the $DegT_{50}$ value of 3.12 days from the evaluation of Manningtree water phase (level P-II) and the geometric total system $DegT_{50}$ values of 2.79 days for the sediment phase were selected.

III. CONCLUSIONS

Kinetic modelling analysis of the data from two aerobic water sediment studies treated with ethephon provided acceptable model fits.

The modelling endpoints for PEC_{sw} derived from the water sediment data are summarised below.

Water sediment system	Whole system (days)		χ^2	Water (days)		χ^2	Sediment (days)		χ^2	Model
	DT_{50}	**DT_{90}**		**DT_{50}**	**DT_{90}**		**DT_{50}**	**DT_{90}**		
Manningtree (P-I)	2.98	9.89	2.48	2.56	8.50	1.43	8.75	29.1	5.55	SFO
Manningtree (P-II)	-	-		**3.12** [B]	10.4	1.53	2.16	7.16	18.05	SFO
Ongar (P-I)	2.61	8.67	5.88	2.19	7.27	5.19	7.65	25.4	5.28	SFO
Mean (P-I)	**2.79** [A,C]	9.26		2.37	7.86		8.18	27.2		

[A)] Suitable for use in FOCUS Steps 1-2 of the modelling assessment and as trigger endpoints
[B)] Suitable for use in FOCUS Step 3 of the modelling assessment for degradation in the water phase
[C)] Suitable for use in FOCUS Step 3 of the modelling assessment for degradation in the sediment phase

The geometric mean total system $DegT_{50}$ values of 2.79 days was deemed appropriate for water, sediment, and total system for FOCUS surface water Step 1 and 2 calculations. For FOCUS Step 3 modelling the $DegT_{50}$ value of 3.12 days from the evaluation of Manningtree water phase (level P-II) and the geometric total system $DegT_{50}$ values of 2.79 days for the sediment phase were selected.

Report:	KCA 7.2.2.3/03; [redacted]; 2017; M-587404-01-1
Title:	Discussion of comments provided by RMS (the Netherlands) in the draft RAR - Volume 3 - Annex B (AS / PPP) - Ethephon - B.8 Environmental fate and behaviour
Report No.:	M-587404-01-1
Document No.:	M-587404-01-1
Guideline(s):	none
Guideline deviation(s):	--
GLP/GEP:	**no**

<u>Request for a new study according to OECD 309/308</u>

RMS requested a study with acidic water/sediment systems. However, the applicant Bayer does not consider a new study necessary for the risk assessment due to the following reasons:

- the available studies were made at pH values representative for the majority of water/sediment systems in Europe. The pH values of 3075 European surface waters were evaluated by [redacted] et al. (2015)[1]. According to this investigation, 95 percent of European surface waters (n equals 3075) with a documented history of AI exposure fall within a rather narrow pH range, between 7.0 and 8.5. It is thus concluded that the risk assessment provided in the submitted Dossier is sufficient to address the risk for the majority of aquatic organisms.

- the PEC_{sw} modelling performed for acidic water/sediment systems using default DT_{50} values of 1000 days for water and sediment, revealed no risk for aquatic organisms in surface water. It is thus concluded, that the risk for organisms in surface water is sufficiently addressed with the available data. A new study is not expected to lead to a more conservative risk assessment here.

<u>Value for persistence assessment</u>
The persistence assessment for water and sediment was made based on the default DT_{50} values of 1000 days proposed for modelling of acidic water/sediment systems (as studies were only made for pH > 7). However, based on the results of the hydrolysis study provided in Section KCA 7.2.1.1/01, the DT_{50} value at pH 5 and 25°C was calculated as 99.1 days. Thus the use of the default value of

1 [redacted] (2015): Narrow pH Range of Surface Water Bodies Receiving Pesticide Input in Europe; Bull Environ Contam Toxicol. 2016 Jan;96(1):3-8. doi: 10.1007/s00128-015-1665-7; M-539960-01-1

1000 days for the persistence assessment seems to be too conservative. We propose to use the DT_{50} value of 99.1 days for the persistence assessment in both, the sediment and the water phase.

CA 7.2.2.4 Irradiated water/sediment study

An irradiated water sediment study is an optional higher tier study which is not required for ethephon.

CA 7.2.3 Degradation in the saturated zone

Ethephon is readily degraded in soil and is not expected to move through the soil profile and into groundwater.

CA 7.3 Fate and behaviour in air

CA 7.3.1 Route and rate of degradation in air

The Atkinson method of calculation had been used to estimate the DT_{50} for degradation of ethephon in air (KCA 7.3.1/01). This report was evaluated during the previous EU review, and the reference is provided below.

Report:	KCA 7.3.1/01; [redacted]; 2001; M-201690-01-1
Title:	Estimation of the degradation of ethephon by photo-oxidation in air Model calculation according to Atkinson
Report No.:	C011869
Document No.:	M-201690-01-1
Guideline(s):	OECD: Monograph 51, 1990
Guideline deviation(s):	
GLP/GEP:	**yes**

A new vapour pressure study (KCA 7.3.1/02) and Henry's Law constant calculation have been conducted. Ethephon has a low vapour pressure, 4.5×10^{-5} Pa at 20 °C, and Henry's law constant 8.1 $\times 10^{-9}$ Pa m^3 mol^{-1} at pH 4 (and < 6.5 $\times 10^{-9}$ Pa m^3 mol^{-1} at pH < 0.2). The compound is an acid with a pK_{a1} of 2.8 and a pK_{a2} of 7.2 and will be ionised to some extent at most environmentally relevant pHs. Thus it would not be expected to be present in significant concentrations in air following use of the compound according to the proposed GAP.

Ethylene is a volatile degradation product of ethephon, formed at a maximum of 62% and 99% of applied ethephon from aerobic soil and water sediment systems, respectively. Ethylene is a naturally-occurring plant hormone produced in significant amounts by all plant tissues. It is a volatile compound with a high vapour pressure [6950 x 10^3 Pa at 25ºC]. Any ethylene formed from ethephon will be present in air because of its physical chemical properties and would not be expected to be found in any significant amounts in soil and water. The rate constants of ethylene reacting with OH radicals, NO_3 radicals and ozone have been measured experimentally and were used as part of the database developed by Atkinson to determine theoretical rates of degradation of organic compounds in air. The half-life of ethylene was determined as 1.45 days using the Atkinson model (OECD SIDS Ethylene, 1998). The new vapour pressure study is summarised below.

Report:	KCA 7.3.1/02; [redacted]; 2015; M-514117-01-1
Title:	Ethephon (AE F016382), pure substance: Vapour pressure
Report No.:	CSL-14-1777.01
Document No.:	M-514117-01-1
Guideline(s):	European Commission Council Regulation (EC) No 440/2008 Method A.4.; OECD Test Guidelines 104 and 113; US EPA Product Properties Test Guideline OCSPP 830.7950
Guideline deviation(s):	not specified
GLP/GEP:	**yes**

Executive Summary

The vapour pressure and thermal stability of ethephon were determined according to the effusion method (vapour pressure balance) and differential scanning calorimetry (DSC) method.

Thermal Stability: Ethephon showed an endothermic effect in the temperature range of 45 - 85 °C, caused by melting of the test item. No further endothermic or exothermic effects were observed up to the maximum test temperature of 300 °C.

Vapour Pressure: The following vapour pressure values for ethephon were extrapolated from the experimental data.

Temperature (°C)	Vapour pressure (Pa)
20	4.5×10^{-5}
25	8.0×10^{-5}
50	1.1×10^{-3}

I. MATERIALS AND METHODS

A. MATERIALS

1. Test material: Ethephon

Chemical name 2-chloroethylphosphonic acid

CA registry number: 16672-87-0

Empirical formula: $C_2H_6ClO_3P$

Molecular weight: 144.49

Batch number: SZBD214XV

Content: 98.5% w/w||

Thermal stability (DSC): A DSC measurement in a closed glass crucible under nitrogen was performed up to a temperature of 300 °C to determine the thermal stability of the test item.

Vapour pressure with the effusion method (vapour pressure balance): The test equipment was brought to vacuum (approximately 10^{-4} Pa) at room temperature before starting the measurements. The vapour pressure was then determined for six temperatures in the range of 58 to 78 °C.

II. RESULTS AND DISCUSSION

Thermal Stability: Ethephon showed an endothermic effect in the temperature range of 45 - 85 °C caused by melting of the test item. No further endothermic or exothermic effects were observed up to the maximum test temperature of 300 °C.

Vapour Pressure: The measured vapour pressure values for ethephon are listed below.

Table 7.3.1- 1: Measured vapour pressure values by the Effusion method

Number	Temperature (°C)	Vapour pressure (Pa)
1	58	2.13×10^{-3}
2	62	4.07×10^{-3}
3	69	5.06×10^{-3}
4	72	7.72×10^{-3}
5	75	1.05×10^{-2}
6	78	1.36×10^{-2}

The vapour pressure at temperatures of 20, 25 and 50 °C was calculated by extrapolation of the measured vapour pressure curve.

Table 7.3.1- 2: Extrapolated vapour pressure values at 20, 25 and 50 °C

Temperature (°C)	Vapour pressure (Pa)
20	4.5×10^{-5}
25	8.0×10^{-5}
50	1.1×10^{-3}

III. CONCLUSIONS

The vapour pressure of ethephon at 20 °C was estimated as 4.5×10^{-5} Pa.

CA 7.3.2 Transport via air

No studies on transport via air had been conducted for ethephon and no new studies have been submitted for Annex I Renewal. Confined volatility studies are optional studies which are not required for ethephon.

The provision of confined volatility studies can be helpful where trigger values for volatilisation are exceeded (vapour pressure = 10-5 Pa (plant) or 10-4 Pa (soil) at 20 °C), when they may be used as a refinement to avoid the need for drift mitigation measures. However as no drift mitigation measures are required for the aquatic risk assessment the studies are not needed for ethephon.

CA 7.3.3 Local and global effects

No studies on local and global effects had been conducted for ethephon and no new studies have been submitted for Annex I Renewal.

For substances that are applied in high amounts, the following effects shall be considered:

— global warming potential (GWP);

— ozone depleting potential (OPD);

— photochemical ozone creation potential (POCP);

— accumulation in the troposphere;

— acidification potential (AP);

— eutrophication potential (EP).

As ethephon is applied once a year at a maximum application rate of 480 g a.s./ha these effects are not considered.

CA 7.4 Definition of the residue

CA 7.4.1 Definition of the residue for risk assessment

Residue definition for soil:

The active substance ethephon had previously been considered in the residue definition for soil.

The metabolite HEPA was observed in aerobic soil studies at a maximum of 7.4% and in tests on soil photolysis at a maximum of 10.6%. In view of new triggers set in EU data requirements, the existing residue definition for soil is now amended to also include HEPA.

Residue definition for groundwater:

The residue definition for groundwater should include by default the compounds defined for soil, i.e. the active substance and now is amended to include the metabolite HEPA.

Residue definition for surface water and sediment:

The residue definition for surface water and sediment should include by default the compounds included for soil and groundwater.

No metabolites were observed in water sediment tests or tests on aerobic mineralisation exceeding the triggers for inclusion in the residue definition. The metabolite HEPA was formed in the water phase of water sediment systems at a maximum of 1.4% but not in sediment. However, HEPA was observed in a natural water photolysis study in both irradiated samples and dark controls, at a maximum of 7.4% AR. In irradiated samples the metabolite exceeded 5% at the two final timepoints. Hence, in view of new triggers set in the EU data requirements, HEPA should be considered in the residue definition for surface water.

Residue definition for air

The active substance ethephon and its degradate ethylene had previously been considered in the risk assessment for air. No additional compounds are included in the residue definition.

CA 7.4.2 Definition of the residue for monitoring

The residue definitions proposed for monitoring are:

Soil:	Ethephon
Groundwater:	Ethephon
Surface water:	Ethephon
Sediment:	Ethephon
Air:	Ethephon and Ethylene

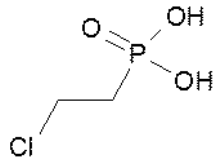
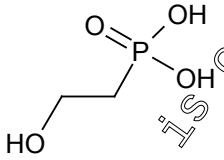
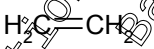
CA 7.5 Monitoring data

Bayer CropScience have not conducted or are aware of any monitoring data for ethephon.

The information and assessments available on the environmental fate and behaviour of ethephon were sufficient to complete an appropriate EU level environmental exposure assessment without monitoring data.

List of metabolites observed in environmental fate testing

A list of metabolites observed in environmental fate testing is included below.

No.	Name, Structure IUPAC name CAS name, [CAS number]	Molecular formula molar mass Other names / codes	Occurrence Major/Minor Compartment(s)
AS 1	Ethephon  2-chloroethylphosphonic acid (IUPAC) (2-chloroethyl)phosphonic acid (CA) CAS No.: 16672-87-0	$C_2H_6ClO_3P$ 144.5 g/mol AE F016382	Active substance
2	HEPA  2-hydroxyethylphosphonic acid (IUPAC) Phosphonic acid (2-hydroxy-ethyl) (CA) CAS No.: 22987-21-9	$C_2H_7O_4P$ 126.1 g/mol 2-HEPA, AE 020271	Soil, aerobic (major) Water (minor, > 5% at final two consecutive timepoints)
3	Ethylene  Ethene (IUPAC) CAS No. 74-85-1	C_2H_4 28.05 g/mol Ethene	Air (major)